Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 3-4 - Session CM1-1-MoM

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

Moderators: Damien Faurie, Université Sorbonne Paris Nord, France, **Barbara Putz**, Empa, Switzerland

10:00am **CM1-1-MoM-1 Exploring Nanostructure Behavior and Ordering Dynamics Through Advanced Electron Microscopy***, **Lilian Vogl (lilian.vogl@berkeley.edu)**,* University of California at Berkeley, USA*; P. Schweizer,* Lawrence Berkeley Lab, University of California at Berkeley, USA*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; A. Minor,* University of California at Berkeley, USA **INVITED**

Characterizing the structure-property relationship and unraveling mechanism on atomic level is not only key for the development of novel nanostructures but also helps to improve the performance of materials on the bulk-scale. *In situ* electron microscopy enables the direct observation of how nano-objects respond to external stimuli, such as mechanical loading or heat treatment. For instance, the significant impact of a disordered crystal structure on the mechanical properties has been widely observed in bulk-alloys. However, the investigation of ordering characteristics in semiconducting and metallic nanostructures (thin films, nanowires) has been largely unexplored. Considering the large surface area to volume ratio of nanostructures, it is expected that local variance within the crystal lattice would have an amplified effect. Therefore, studying the precise characteristics of local ordering in nanostructures becomes all the more important to better tailor their behavior.

By using our unique small-scale model systems of alloyed nanowires, we investigate the transition from the disordered state to intermetallic phases by *in situ* heating experiments. With increasing degree of ordering, microdomains are observed showing characteristic long-rang periodicity. Visualized by 4DSTEM, such local ordering induces strain at the order-disorder domain boundary. For metallic nanowires, the size effect of “smaller is stronger” has been established, showing that nanostructures have superior mechanical properties compared to their bulk counterpart. Now, alloyed nanowires offer the opportunity to further optimize the mechanical response by tuning the ordering degree. *In situ* mechanical testing (including the acquisition of stress-strain curves) of single-crystalline nanowires with different degree of ordering demonstrate the slip-to-twin transition. While solid-solution nanowires deform via twinning, ordered ones show distinct slipping mechanism.

But ordering isn't limited to its pivotal role in alloyed systems. In the case of designing semiconducting thin films, in addition to composition, short-range ordering (SRO) can be utilized to adjust the band gap. The presence of preferential neighbors in the range of 1-2 unit cells in an otherwise random lattice induces diffusive intensity distributions in the diffraction pattern which can be visualized by energy filtered 4DSTEM. In order to manipulate the short-range ordering within the thin films, they undergo heating or irradiation, inducing atoms to exchange positions and thereby altering the local ordering.

10:40am **CM1-1-MoM-3 Autonomous Health Tracking in Self-Reporting MAX and MAB Phases***, **Peter Pöllmann (poellmann@mch.rwth-aachen.de)**[8], S. Lellig, D. Bogdanovski, A. Navid Kashani, M. Hans,* Materials Chemistry RWTH Aachen University, Germany*; P. Schweizer,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; D. Holzapfel, C. Azina, P. Zöll,* Materials Chemistry RWTH Aachen University, Germany*; D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J. Schneider,* Materials Chemistry RWTH Aachen University, Germany

Materials health defining mechanisms including chemical changes induced by annealing and oxidation have been tracked via contact-based *in-situ* resistivity measurements. The resulting changes in structure and composition have been analyzed by scanning transmission electron microscopy (STEM), selected area electron diffraction (SAED), high-energy X-ray diffraction (HEXRD), as well as differential scanning calorimetry (DSC) and related to the resistivity data. From this comparison, it is evident that Cr_2AlC, MoAlB as well as $(CrB_2)_nCrAl$ (n=1,2) exhibit autonomous self-reporting behavior as it was demonstrated that structural and chemical changes, influencing materials health, can be readily tracked by contact-based *in-situ* resistivity measurements in an application-relevant temperature regime.

Furthermore, a proof of concept for contactless materials health monitoring has been demonstrated for the first time. This contactless resistance measurement was benchmarked with respect to contact-based resistivity measurements as well as the methods mentioned above to probe structure and composition. It was shown that phase changes, decomposition, and oxidation can be tracked contactless. The proposed method can hence be utilized in the future to track the remaining lifetime of complex-shaped, fast-moving components enabling efficient and therefore more sustainable component utilization.

11:00am **CM1-1-MoM-4 Correlation of Laser-Reflection and Thermionic Emission of Thermally Loaded Coatings Under UHV Conditions***, **Lukas Wimmer (lukas.wimmer@tuwien.ac.at)**,* Vienna University of Technology, Austria*; C. Bienert, R. Schiftner,* PLANSEE SE, Austria*; C. Eisenmenger-Sittner,* Vienna University of Technology, Austria

In (ultra) high vacuum conditions the evaporation of materials at high temperatures is an important issue, which may significantly reduce the lifetime of thin coatings. To analyze the behavior of film evaporation at high temperatures, the surface evolution has been monitored in-situ using thermionic remission and a laser reflection setup. The temperature during the investigations was regulated by a pyrometer on a designated spot via direct resistive sample/substrate heating. The identified correlation between these two signals showed the capabilities of the measurement system and technique to develop new materials for high temperature applications, such as thermal barrier or thermionic emission coatings.

Within this study different oxide coatings have been analyzed, based on reactive magnetron sputtered ZrO_2 and Y_2O_3 films on tungsten substrates. Depending on the thermal stability of the respective materials, the coatings of various thickness were tested at temperatures in the range of 1200-1800°C while keeping the total pressure below 10^{-5} Pa. Even though the thermionic emission of the oxide coatings provides information regarding the coating breakdown, the reflection signal is more decisive. The reflection signal shows a strong dependence on the thickness of the “transparent” oxide coatings, allowing to obtain close information on the film evolution. For instance, the evaporation rate of ZrO_2 at 1700 °C was determined to be appr. 10 nm/h for pressures below 10^{-5} Pa. The combination of the reflection signal and thermionic emission on the other hand allows an observation of the chemical stability of the film. The investigated oxide coatings thereby maintain their chemical composition throughout the high temperature process and eventually evaporate completely.

11:20am **CM1-1-MoM-5 Bill Sproul Award and Honorary ICMCTF Lecture: When Stressed Condensed Matter Reveals Its Ultimate Secrets: Thin Film Growth Dynamics Probed by Real-Time Diagnostics***, **Gregory Abadias (gregory.abadias@univ-poitiers.fr)**[8], K. Solanki,* Institut PPrime - CNRS - ENSMA - Université de Poitiers, France*; M. Kaminski,* Karlsruhe Institute of Technology (KIT), Germany*; A. Michel,* Institut PPrime - CNRS - ENSMA - Université de Poitiers, France*; A. Vlad, A. Resta, A. COATI,* Synchrotron SOLEIL, France*; B. Krause,* Karlsruhe Institute of Technology (KIT), Germany*; D. Babonneau,* Institut PPrime - CNRS - ENSMA - Université de Poitiers, France **INVITED**

Metallic thin layers grown by physical vapor deposition (PVD) are ubiquitous in many technological areas, as key components of optoelectronic devices, architectural glazing or sensors. Due to the non-equilibrium nature of PVD, the formation of a thin solid layer from condensation of a vapor flux onto a substrate is inevitably accompanied by the development of a stress build-up [1]. The accumulated stress can significantly reduce the performance, integrity and durability of the material, so that a fundamental understanding of intrinsic stress sources, being either of tensile or compressive type, is needed. In recent years, significant progress has been gained thanks to the potentiality offered by real-time and in situ diagnostics [1-4].

We will present some recent advances on stress evolution during growth of polycrystalline metal layers based on a series of real-time wafer curvature and X-ray synchrotron experiments, and physical models. In contrast to epitaxial systems, where the stress evolution is often dominated by interface-related stresses, polycrystalline layers growing on weakly-interacting substrates reveal a complex stress evolution resulting from a subtle interplay between interface formation and microstructural evolution.

[8] **Graduate Student Award Finalist**

[8] **Bill Sproul Awardee**

Through several illustrative examples covering a broad range of sputter-deposition conditions (working pressure, temperature, particle flux, bias voltage, ionization degree) and spanning different film/substrate interaction, the influence of kinetics and energetics on growth morphology and stress development will be discussed [5], with main emphasis laid on the early growth stages. The impact of energetic particle bombardment on the compressive stress build-up observed during sputter-deposition of refractory metal layers will be explored, and the results discussed in the frame of a kinetic model which includes the influence of grain size, deposition rate and adatom mobility [6].

We will also show that nanoscale phase transformation during the course of film growth can be unraveled from the combination of real-time optical/electrical and surface-sensitive X-ray methods [3,4,7]. Finally, recent findings on the impact of gas additives and wetting agents on the growth morphology of ultrathin Ag layers will be highlighted, with the ultimate goal to produce ultrathin and ultrasmooth Ag layers for use as transparent conductive electrodes [8]. On a broader context, the knowledge gained from these real-time and in situ diagnostics may provide guidelines for efficient growth manipulation strategies in order to target specific applications.

[1] G. Abadias et al., “Review Article: Stress in thin films and coatings: Current status, challenges, and Prospects”, J. Vac. Sci. Technol. A 36 (2018) 020801

[2] E. Chason, P. Guduru, “Tutorial: Understanding residual stress in polycrystalline thin films through real-time measurements and physical models”, J. Appl. Phys. 119 (2016) 191101

[3] A. Fillon, G. Abadias et al., “Influence of Phase Transformation on Stress Evolution during Growth of Metal Thin Films on Silicon”, Phys. Rev. Lett. 104 (2010) 096101

[4] J. Colin et al., “In Situ and Real-Time Nanoscale Monitoring of Ultra-Thin Metal Film Growth Using Optical and Electrical Diagnostic Tools”, Nanomaterials 10 (2020) 2225

[5] A. Jamnig, N. Pliatsikas, K. Sarakinos, G. Abadias, “The effect of kinetics on intrinsic stress generation and evolution in sputter-deposited films at conditions of high atomic mobility”, J. Appl. Phys. 127 (2020) 045302

[6] E. Chason et al., “A kinetic model for stress generation in thin films grown from energetic vapor fluxes”, J. Appl. Phys. 119 (2016) 145307

[7] B. Krause, G. Abadias et al., “In Situ Study of the Interface-Mediated Solid-State Reactions during Growth and Postgrowth Annealing of Pd/a-Ge Bilayers”, ACS Appl. Mater. Interfaces 15 (2023) 11268

[8] K. Sarakinos et al., “Unravelling the effect of nitrogen on the morphological evolution of thin silver films on weakly-interacting substrates”, Appl. Surf. Sci. 649 (2024) 159209

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Author Index

Bold page numbers indicate presenter