Tribology and Mechanics of Coatings and Surfaces
Room Palm 5-6 - Session MC2-1-TuA

Mechanical Properties and Adhesion I
Moderator: Alice Lassnig, Austrian Academy of Sciences, Austria

1:40pm **MC2-1-TuA-1 Nanoscale Interface Engineering for Thin Films on Polymer Substrates***, **Barbara Putz [barbara.putz@empa.ch]**,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland **INVITED**

Atomic layer deposition (ALD) holds enormous potential to design interfaces, due to the unique way in which a material is built in an atomic layer-by-layer fashion. When combined with other thin film techniques, such as magnetron sputtering (PVD), without breaking vacuum, the layer-by-layer nature of ALD can be harvested to design (sub)nanoscale interface architectures. An interesting area for this combined deposition are metal-polymer interfaces, where thin amorphous interlayers (IL, 5 nm thick) between metal film and polymer substrate favour strong and stable interfaces [1-3]. Until now, interlayer formation is governed by the film/substrate chemistry and deposition method, preventing high interface quality for the majority of material combinations and fabrication routes. Since ultrathin ALD layers uniquely resemble the reported interlayer in structure and chemistry, interlayer formation can, for the first time, be mimicked artificially to clarify the role of these structures in thin film delamination.

Through a combined ALD/PVD setup, we fabricate and study Al thin films (150 nm) with different ALD interlayer thicknesses (Al_2O_3 + H, 0.12 - 25 nm) on a polyimide substrate. Mechanical properties are measured via uni- and equi-biaxial tensile loading [4] with in-situ X-ray diffraction and electrical resistivity measurements from the evolution of Al film stress, width of the Al diffraction peak and electrical resistivity as a function of IL thickness and applied strain. Adhesion energy between metal film and polymer substrate is calculated using the tensile induced delamination method.

In our study, differences in the system's mechanical behaviour (yield strength, crack onset strain) are found to be driven by the microstructure of the metallic Al layer (film thickness and grain size), while the crack propagation (electrical failure strain) and adhesive performance (buckle density) is dominated by the interface structure. Significant embrittlement and fracture is only observed for thick interlayers (>= 25 nm).

[1] Putz, B. et al., Adv. Eng. Mater. (2022), 2200951

[2] Putz, B. et al. Surf. Coat. Technol. 332, 368–375 (2017)

[3] S. Oh. Et al., Scripta Materialia 65 (2011) 456–459

2:20pm **MC2-1-TuA-3 Trilayer Fracture and Adhesion Investigated with in-Situ Synchrotron Radiation***, **Megan J. Cordill [megan.cordill@oeaw.ac.at]**,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; Shuhel Altaf Husain,* Université Sorbonne Paris Nord, France*; Claus O.W. Trost,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; Damien Faurie,* Université Sorbonne Paris Nord, France*; Pierre O. Renault,* University of Poitiers, Pprime Institute, France

Flexible and wearable electronics use multiple metal films on polymer substrates to achieve functionality where the resistance to through thickness fracture and the adhesion to the polymer substrates determines device performance. Commonly, flexible material systems are made of layers ductile metals of copper or aluminum as the conducting layers with more brittle molybdenum and chromium used as interlayers to improve adhesion to the polymer substrate or as protective capping layers. In this work, in-situ uniaxial tensile straining was used to investigate the fracture and delamination behavior of brittle-ductile-brittle trilayers. The method uses uniaxial straining to cause fracture of the film system perpendicular to the tensile loading direction and film delamination parallel to the tensile loading direction, which allows the adhesion energy to be evaluated. Experiments on the differently layered samples, namely Mo-Cu-Cr and Nb-Cu-Mo, were performed with in-situ resistance measurements and X-ray diffraction (XRD). Combined with post-straining confocal laser scanning microscopy, XRD provided the film stress evolution simultaneously in every layer to understand fracture of trilayer systems and how adhesion can be measured using tensile induced delamination. The main aspects presented will be adhesion energy along with the stress evolution under uniaxial tensile loading of the various trilayer architectures. Results indicated that the position of the Mo layer can influence the fracture behavior. It was also observed that only the presence of a brittle layer, rather than the position (interface layer vs. top layer), aids delamination in trilayers. Compared to single layer films of similar thickness, no significant change in the calculated adhesion energy of the same trilayer interfaces was found.

2:40pm **MC2-1-TuA-4 The Model to Explain the Origin of Residual Thin Film Stress***, **Tong Su [tong_su@brown.edu]**, Eric Chason,* Brown University, USA

Residual stress has been a long-standing problem in thin film deposition, and it is critical to the adhesion and physical properties of their applications. In previous works, we have studied the mechanisms and used modeling to explain the stress evolution in the post-coalescence stage (typically 50 nm ~ 400 nm) and steady state (>400 nm or when the stress does not change significantly). The early stage of growth (<50 nm) is not as well studied as the others and yet this state is important to the origin of the thin film stress. Here we present a model to explain the behavior of residual stress in the early stage with the assumption that the deposited particles form hemisphere islands on the substrate. The model is applied to analyze stress measurements of e-beam evaporated Ag and Ni from the wafer curvature measurements. The results suggest that the end of the coalescence stage may not be sufficient to explain the occurrence of the tensile peak in the early state. Rather, the balance between tensile and compressive stress mechanisms as the grain boundary is formed between islands needs to be considered.

3:00pm **MC2-1-TuA-5 Novel Approach for Scratch Analysis of Ductile Metallic Layers on Fragile Substrates***, Mohammad Arab Pour Yazdi, Pavel Sedmak,* Anton Paar TriTec SA, Switzerland*; Parth Kotak,* Anton Paar USA*; Jiri Nohava,* Anton Paar TriTec SA, Switzerland*; **Mark Haase [mark.haase@anton-paar.com]**,* Anton Paar, USA

In the electronics and semiconductor industries, there is a growing demand for precise characterization of adhesion properties in soft metallic multilayers on fragile substrates, such as semiconductor wafers and glass. Consequently, nondestructive testing methods have become essential to prevent damage to these sensitive substrates during testing. Conductive metallic layers including gold (Au), platinum (Pt), copper (Cu), and silver (Ag) are critical for microchip pathways; however, their ductility poses challenges for adhesion testing on brittle substrates. Traditional nanoscratch methods, which use sphero-conical indenters, rapidly traverse these soft layers and exert significant stress on the fragile substrates. This often results in substrate failure rather than yielding valuable insights into the interfacial adhesion of the layers.

In this study, we introduce a novel scratch testing method specifically designed for soft metallic layers or multilayers on fragile substrates. This approach employs a micro wedge blade indenter, rather than the conventional spheroconical indenter, along with a two-axis tilt stage sample holder, enhancing precision and reducing substrate damage to yield more reliable adhesion measurements. This method is particularly suited for ductile metallic coatings deposited via PVD, CVD, and ALD, providing a robust solution for accurately assessing the adhesion properties of soft metallic coatings on sensitive substrates.

Keywords: Ductile coatings; Fragile substrates; Adhesion testing; Wedge blade indenter; Nanoscratch testing.

4:00pm **MC2-1-TuA-8 The Comparison in Microstructure and Mechanical Properties of MoN Films Deposited by RFMS and HiPIMS Techniques***, **Chi-Yueh Chang [w6208asx@gmail.com]**,* National United University, Taiwan

The MoN films are gathering increasing attentions for their high-performance characteristics, making the production of high-quality MoN films an important research focus. In this study, Mo-N thin films are coated using radio frequency magnetron sputtering, RFMS, and high intensity power impulse magnetron sputtering, HiPIMS, techniques. The input power and Ar/N_2 ratio are adjusted from 150 to 200W and 15/5 to 18/2 sccm/sccm to control the microstructure. The duty cycle of the HiPIMS from 4 to 10% is also manipulated to trigger higher peak power density and current. A columnar structure feature was observed across all thin films. Nevertheless, the phase of the Mo-N changes under different parameters. Through RFMS, as the Ar/N_2 ratio was raised from 15/5 to 18/2 sccm at 150 W input power, a significant evolution of major Mo_2N to MoN phase was observed. With higher peak current and power density through HiPIMS deposition, a multiple phase feature with decreased grain size of Mo-N phases were discovered. The microhardness, elastic modulus, wear resistance and indentation cracking behavior were investigated. The correlation between microstructure evolution and the mechanical properties were also discussed.

Keywords:RefractoryThin film coatingsMoNHipims

4:20pm **MC2-1-TuA-9 Quantitative 3D FIB-SEM Characterization of Single Cu Particle Impacts for Cold Spray Applications***, **Veera Panova [vpanova@mit.edu]**,* Massachusetts Institute of Technology, USA*; Christopher Schuh,* Northwestern University, USA

Cold spray is a solid-state additive manufacturing process that produces coatings and standalone parts by accelerating micron-sized metallic particles to supersonic velocities. Upon impact, the particles and substrate undergo plastic deformation, surface oxide layers get disrupted, and direct particle-substrate contact is achieved to attain metallurgical bonding. Our recent works take advantage of the Laser-Induced Particle Impact Test (LIPIT) to produce single microparticle impacts under carefully controlled conditions, providing a unit-process understanding of cold spray physics. Each launched particle is well-characterized: its size, morphology, microstructure, velocity, and in-flight behavior are known. We then analyze impact sites using focused ion beam-scanning electron microscopy (FIB-SEM) to study multiple aspects of the impact event: bonding at particle-substrate and particle-particle interfaces, deformation at high strain rates, and microstructural evolution. The major advantage of this approach is that it is tomographic, providing direct 3D observations of the interfaces, as well as quantitative measurements of the bonded area and microstructural changes around the impact site.

This talk will review several observations that 3D tomography of the impact sites reveals about structure development in cold spray. First, we observe generally non-symmetrical bonding at the particle-substrate interface and conclude that bonding takes place top-down; regions experiencing high strain bond first. These insights conform to a model for particle-substrate bonding through oxide-layer rarefication and provide guidelines for how to optimize processing parameters to produce well-bonded cold spray coatings. Second, our microstructural observations reveal limiting conditions for the development of recrystallization structures. Such information speaks to the development and dissipation of adiabatic heat upon impact.

4:40pm **MC2-1-TuA-10 Mechanical Properties and Deformation Mechanisms of Metallic Thin Films Synthetized by Pulsed Laser Deposition***, Francesco Bignoli, Davide Vacirca, Philippe Djemia,* Laboratoire des Sciences des Procédés et des Matériaux (LSPM) – CNRS, France*; Andrea Li Bassi,* Department of Energy, Politecnico di Milano, Italy*; James Paul Best, Gerhard Dehm,* Max-Planck Institut für Eisenforschung, Germany*; **Matteo Ghidelli [matteo.ghidelli@lspm.cnrs.fr]**,* Laboratoire des Sciences des Procédés et des Matériaux (LSPM) – CNRS, France

The ongoing trend toward miniaturization in device components across key technologies demands the synthesis of high-performance nanostructured films with exceptional combination mechanical properties such as high yield strength and plasticity which, however, are mutually exclusive. In order to overcome such trade off, it is crucial to control the atomic composition and the microstructure, going beyond currently nanoengineering design approaches for thin films. One main limitation arises from conventional thin film deposition techniques (sputtering) with limited possibility to fabricate novel microstructures such as with ultrafine grains or nanoscale laminates alternating layers of different compositions and phases with intrinsic dimensions on the order of a few nanometers. Such features could induce mechanical size effects, influencing deformation mechanisms and enabling highly tunable and enhanced mechanical properties.

Here, I will show the potential of Pulsed Laser Deposition (PLD) as a novel technique to synthetize advanced metallic thin films, reporting the fabrication of a variety of microstructures with tailored composition and nanoscale features including compact, nanogranular and crystal/glass ultrafine nanolaminates and focusing on the deformation behavior and mechanical properties.

First, I will focus on the on the fabrication of thin film metallic glasses with different composition ZrCu, ZrCuAl (with also O addition) and controlled microstructure, compact and nanogranular [1]. The mechanical characterization with optoacoustic techniques, nanoindentation and *in situ* SEM micropillar compression reports large and tailored mechanical properties, above sputter-deposited counterparts, reaching ultimate yield strength (>4 GPa) and ductility (>15 %) for ZrCuAl/O films. Then, I will show the fabrication of ultrafine glass/crystal (ZrCu/Al) nanolaminates with high and tunable density of interfaces (nanolayer thickness <5 nm), reporting shear bands blocking and homogenous deformation, in combination with large plasticity (> 10%) and yield strength (>3.4 GPa) [2].

Lastly, I will focus on the PLD synthesis of CoCrCuFeNi crystalline high entropy alloys showing unique microstructure and ultrafine grains (≈10 nm), triggering Hall-Petch strengthening resulting in high hardness (≈10.5 GPa) and yield strength (1.9 GPa) significantly above sputter-deposited counterparts, while retaining large plastic deformability (30%) [3].

[1] M. Ghidelli *et al.*, Acta Mater., 213, 116955, 2021.

[2] F. Bignoli *et al.*, ACS Appl. Mater. Interfaces, 16, 27, 35686–96, 2024.

[3] D. Vacirca *et al*., Submitted to Acta Mater, 2024.

5:00pm **MC2-1-TuA-11 The Forgotten Method: Coatings Mechanical Properties Calculated According to ISO Standard 14577***, **Esteban Broitman [ebroitm@hotmail.com]**,* EDB Engineering Consulting, France

When an indenter penetrates the surface of a film deposited onto a substrate, the mechanical response of the film will be influenced by the mechanical properties of the substrate, according to its penetration depth h and the film thickness *t*. As the depth of penetration h increases, more of the mechanical contribution will come from the substrate.

From the first work published by H. Bückle in 1959 for microindentations, there have been many theoretical and experimental published research works trying to show how the hardness and elastic modulus of the coatings should be calculated in order to avoid any influence of the substrate [1].

ISO Standard 14577 “Metallic Materials—Instrumented Indentation Test for Hardness and Materials Parameters” published for first time in 2002, was written to make some order in the way to use nanoindenters. The standard included originally 3 parts: Part 1: Test method; Part 2: Verification and calibration of testing machines; and Part 3: Calibration of reference blocks. Some years later, the standard included a new Part 4: Test method for metallic and non-metallic coatings. This section of the Standard contains a method that has been ignored by most of researchers.

In this presentation, we will review the four parts of ISO standard 14577. In particular, we will analyze the simple experimental methodology established in Part 4 that, in most of cases, gives the correct values for hardness and elastic modulus, independently of the coating/substrate system.

[1] E. Broitman, Indentation Hardness Measurements at Macro-, Micro-, and Nanoscale: A Critical Overview. Tribol. Lett. 65 (2017) 23.

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