Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H1-2-MoA

Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces II

Moderators: Dr. Damien Faurie, Université Sorbonne Paris Nord, France, **Dr. Michael Tkadletz**, Montanuniversität Leoben, Austria

1:40pm **H1-2-MoA-1 Multimodal and *in Situ* Electron Microscopy to Understand Local Deformation Mechanics*, Josh Kacher,*** Georgia Institute of Technology, USA **INVITED**

Understanding dislocation generation mechanisms and interactions with obstacles such as grain boundaries and other dislocations is central to understanding the mechanical behavior of metals and alloys, including thin films. This has motivated decades of research into the unit processes governing dislocation interactions by *in situ* transmission electron microscopy (TEM) mechanical testing, resulting in the establishment of basic rules that govern how these interactions occur. However, much of this research has been largely observation based with direct quantification of the interactions in terms of the local and global stress state limited. With the advent of high speed electron detectors and the continued improvement of quantitative *in situ* mechanical testing platforms, it is now possible to extract accurate information on the material stress state associated with dislocation generation and their interactions with surrounding microstructural features, spurring renewed interest into these fundamental dislocation interactions. These advances have necessitated the increased integration of data analytics based analysis of results as data acquisition rates now exceed what can be manually processed and understood. They also open new spaces for integration with computational simulations, beyond simple visual comparisons that are prone to human bias.

In this talk, I will discuss the development of advanced *in situ* TEM testing techniques, including local stress mapping and multimodal imaging via scanning nanobeam diffraction as well as quantification of the global sample stress state using MEMS-based nanomechanical testing platforms. I will discuss these advances in terms of two materials systems: understanding transgranular and intergranular dislocation mechanisms in ultrafine grained thin films and understanding the influence of the deformation-induced grain boundary state on dislocation/grain boundary interactions in coarse-grained thin films. For both of these systems, I will also discuss how irradiation induced defects affect local strain accommodation and active deformation mechanisms.

2:20pm **H1-2-MoA-3 Nanomechanical Characterization and Residual Stress Analysis in Thin ALD Coatings on 3D Printed Nano-Ceramics*, Marco Sebastiani,*** Università degli studi Roma Tre, Rome, Italy

Recently, Nano-Architected Mechanical Metamaterials (NAMM) have been proposed as a novel class of lightweight and sustainable materials, where a unique combination between high strength and low density is achieved. Such materials are usually produced by Two-Photon Lithography (TPL) Direct Laser Writing (DLW) method, which allows for fast 3D printing with nanoscale spatial resolution.

Unfortunately, the improvement of strength is usually not accompanied by a similar improvement of toughness and ductility, because of the effects of imperfections and flaws on structural reliability.

In this work, we explore the effects of this ALD coatings, by different materials, on the strength and toughness of NAMM.

In particular, we present a detailed study on the effect of the coatings' residual stress on the apparent fracture toughness, showing that a significant change in the crack propagation mechanisms for different residual stress states in the thin film.

The residual stress in the films with thickness below 50 nm is measured by an improved FIB-DIC method, which was specifically optimized to achieve sub-micrometer lateral and depth resolution.

This study demonstrated that fracture toughness in additively manufactured nano-ceramics is, in contrast to macroscopic ceramics, is a surface dominated characteristic, where surface residual stress states can have a paramount effect on reliability and durability

2:40pm **H1-2-MoA-4 *In-Situ* Monitoring of Stress Evolution in Hipims-Deposited Ti-Al-N Films: Effect of Substrate Bias and Temperature*, Pedro Renato Tavares Avila,*** *O. Zabeida, L. Varela Jiménez, J. Klemberg-Sapieha, L. Martinu,* Polytechnique Montréal, Canada

The origin of stress during film deposition is a topic of interest in the surface engineering community and requires appropriate investigation tools to explain the different mechanisms acting on the evolution of stress, and how they relate to process conditions and materials characteristics. The use of a single stress analysis methodology relying on *ex-situ* results cannot provide a complete insight into stress formation and makes the distinction among the different stress contributors difficult.

In the present work, we used *in-situ* curvature stress probing combined with *ex-situ* techniques such as $Sin^2\psi$ in depositions of TiAlN films, to understand the mechanisms underlying stress evolution. Films were prepared at room temperature (RT) and 300 °C, and four bias strategies, namely two conditions with constant values of 0 V and -75 V, and two conditions with a superposition of layers with alternating high and no bias have been applied.

At RT, the bias increase changed the stress from slightly tensile to compressive, with a small rise in hardness (H), while at 300°C, the use of higher bias increased the compressive intrinsic stress by 3 GPa along with H from 14 to 30 GPa. The combined stress analysis revealed three mechanisms acting in the evolution of intrinsic stress: 1) grain boundary (GB) closing (tensile), dominating at conditions of low adatom mobility and low ion energy bombardment; 2) atom insertion in GB (compressive), dominating at high mobility and low energy of bombardment, and 3) defect generation (compressive), dominating at highly energetic bombardment and low temperature.

In-situ stress probing allowed direct calculation of thermal stress (TS) and determination of the Coefficient of Thermal Expansion (CTE) and Poisson's ratio (v) of TiAlN. CTE increased from 6.6 to 12.4 x 10^{-6} K^{-1} for higher bias, while v was found to be 0.22.

The use of alternating bias showed a dependence of the structure and stress on the conditions of previous layers. When growing dense on porous films, the porous surface is initially filled, stopping the propagation of the less dense structure, resulting in an intermediate morphology between the conditions of 0 V and -75 V. In contrast, when growing porous on dense film, less structural change is observed, and the film resembles a dense layer deposited at a single high bias condition. Films with alternating -75/0/-75 V bias sequence presented the same H as films deposited at a single -75 V condition, but with stress 20% lower. Based on the above-described results, we will discuss the overall strategies to tailor the film stress level with respect to the specific applications and coating durability.

3:00pm **H1-2-MoA-5 High Strength and Deformability in 3D Interface Cu/Nb Nanolaminates Under Multiple Loading Orientations*, Justin Y. Cheng,*** University of Minnesota, USA*; S. Xu,* University of Oklahoma, USA*; J. Baldwin,* Los Alamos National Laboratory, USA*; M. De Leo,* University of Minnesota, USA*; I. Beyerlein,* University of California Santa Barbara, USA*; N. Mara,* University of Minnesota, USA

Bimetallic nanolamellar composites have been studied extensively to probe the influence of interface structure on mechanical properties in nanocrystalline alloys. Previously, we have shown that Cu/Nb nanolaminates incorporating 3D interfaces (3D Cu/Nb) containing chemical, crystallographic, and structural nanoscale heterogeneities in all spatial dimensions have remarkable strength and deformability compared to 2D interface counterparts (2D Cu/Nb) under *in situ* micropillar compression normal to interface planes. This work also demonstrated the role of 3D interface thickness relative to layer thickness in optimizing mechanical behavior. However, a detailed investigation of post-deformation microstructures was not completed. In this work, present *in situ* micropillar compression results on 3D Cu/Nb at normal and 45° inclination to interfaces to show that 3D Cu/Nb behaves more isotropically than 2D Cu/Nb and that 3D interfacial shear strength exceeds that of 2D interfaces. *Post mortem* TEM characterization of deformed 3D Cu/Nb microstructures provides insight on the effect that 3D interfaces have on energetically favored slip pathways in different loading conditions. Experimental results reveal key microstructural features indicating delayed shear instability, providing insight on possible methods for increasing strength and deformability in nanostructured alloys by controlling interface structure.

3:20pm **H1-2-MoA-6 Multiaxial Stress-Strain Transfer Across Indenter-Sample Interface During *in Situ* Indentation of Nanocrystalline Thin Films**, ***Michael Meindlhumer**, J. Todt,* Montanuniversität Leoben, Leoben, Austria*; A. Medjahed,* ESRF, The European Synchrotron, Grenoble, France*; M. Burghammer,* ESRF, The European Synchrotron, France*; M. Zitek, R. Daniel,* Montanuniversität Leoben, Leoben, Austria*; D. Steinmüller-Nethl,* CarbonCompetence GmbH, Wattens, Austria*; J. Keckes,* Montanuniversität Leoben, Leoben, Austria

Nanoindentation is routinely used to determine local mechanical properties of materials such as hardness and Young's modulus. Especially for the testing of thin films, the versatile nanoindentation method is used also on materials approaching a stiffness and hardness regime close to diamond, typically the indenter tip's material. Yet, up to now, the stress-strain response in the indenter tip remained unknown during testing of materials of extremely high hardness.

Contrary, in recent years, *in situ* cross-sectional X-ray nanodiffraction coupled with an indenter system has given new insights into the elasto-plastic deformation of thin films during indentation with a resolution down of 500 nm. In this work, the *in situ* indentation setup developed for the ID13 beamline at the ESRF was used for the first time to determine experimentally the multi-axial stress distributions across both the indenter and the tested material with a resolution below ~100 nm.

For this purpose, a 75 µm wide diamond wedge indenter tip with an opening angle of 60 deg and a tip radius of 2 µm, was coated using chemical vapour deposition with a nanocrystalline diamond thin film of 4 µm thickness. In order to test the mechanical response of the indenter-sample system, wedge samples with a thickness of ~70 µm were prepared by means of consecutive mechanical polishing, femtosecond laser ablation and focused ion beam milling steps from nanocomposite AlCrSiN, a biomimetic CuZr-ZrN multilayer and a nanocrystalline diamond thin films.

Prior to the *in situ* cross-sectional X-ray nanodiffraction experiment, the coated indenter tip is aligned parallel to the incident beam and perpendicular to the smaple using small-angle X-ray scattering microscopy. The samples of highly different elasto-plastic behaviour are loaded to the same indentation depths, which depending on the stiffness yields highly different loads. Therefore, unique multiaxial stress-strain transfer across the indenter tip-sample interface was evaluated for each sample system depending on the Young's modulus, hardness and the ability for plastic deformation of the indented material.

This new kind of indentation experiment allows for tor the first time to directly assess the multi-axial stress distributions in the contact area for both tip and tested volume. The thereby gathered results give unprecedented insights into the deformation of both indenter and tested (thin film) material.

3:40pm **H1-2-MoA-7 Film Thickness Effect on Stress Sign Transition in ITO Thin Films**, ***Jianhui Liang**, J. Zhang, K. Rubin, W. Johnson,* KLA Corporation, USA*; R. Schelwald,* KLA Corporation, Germany*; O. Amster,* KLA Corporation, USA*; B. Cuénod, R. Juttin,* EPFL, Switzerland

Indium tin oxide (ITO) is widely used as a transparent conductive thin film in the production of semiconductor devices including solar cells, liquid crystal displays (LCDs), light emitting diodes (LEDs), and sensors. However, various stress configurations are usually generated during ITO film growth, which can impact device performance. Stress-induced wafer bow changes the device planarity, impacting subsequent production processes. Stress can dramatically change the physical properties of the ITO film, potentially causing a failure of the ITO device. Quantitatively determining the stress generated during the ITO film formation and investigating the origin of the stress from a micro perspective provide tools to improve the quality of the ITO films and devices.

In this work, we report on the results of a quantitative study on the stress of ITO films with various thicknesses. ITO films were deposited on glass wafers by standard radio frequency sputtering at room temperature. The film thickness was characterized using optical reflectometry and the stress was characterized by high-precision stylus profilometry. A stress-type transition from tensile to compressive was observed with increased ITO film thickness. The highest tensile stress was 1.9GPa for the 13.7nm thick ITO film, and the highest compressive stress of -0.4GPa was found in ITO films thicker than 300nm.

A separate investigation of the surface morphology of the ITO suggests that the film follows Volmer-Weber growth, and the tensile stress originates from the impingement and coalescence of the newly-deposited film islands [1]. With the continuous deposition of the film, the grain size becomes larger and the structure transitions to a nanorod shape - fewer new islands emerge, thus decreasing the tensile stress. Compressive stress dominates and stabilizes at -0.4GPa for thicker ITO films. The origin of the post-coalescence compressive stress is consistent with the incorporation of excess material in the grain boundaries. This study reveals the thickness effect on the ITO film stress evolution, which can be a reference for the ITO film stress monitor and modulation during production process control.

1. Brian W. Sheldon, K. H. A. Lau, and Ashok Rajamani, Intrinsic stress, island coalescence, and surface roughness during the growth of polycrystalline films, Journal of Applied Physics 90, 5097 (2001).

4:00pm **H1-2-MoA-8 Reactions of Metal-Tmhd Compounds in the Gas-Phase: Insights from Microreactor Studies Using Synchrotron Radiation**, ***Sebastian Grimm**,* Institute for Combustion and Gas Dynamics, University of Duisburg-Essen, Germany*; P. Hemberger,* Paul Scherrer Institute, Switzerland*; B. Atakan,* Institute for Combustion and Gas Dynamics and CENIDE, University of Duisburg-Essen, Germany

In CVD deposition processes gas-phase reactions are often the inital steps, but gaseous intermediates can lead to unwanted film morphology, unsatisfactory purity or a depletion of the precursor, and consequently a reduction in growth rate. Understanding the decomposition mechanisms, especially the sequence of bond dissociation steps, is important for improving and modelling such processes.

Consequently, the analysis of the inital stages of growth is important and requires analytical techniques with sufficiently low detection limits for elusive gas-phase species. Because of limitations in various experimental techniques, it was until recently not possible to detect most of the postulated intermediate species and their temperatue-depdenent kinetics often remained unknown.1

We have overcome some of these challenges and demonstrated for various metal-organic precursors that by using a microreactor coupled to a very mild ionization source, we can detect and characterize elusive species, especially metal-containing intermediates, with short liftetimes below 50 µs.2,3

Here, the vacuum pyrolysis of aluminium and zirconium 2,2,6,6-tetramethyl-3,5-heptanedionate, Al(tmhd)3 and Zr(tmhd)4, is investigated. In brief, the precursor is sublimed, subsequently transported by helium carrier gas and expanded through a pinhole into a resistively heated 1 mm inner diameter SiC-microreactor of 10 mm length. Species leaving the reactor are ionized by tuneable vacuum ultraviolet (VUV) synchrotron radiation, and characterized by imaging photoelectron photoion coincidence spectroscopy (i2PEPICO) and mass spectrometry at the Swiss Light Source.

In the experiments, hydrocarbons, oxygenated and metal-containing species were detected and characterized unambigously in the gas-phase at temperature from 450-950 K, which provides insights in the underlying decomposition mechanisms. Most importantly, we detected and characterized metal-bis(diketo)acetylacetonate-H, M(C11H19O2)(C11H18O2) as major inital decomposition product in the gas-phase at temperatures above 650 K, which subsequently forms M(C11H19O2)(C10H15O2) by a methyl loss. The temperature-dependent formation mechanisms of the assigned species will be discussed and compared to previous results on M(acac)x precursors.

References:

1. Y. Jiang, M. Liu, Y. Wang, H. Song, J. Gao and G. Meng, J. Phys. Chem. A, 2006, 110(50), 13479.

2. S. Grimm, S.-J. Baik, P. Hemberger, A. Bodi, A. M. Kempf, T. Kasper and B. Atakan, Phys. Chem. Chem. Phys., 20221, 23(28), 15059

3. S. Grimm, S.-J. Baik, P. Hemberger, T. Kasper, A.M. Kempf and B. Atakan, J. Mat. Research, 2022, 37(9), 1558.

4:20pm **H1-2-MoA-9 How to Simultaneously Determine Absolute Thickness, Chemistry, and Other Properties of Crystalline Layers Using XRD**, ***Thomas Degen**, M. Sadki, N. Norberg,* Malvern Panalytical, Netherlands*; N. Shin,* Deep Solution Inc., Korea (Democratic People's Republic of)

For the in-line absolute thickness analysis of FeZn layers on galvanized steel, we developed a Rietveld [1] based, full-pattern fitting method that fits a general layered structural model to a measured XRD Scan. The fitted model then delivers both the absolute layer thicknesses as well as the chemical composition of the layers and other key information like unit cell sizes, size/strain, and texture-related information for all phases of the model. The method is implemented in the Malvern Panalytical software package HighScore Plus [2] V5.1.

The layer thickness modeling is based on the variable and increasing absorption of X-rays in the layers with different chemistry and thickness. Basically, by integrating over all beam paths, we accumulate the reduction in the intensity of the total beam. Each layer adds a new absorption term with its own linear absorption coefficient. The method is theoretically correct, still, in practice, we need to know the packing factor and density of each layer. To solve that, we introduced an instrument-dependent (alignment, tube aging, etc) calibration factor for each layer. These calibration factors are determined from a dedicated data set, where many samples are characterized using multiple methods like SEM, wet analysis, etc.

The initial fit model comprises:

1. Initial/expected thickness values, for all the phases
2. Calibration factors for all phases determined based on analyzed knowns
3. Intensity calibration factor to counteract tube aging
4. Atomic phase models, typically taken from structural databases

Output after fit:

1. Absolute thickness for all as layer-marked phases
2. All other fit model parameters, like unit cells, size/strain information, texture index, and more, including estimated standard deviations
3. Quality of fit indicators, Chi-Square, R_{wp} etc.

[1] H.M. Rietveld, *A profile refinement method for nuclear and magnetic structures*, J. Appl. Cryst. (1969), **2**, 65-71.

[2] *T. Degen, M. Sadki, E. Bron, U. König & G. Nénert*, *The HighScore Suite*, *Powder Diffr*. Vol. **29**, (2014), 13-18.

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