

## Protective and High-temperature Coatings Room Town & Country D - Session MA4-2-WeM

### High Entropy and Other Multi-principal-element Materials II

**Moderators:** Jean-François Pierson, IJL - Université de Lorraine, Frederic Sanchette, Université de Technologie de Troyes

8:00am **MA4-2-WeM-1 Oxidation Resistance of High Entropy Nitride Thin Films Deposited by Magnetron Sputtering**, *Djaljel Eddine Touaibia, Abdelhakim Bouissil, Sofiane Achache, Mohamed El Garah, Frederic Sanchette*, Université de Technologie de Troyes, France **INVITED**

In the last decades, Refractory High Entropy Alloys (RHEAs) thin films have attracted more attention owing to their enhanced mechanical properties and better thermal stability at high temperatures, compared to conventional alloys. TiTaZrHfW-N and TiTaZrHfAl-N RHEAs thin films were deposited by reactive magnetron sputtering technology at different N<sub>2</sub> flow rates. For both systems, nitrogen-free films are amorphous, and the nitrides are columnar, single-phased with an FCC-NaCl type structure. The strong Me-N bonds lead to hardness up to 29 GPa and a Young's modulus up to 257 GPa, for the TiTaZrHfW-N system whereas the highest hardness and Young's modulus for the TiTaZrHfAl-N system are 25.3 GPa and 201.3 GPa respectively. Unlike metallic films, TiTaZrHfW-N and TiTaZrHfAl-N nitride films are thermally stable at 800 °C under vacuum and have a much better oxidation resistance. Nanolayered architectures TiTaZrHfW-N/Si<sub>3</sub>N<sub>4</sub> and TiTaZrHfAl-N/Si<sub>3</sub>N<sub>4</sub> result in a significant improvement of the oxidation resistance at 800 °C due to the formation of amorphous Si-N barrier nanolayers, hindering the oxygen diffusion.

8:40am **MA4-2-WeM-3 Plasmonic Behaviour of Multi-Component Nitride (TiVZrNbTa)<sub>x</sub> Thin Films**, *Miguel Piñeiro*, Institut Jean Lamour - Université de Lorraine, France, Peru; *Salah-Eddine Benrazouq*, Institut Jean Lamour - Université de Lorraine, France, Morocco; *Valentin Milichko, David Pilloud, Thomas Easwarakhanthan*, Institut Jean Lamour - Université de Lorraine, France; *Frank Mücklich*, Saarland University, Germany; *Jean-François Pierson*, Institut Jean Lamour - Université de Lorraine, France

Although transition metal nitrides such as TiN or ZrN have been widely studied as plasmonic properties, the optical and electrical properties of multi-component nitride thin films are rather lacking in the literature for plasmonic applications, in spite of their well-known mechanical properties [1]. We attempt in this paper to alleviate this drawback by depositing the multi-component nitride (TiVZrNbTa)<sub>x</sub> films on silicon substrates by using reactive magnetron sputtering under different nitrogen flow rates (R<sub>N<sub>2</sub></sub>) and at different working pressures. The X-ray diffractograms of the as-deposited films have shown that they crystallize in a single-phase with a rocksalt-like structure. Moreover, the plasmonic potential of the films was investigated from their dielectric function determined by variable angle spectroscopic ellipsometry. The films prepared at low working pressures exhibit optimal metallic behaviour with the real part of their dielectric function displaying zero-crossover. In contrast, those fabricated at high working pressure show non-metallic behaviour without any zero-crossover and with low absorption in the near-infrared region. In particular, the real part of the dielectric function of the film produced at 0.5 Pa has a notable feature of double epsilon-near-zero (2ENZ) comparable to other transition metal nitrides such as TiN, ZrN and NbN [2-4]. The dielectric function of (TiVZrNbTa)<sub>x</sub> can be tuned by tailoring the deposition parameters such as working pressure to some desired plasmonic application. Specifically, the screened plasma energy (E<sub>ps</sub>) is tuneable from near UV to visible ranges, from 3.4 to 2.1 eV. Their plasmonic performance were evaluated by calculating their intrinsic quality factor for surface plasmon polaritons (SPP). Additionally, the free-carrier density, the scattering time and the electrical resistivity of the films were also determined by means of Drude model for the free charge carrier contribution to the dielectric function [2]. Drude parameters were compared with additional electrical measurements performed by four-point probe method.

### References

[1] Von Fieandt, K., Pilloud, D., Fritze, S., Osinger, B., Pierson, J. F., & Lewin, E. *Vacuum*, 2021, 193, 110517.

[2] Kassavetis, S., Hodroj, A., Metaxa, C., Logothetidis, S., Pierson, J. F., & Patsalas, P. *Journal of Applied Physics*, 2016, 120(22).

[3] Guo, Q., Wang, T., Ren, Y., Ran, Y., Gao, C., Lu, H., ... & Wang, Z., *Physical Review Materials*, 2021, 5(6), 065201.

[4] Ran, Y., Lu, H., Zhao, S., Guo, Q., Gao, C., Jiang, Z., & Wang, Z., *Applied Surface Science*, 2021, 537, 147981.

9:00am **MA4-2-WeM-4 Temperature Stability of High Entropy Ceramic Cr-Hf-Mo-Ta-W-N Refractory Metal Coatings**, *Pavel Soucek, Stanislava Debnarova, Matej Fekete*, Masaryk University, Czechia; *Sarka Zuzjakova*, University of West Bohemia, NTIS, Czechia; *Shuyao Lin*, Technische Universität Vienna, Austria; *Ondrej Jasek, Tatiana Pitonakova*, Masaryk University, Czechia; *Nikola Koutna*, Technische Universität Vienna, Austria; *Petr Zeman*, University of West Bohemia, NTIS, Czechia

High entropy alloys (HEAs) are multi-component materials composed of five or more principal elements, with each element's content ranging from 5 to 35 atomic percent. The properties of HEAs arise from four core effects: the high entropy effect, severe lattice distortion, sluggish diffusion, and the cocktail effect. This high entropy concept also extends to ceramics, including oxides, nitrides, borides, and carbides.

In this study, we are examining the temperature stability of high entropy nitrides from the Cr-Hf-Mo-Ta-W-N system. We utilized magnetron co-sputtering of segmented elemental targets for all depositions, which were performed on silicon and sapphire substrates. The first set of depositions was conducted at ambient temperature, while an elevated temperature of 700°C was used for the second set to enhance coating crystallization.

All the deposited coatings exhibited strong diffraction peaks corresponding to a face-centred cubic (fcc) lattice, which is anticipated for the formation of these high entropy ceramics. The coatings were annealed at temperatures of 1000°C, 1200°C, and 1400°C to observe changes in their chemical composition, phase, crystal structure, morphology, and mechanical properties.

We will discuss the significant role of coating adhesion in withstanding annealing, the impact of nitrogen loss on changes in the coating structure, and the influence of the inherent multilayered structure of the coatings on phase emergence and stability. Furthermore, we will identify critical elements that enhance the temperature stability of the coatings and discuss the limits of high entropy stabilization in the studied nitride system.

9:20am **MA4-2-WeM-5 Influence of Si on Structural, Mechanical, and Thermal Properties of High Entropy Carbide Thin Films Based on (Hf, Ta, Ti, V, Zr)**, *Muhammad Awais Altaf, Alexander Kirnbauer, Balint Hajas*, TU Wien, Institute of Materials Science and Technology, Austria; *Szilard Kolozsvari*, Plansee Composite Materials GmbH, Germany; *Paul Mayrhofer*, TU Wien, Institute of Materials Science and Technology, Austria

In this research work, high-entropy carbide thin films based on (Hf, Ta, Ti, V, Zr) with Si addition were developed by magnetron sputtering to explore the effects of Si on their structural, mechanical, and thermal properties. XRD results indicate that all films have a single-phase face-centered cubic (fcc) structure (Fm-3m, space group number 225). Si addition leads to an increased hardness (30 GPa to 36 GPa) and elastic modulus (396 GPa to 427 GPa). SEM Images of fractured cross-sections show that films containing Si have a higher thickness and less pronounced columnar growth. With the addition of Si, the onset temperature for an exothermic reaction during a thermal treatment increased from 665 °C to 703 °C. All the samples (without and with Si) retained their single-phase fcc structure even when annealed at 900 °C for 10 min in a vacuum. However, their elastic modulus slightly increased (e.g., from 423.34 GPa to 442.21 GPa for the film) while the hardness decreased (e.g., from 33.12 GPa to 29.08 GPa) with 21.72 at% Si in vacuum annealing. In summary, the structural, mechanical, and thermal properties of high-entropy carbide thin films were improved with the addition of Si.

11:00am **MA4-2-WeM-10 The Microstructure, Mechanical Properties and Performance of High-Entropy (AlCrTiMoVNi)<sub>x</sub>N Coatings Produced by Cathodic Arc Evaporation**, *Qi Yang*, National Research Council of Canada; *Alex Lothrop, Xiao Huang*, Carleton University, Canada

High-entropy (AlCrTiMoVNi)<sub>x</sub>N coatings were prepared using cathodic arc evaporation. The target composition was varied to investigate the effect of nickel concentration on the microstructure, mechanical properties and tribological performance of the coatings. All coatings assume a B1 face centered cubic structure, and contain many small droplet and large splat defects; and the amounts of those defects increase with the concentration of Ni. All coatings showed excellent high-temperature phase stability. The hardness and elastic modulus of the coatings reached maximum values at 2% Ni and then, decreased as the Ni content increases. In terms of performance, the coating with 2% Ni had the lowest wear rate while in

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erosion testing the coating free of Ni had the lowest erosion rates. Overall, the presence of droplets/splats had a significant influence on the tribological performance of the coating.

11:20am **MA4-2-WeM-11 Correlating the Structural and Mechanical Properties of (AlCrNbSiTi)N Thin Films as a Function of Substrate Bias, Vinay Joru, Sudharshan Phani Pardhasaradhi, Venkata Girish Kotnur, University of Hyderabad, India**

This study investigates the relationship between the structural and mechanical properties of (AlCrNbSiTi)N thin films deposited on Si (100) substrates using direct current magnetron sputtering (DCMS), varying the substrate bias from 0 to -200 V. Characterization techniques employed include X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) for crystal structure analysis, along with field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) for microstructural assessment. Mechanical properties were evaluated through nanoindentation. The results indicate that all films exhibit a NaCl-type face-centred cubic (FCC) crystal structure with a predominant (200) orientation. Notably, surface morphology transitioned from granular to triangular facets, eventually leading to a featureless and smooth appearance as substrate bias increased from 0 V to -200 V. The growth morphology shifted from columnar to dense and featureless with increasing bias. Additionally, film thickness decreased from 950 nm to 650 nm due to ion bombardment during growth. Mechanical properties improved significantly, with hardness rising from 18 GPa to 31 GPa and film modulus increasing from 173 GPa to 261 GPa as substrate bias changed from 0 V to -200 V. The ratios  $H/E$  and  $H^3/E^2$  for the film at -200 V were found to be 0.12 and 0.44, respectively, surpassing values reported in existing literature for the (AlCrNbSiTi)N system. This enhancement in mechanical properties will be reported in correlation with their structural characteristics.

**Keywords:** (AlCrNbSiTi)N thin films, substrate bias, growth mechanism, and mechanical properties.

11:40am **MA4-2-WeM-12 Effect of Elemental Concentration on Mechanical and Tribological Properties of (AlNbSiTiZr)N Thin Films, Tongyue Liang, Stéphanie Bessette, Raynald Gauvin, Richard Chromik, McGill University, Canada**

(AlNbSiTiZr)N thin films were deposited on silicon wafer and steel substrates using pulsed DC magnetron sputtering with four distinct targets (AlSi, Ti, Nb, Zr). The elemental concentration of each constituent was tuned by adjusting the discharge current applied to each target. The thickness of the deposited films was maintained at approximately 1.3  $\mu\text{m}$ . Three different (AlNbSiTiZr)N thin films with slight variations in elemental concentrations were studied to assess the impact of compositional changes on their structure and properties. The films were characterized for surface and cross-sectional morphology, microstructure, roughness, and mechanical properties. A minor increase in the concentrations of Nb and Zr (5 at.% for each) led to a significant improvement in hardness, increasing from  $12.7 \pm 0.7$  GPa to  $20.8 \pm 0.5$  GPa. The tribological properties of the films were studied using a ball-on-plate tribometer under dry air conditions with a load of 0.5 N for 1000 sliding cycles. The results indicate that the wear resistance of the (AlNbSiTiZr)N thin films improved with the increased concentrations of Nb and Zr.

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