Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 1-2 - Session CM1-2-ThA

Spatially-resolved and in situ Characterization of Thin Films, Coating and Engineered Surfaces II

Moderators: Damien Faurie, Université Sorbonne Paris Nord, Barbara Putz, Empa Thun, Aparna Saksena, MPI für Eisenforschung GMBH, Germany

1:20pm **CM1-2-ThA-1 Crystalline-Amorphous Interface Fracture Explored Across Different Length Scales***, **Alice Lassnig**,* Montanuniversitat Leoben, Austria*; Michael Meindlhumer,* Montanuniversität Leoben, Austria*; Stanislav Zak,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; Megan Cordill, Christoph Gammer,* Austrian Academy of Sciences, Austria*; Andrew Minor,* Lawrence Berkeley Lab, USA **INVITED**

Interfaces separating bi- and multilayered thin film structures, are susceptible to premature failure due to the challenge of bridging distinct physical properties of adjacent materials. Thus, the reliability of these interfaces significantly influences the overall lifespan of such structures. Consequently, a thorough investigation of their reliability and a comprehensive understanding of the underlying failure mechanisms are essential for enhancing novel material composites and combinations.

In this study, we investigate the fracture behavior of model crystalline-amorphous interfaces, specifically focusing on Cu thin films delaminating from bulk glass substrates and nanocrystalline Cu – amorphous CuZr multilayers. Utilizing advanced characterization techniques, we aim to study the delamination behavior, interface adhesion, and fracture under static and cyclic loading of such structures using advanced experimental techniques spanning both the meso-scale and nanoscale, incorporating in situ transmission electron microscopy for a detailed exploration of these phenomena.

2:00pm **CM1-2-ThA-3 Tailoring Structure and Mechanical Properties of TiZrHfTa Refractory Alloy Thin Films***, **Gregory Abadias**, Hocine Slimani,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; Pietro Vecchietti,* Politecnico Milano, Italy*; Meriadeg Chalopin,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; Ferenc Tasnádi,* Linköping University, IFM, Sweden*; Matteo Ghidelli, Philippe Djemia,* Laboratoire des Sciences des Procédés et des Matériaux (LSPM) – CNRS, France

Complex concentrated alloys (CCAs), including medium- and high-entropy alloys, offer attractive thermomechanical properties which make them promising candidates for various technologies such as corrosion resistant or radiation tolerant structural materials. Among the various CCAs, alloys with multi-principal refractory elements (RCCA) have drawn significant attention for hydrogen (H) storage applications [1-3] due to their ability to reversibly absorb H in the form of metal hydrides. However, up to now, studies on RCCA for H storage have only focused on bulk materials, with limited attention to thin film counterparts, which could be considered as model materials enabling an easy tailor of composition, phase and microstructural features (grain size, porosity or texture), providing valuable insights on the mechanisms of hydride formation and dissolution in RCCAs.

In this work, $(TiZrHf)_{100-x}Ta_x$ thin films, with thickness up to 700 nm and Ta content ranging from 0 to 60 at.%, were synthesized by co-sputtering deposition. The phase composition, crystal structure, morphology and elemental composition was determined using a combination of analytical techniques (XRD, SEM/TEM, EDS), while the intrinsic stress was measured *in situ* during deposition by wafer curvature method. The mechanical properties of the films were assessed by nanoindentation and opto-acoustics (Brillouin light scattering and picosecond laser ultrasonics) methods. By tuning the Ta content, different phases were stabilized in these quaternary alloys, from hcp to bcc and amorphous. These structural changes are accompanied by variation in growth morphology (evolving from nanocolumns to vein-like patterns), stress reduction and a progressive softening of hardness, shear and elastic modulus with increasing Ta content. The experimental findings are discussed and compared with results obtained from atomistic models of random alloys and amorphous phases, using *ab initio* molecular dynamics simulations combined with machine-learned interatomic potentials, as well as relevant data from the existing literature [4].

References:
1. Marques, F., Balcerzak, M., et al., *Review and outlook on high-entropy alloys for hydrogen storage*. Energy Environ. Sci. 14, 5191 (2021)
2. Kong, L., Cheng, B., Wan, D., Xue, Y., *A review on BCC-structured high-entropy alloys for hydrogen storage*, Front. Mater. 10, 1135864 (2023)
3. Shahi, R. R., Gupta, A. K., Kumari, P., *Perspectives of high entropy alloys as hydrogen storage materials*, Int. J. Hydrogen Energy 48, 21412 (2023)
4. Huang, S., Li, W., Holmström, E., Vitos, L., *Phase-transition assisted mechanical behavior of TiZrHfTax high-entropy alloys*, Sci. Rep. 8, 12576 (2018)

2:20pm **CM1-2-ThA-4 Exploring Mechanical Properties of Thin Films Through Synchrotron X-Ray Diffraction, Digital Image Correlation and Electrical Resistivity Measurements***, **Pierre-Olivier Renault**,* University of Poitiers, France **INVITED**

Mechanical behavior of thin films deposited on polymeric substrates was investigated under in-situ controlled tensile biaxial loading conditions. The study employed synchrotron X-ray diffraction (XRD), digital image correlation (DIC) techniques, and electrical resistivity measurements. The combination of X-ray diffraction and digital image correlation provides classical stress-strain curves.

The three complementary measurement techniques allow for a comprehensive analysis of the deformation characteristics of each component of the thin film. This approach helps to identify and distinguish the various deformation regimes that arise during mechanical loading. Beyond the yield stress, distinct mechanical behaviors are observed in the stress-strain curves, which can be attributed to plasticity and fracture phenomena. These behaviors are identified as characteristic signatures of material failure modes.

Additionally, the experimental setup offers the capability to assess whether deformations are fully transmitted through the interfaces between the thin film and the substrate, providing also insight into the interaction between different layers in a multilayer coating.

After describing the experimental setup, examples of the mechanical behaviors observed in metallic bilayer or trilayer systems and, oxide-metal films deposited on polyimide substrates will be presented. These examples illustrate the range of deformation responses that can arise in such multilayer systems. Differences in the mechanical behavior of films are shown to be influenced by factors such as type of interface or the presence of residual stresses in the as-deposited films, as well as variations in film thickness and grain size. These factors play a key role in determining the overall mechanical performance of the thin film systems.

3:00pm **CM1-2-ThA-6 A Combined X-ray Microdiffraction and Micromechanical Testing Approach for Direct Measurement of Thin Film Elastic Constants***, **Rainer Hahn**,* CDL-SEC, TU Wien, Austria*; Rebecca Janknecht,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; Nikola Koutná,* Institute of Materials Science and Technology, TU Wien, Austria*; Anna Hirle,* CDL-SEC, TU Wien, Austria*; Anton Davydok,* Helmholtz-Zentrum Hereon, Germany*; Klaus Boebel,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; Szilárd Kolozsvári, Peter Polcik,* Plansee Composite Materials GmbH, Germany*; Christina Krywka,* Helmholtz-Zentrum Hereon, Germany*; Paul H. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; Helmut Riedl,* CDL-SEC, TU Wien, Austria

The direct measurement of elastic constants for thin films is not yet a routine procedure and presents a number of significant technical and analytical challenges when compared to the analysis of bulk materials. Ab initio density functional theory calculations can provide a theoretical basis for understanding the properties of materials. However, discrepancies between model systems and real-world properties persist, primarily due to a lack of available experimental data for newly emerging material systems. Furthermore, computationally affordable models are typically constrained to defect-free single crystals, thereby excluding microstructural effects that exert a pronounced influence on the material's behavior.

This study addresses this gap by proposing a novel experimental approach to measure direction-dependent elastic constants, combining synchrotron microdiffraction and micropillar compression. The approach was tested on a polycrystalline face-centered cubic TiN thin film, where linear elastic failure prevails. An advanced in-situ testing environment has been established to enable the continuous recording of the load-displacement of the indenter, while simultaneously collecting the material's deformation response to uniform uniaxial compression. This dynamic approach permits the evaluation of the orientation-dependent elastic strain components and the macroscopic uniaxial compressive stresses, each over time, thereby enabling a differential analysis to assess the elastic and X-ray elastic constants.

The excellent agreement between experimental and ab initio data serves to corroborate the here-proposed robust method for direct elastic constant measurements, which is of crucial importance for advancements in thin film material testing.

3:20pm **CM1-2-ThA-7 Real-Time Particle Detection for Enhanced Coating Deposition Processes**, ***Constant Boris Rieille***, *Sylvain LeCoultre*, Berner Fachhochschule BFH, Switzerland

Industries in photonics, optics, and semiconductors are increasingly challenged by particles emitted during PVD/ALD deposition processes. As device miniaturization advances, stricter requirements on defect size and particles inclusions make effective control essential to ensure product conformity.

Currently, these industries rely on preventive maintenance schedules that do not account for unexpected particle emissions or variations in machine usage. When particles appear, repeated maintenance is required due to the lack of a system to detect or locate their source. Integrating a real-time particles sensor into machines would transform this approach by enabling predictive monitoring, reducing downtime, and improving operational efficiency.

This session will deliver key insights into particle emissions during PVD deposition, explore market trends, and present business cases for the PVD/ALD market.

4:00pm **CM1-2-ThA-9 Real-Time Monitoring of Sputter Deposition Process: Application in the Context of Ag-Based Low-Emissive Coatings**, ***Rémi Lazzari***, CNRS/Sorbonne Université, France **INVITED**

The challenge of green-house gas reduction pushes towards a better thermal insulation of housing. In this context, glass industry strives to decrease the infra-red radiative transfer across windows while keeping transparency. In the so-called low-E or solar control glazings, the functionality is provided by a complex stack of layers deposited by magnetron sputtering in which the active component is a ~10 nm thick Ag film encapsulated in between ZnO dielectric layers. Because of its noble character, Ag follows intrinsically a Volmer-Weber growth mode and is prone to dewetting upon thermal treatments such as windows tempering. Thus, there is tremendous need of understanding and control of its out-of-equilibrium growth process.

In this context, this presentation will illustrate the interest of combining real-time measurements (UV-vis spectroscopy[1,2]; stress measurement via wafer curvature and digital image correlation[3]; film resistivity) with *in situ* photoemission spectroscopy to have a full overview on the Ag growth mechanism. Among others, the impact of sputtering deposition parameters and of gas additives on stress build-up and relaxation, on film percolation and on Ag chemistry will be discussed[4-6]. The second part of the talk will show the contribution of model experiments in understanding the epitaxy at Ag/ZnO interface[7], the reactivity[8] and band alignment[9] at metal/ZnO interfaces as seen by *in situ* hard x-ray photoemission and the various contributions to Ag film resistivity[7].

[1] I. Gozhyk, L. Dai, Q. Hérault, R. Lazzari, and S. Grachev. *J. Phys. D: Appl. Phys.*, 52:095202, 2018.

[2] R. Lazzari, J. Jupille, R. Cavallotti, E. Chernysheva, S. Castilla, M. Messaykeh, Q. Herault, and E. Meriggio. *ACS Appl. Nano Mater.*, 3:12157–12168, 2020.

[3] S. Grachev, Q. Hérault, J. Wang, M. Balestrieri, H. Montigaud, R. Lazzari, and I. Gozhyk. *Nanotechnology*, 33:185701, 2022.

[4] Q. Hérault, I. Gozhyk, M. Balestrieri, H. Montigaud, S. Grachev, and R. Lazzari. *Acta Mater.*, 221:117385, 2021.

[5] R. Zapata, M. Balestrieri, I. Gozhyk, H. Montigaud, and R. Lazzari. *ACS Appl. Mater. Interfaces*, 15:36951–36965, 2023.

[6] R. Zapata, M. Balestrieri, I. Gozhyk, H. Montigaud, and R. Lazzari. *Appl. Surf. Sci.*, 654:159546, 2024.

[7] F. Corbella, V. Haspot, Y. Zheng, D. Guimard, H. Montigaud, and R. Lazzari. *submitted*, 2024.

[8] E. Chernysheva, Rensmo H. Philippe, B., O. Karis, M. Gorgoi, E. Burov, S. Grachev, M. Montigaud, and R. Lazzari. *Appl. Surf. Sci.*, 680:161409, 2023.

[9] E. Chernysheva, W. Srour, B. Philippe, B. Baris, S. Chenot, R. F. Duarte, M. Gorgoi, H. Cruguel, H. Rensmo, H. Montigaud, J. Jupille, G. Cabailh, S. Grachev, and R. Lazzari. *Phys. Rev. B*, 97:235430, 2018.

4:40pm **CM1-2-ThA-11 A Combination of Real-Time Diagnostics Probing the Impact of N_2 on Ag Thin Film Growth**, ***Michal Kaminski***, KIT, Germany; *Gregory Abadias, David Babonneau*, Institute Pprime, France; *Alessandro Coati, Yves Garreau*, Synchrotron SOLEIL, France; *Anny Michel*, Institute Pprime, France; *Anton Plech*, KIT, Germany; *Andrea Resta*, Synchrotron SOLEIL, France; *Karan Solanki*, Institute Pprime, France; *Alina Vlad*, Synchrotron SOLEIL, France; *Baerbel Krause*, KIT, Germany

Silver thin films are used in a number of applications (e.g., transparent and conductive electrodes and plasmonic devices) which require a continuous layer with thickness below a few nanometers. However, Ag films grown by magnetron sputtering have the tendency to form 3D-structures on weakly interacting substrates, what prevents their application as transparent and conductive layers. It is reported that the use of gas additives (particularly N_2 [1]) allows for obtaining a continuous layer at earlier deposition stage.

A thorough understanding of the nanoscale mechanisms of thin film formation requires real-time techniques [2]. In particular the widely used *ex situ* diagnostics can provide misleading information, as the structure of the thin film can evolve even under high vacuum conditions. We employ a simultaneous combination of real-time grazing incidence small-angle x-ray scattering (GISAXS), grazing incidence diffraction (GID), and substrate curvature measurements to get information about polycrystalline thin film evolution during growth. In particular, GISAXS reveals changes in nanoscale morphology, GID gives insight into the crystallinity of thin films, and substrate curvature measurements provide information about the average intrinsic stress. With our methodology we can study the interdependence between stress state, thin film structure and morphology, using the quantitative information obtained from the scattering techniques. Since the influence of the substrate curvature can be crucial for grazing incidence condition x-ray techniques, we show that in the curvature regime encountered in our experiment the effect on GISAXS is negligible.

Using the information from all three techniques, we will discuss the impact of nitrogen additive on all growth stages (from initial stages of island nucleation, growth, and coalescence, up to formation of percolated and continuous films), including the relaxation of the film during growth interruptions.

Acknowledgements: The work is performed within the frame of the ANR-DFG project IRMA (491224986).

Literature:

[1] A. Jamnig et al., ACS Appl. Nano Mater. 3, 4728-4738 (2020)

[2] B. Krause et al., ACS Appl. Mater. Interfaces 15, 11268-11280 (2023)

Author Index

Bold page numbers indicate presenter