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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Advanced Characterization, Modelling and Data Science for Coatings and Thin Films

Room Town & Country C - Session CM4-1-MoM

Simulations, Machine Learning and Data Science for Materials Design and Discovery I

Moderator: Davide G. Sangiovanni, Linköping University, Sweden

10:00am **CM4-1-MoM-1 High-Throughput Rapid Experimental Alloy Development (HT-READ)***, Kenneth Vecchio (kvecchio@ucsd.edu),* University of California at San Diego, USA **INVITED**

The development of high-throughput materials development strategies in the thin-film field have moved forward more quickly than bulk material high throughput strategies, primarily due to the need in bulk materials to account for microstructure effects on properties.In addition, the current bulk materials discovery cycle has several inefficiencies from initial computational predictions through fabrication and analyses. Much of the information and knowledge generated existed in isolated data silos making integrated approaches more challenging. This was the motivation for the 2011 Materials Genome Initiative, which sparked advances in many high-throughput computational techniques related to materials development. However, computational techniques ultimately rely on experimental validation.Furthermore, bulk materials are generally evaluated in a singular fashion, relying largely on human-driven compositional choices and analysis of the volumes of generated data, thus also slowing validation of computational models. Thus, increasing the rate of materials experimentation is fundamental to improving materials research, and requires parallelizing, automating, and miniaturizing key steps in experimental materials research, including computation, synthesis, processing, characterization, and data analysis.

To overcome these limitations, we developed a High-Throughput Rapid Experimental Alloy Development (HT-READ) platform and methodology that comprises an integrated, closed-loop material screening process inspired by broad chemical assays and modern innovations in automation. Our method is a general framework unifying computational identification of ideal candidate materials, fabrication of sample libraries in a configuration amenable to multiple tests and processing routes, and analysis of the candidate materials in a high-throughput fashion. An artificial intelligence agent is used to find connections between compositions and material properties.New experimental data can be leveraged in subsequent iterations or new design objectives. The sample libraries are assigned unique identifiers and stored to make data and samples persistent, thus preventing institutional knowledge loss.This integrated approach paves the way for truly compositionally-accurate and microstructurally-informed bulk materials development in a highly accelerated manner.This overall strategy has enabled our group to achieve the ability to design, fabricate, and fully characterize more than 800 bulk alloy samples per year with a single researcher.

10:40am **CM4-1-MoM-3 Fundamental Investigation for Film Quality Prediction Based on Zone Model in Magnetron Sputtering***, Kohei Kuroshima (kohei-kuroshima@osakavacuum.co.jp),* *I. Ikeda,* Osaka Vacuum, Ltd., Japan*; Y. Gotoh,* Department of Electronic Science and Engineering, Kyoto University, Japan*; M. Iguchi, S. Sugimoto,* Osaka Vacuum, Ltd., Japan

There are diagrams for film structures that are closely related to film properties, called the structure zone model. Thornton's model[1] uses a pressure for one axis, so the model may vary depending on the sputtering apparatus. Anders[2] argued the structure zone diagram (SZD) for the films deposited under presence of energetic particles. In the SZD, the axes are the normalized energy of the particles incident on the substrate, E* and the generalized temperature, T*.

Although it is said that this model cannot be used to predict film structure at points on the E*-T* plane, a trial to predict the structure on the SZD was done in this study. We focused on magnetron sputtering and calculated E* using only the kinetic energy when sputtered particles are incident on the substrate, and with measured substrate temperature, and verified whether Anders' SZD could be applied. We developed a sputter particle transport simulation software and calculated E*. This simulation includes the thermal motion effect of the process gas[3]. For validation, two common types of magnetron sputtering equipment were used to deposit film samples at several combinations of sputtering pressure (0.3-4.0 Pa), target-to-substrate distance (50-100 mm), and substrate temperature (RT-450 ℃). The input power was constant at 300W DC. We observed the surface and cross section of the samples by Scanning Electron Microscope (SEM). It was confirmed whether the structure of the film deposited with the condition which is represented by a certain point on the SZD was consistent with the structure represented by the ZONE.

As a result, under the conditions corresponding to the film structures of ZONE 1 and ZONE 2 on the SZD, the SEM images of the film had the characteristics of each ZONE. On the other hand, under conditions corresponding to the ZONE T, which is the transition region, it was found that the film structure did not show the texture of ZONE T so much, but strongly showed the structure of the adjacent ZONE, especially in the area near the boundaries of the zones.

Following SZD, we are developing a new diagram which exhibits film properties instead of film structure[4].

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References

[1] J. A. Thornton, J. Vac. Sci. Technol. 11, 666 (1974).

[2] A. Anders, Thin Solid Films, 518, 4087 (2010).

[3] T. Nakano, Appl. Surf. Sci., 113/114, 642 (1997).

[4] I. Ikeda et al., International Conference on Metallurgical Coatings & Thin Films 2024, Sandiego, May 19-24, 2024 (submitted).

11:00am **CM4-1-MoM-4 Are ML Potentials Useful to Understand Deformation and Fracture of Ceramics?**, ***Nikola Koutná (nikola.koutna@tuwien.ac.at)***, *S. Lin,* TU Wien, Austria*; L. Hultman,* Linköping University, Sweden*; P. Mayrhofer,* TU Wien, Austria*; D. Sangiovanni,* Linköping University, Sweden **INVITED**

Theoretical understanding of atomic-scale mechanisms underlying deformation and crack growth in ceramics enables rational design of alloys, superlattices, or nanocomposites with optimized combination of hardness and toughness. Simulations represent an important counterpart to experiment, being relatively inexpensive and allowing to impose well-defined loading conditions, thus making fair comparisons within one material class. Certain comprehension of how ceramics behave subject to mechanical loads can be achieved by *ab initio* methods, however, experimentally-relevant predictions require a combination of finite-temperature effects and large-enough models to consider extended crystallographic defects. In this talk I will discuss the exciting and rapidly growing field of machine-learning interatomic potentials (MLIPs) for molecular dynamics and how these can be used to study the onset of fracture. Transition metal diborides and MAB phases (i.e. atomically-thin laminates of ceramic/metallic-like layers) will serve as model materials to showcase a possible training strategy for the MLIP development and challenges upon up-scaling beyond length scales of *ab initio* reach. Furthermore, simulations of crack initiation in TiB_2 as well as the formation of ripplocations in Ta_2AlB_2 and other MAB phases under certain loading conditions will be interpreted in the light of experimental data available via collaborators. The ML potentials will turn out to be quite useful.

11:40am **CM4-1-MoM-6 Impact of TM Elements on Structural, Thermodynamic and Mechanical Properties of CrN**, ***David Holec (david.holec@unileoben.ac.at)***, Montanuniversität Leoben, Austria*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

CrN belongs to a family of transition metal nitrides used as protective coatings in automotive, aerospace, tooling and other applications. It poses a specific challenge for *ab initio* modelling due to its genuine magnetic properties: it has an antiferromagnetic (AFM) orthorhombic structure below the Néel temperature (T_N~room temperature) and adopts paramagnetic (PM) cubic B1 above T_N.

In this contribution, we use *ab initio* calculations to study the alloying impact of TM elements (Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Mo, W) on CrN in its application-relevant PM-B1 phase. Apart from V, all other elements increase the lattice parameter of CrN consistently with the corresponding binary TMNs. The enthalpy of isostructural mixing is the largest for Y due to large internal strains, followed by the group IVB elements. Interestingly, $H_{mix}$is negligible in the whole compositional range for Sc and V and becomes even negative (stable solid solutions) for $Cr_{1-x}Ta_xN$. Nb, W and Mo exhibit more complicated, composition-dependent behaviour. As quantified by the *B/G* ratio and the Cauchy pressure (C_{12}-C_{44}), the mechanical properties strongly correlate with the valence electron concentration of the ternary $Cr_{0.89}TM_{0.11}N$ solid solutions. While Mo and W are the most potent ductility enhancers, Sc and Y are predicted to embrittle CrN.

12:00pm **CM4-1-MoM-7 Machine-Learning Potential for Accurate Predictions of Elastic Properties in Amorphous W-B-C**, ***Pavel Ondracka (ondracka@mail.muni.cz)***, *J. Ženíšek,* Masaryk University, Czechia*; G. Nayak,* RWTH Aachen University, Germany*; D. Holec,* Montanuniversität Leoben, Austria*; P. Vašina,* Masaryk University, Czechia

Amorphous tungsten boron carbide is a prospective material for protective coatings, with superior ductility and crack resistance [1], and yet the subtle details of its atomistic structure and origin of its excellent mechanical properties are still unclear. Due to the small sizes of representative models and limited timescales of *ab initio* molecular dynamics based on density functional theory, it is difficult for this standard methodology to reliably predict structural and mechanical properties of amorphous W-B-C. Such predictions lead to strongly anisotropic mechanical properties and large uncertainties in the results. We solved the issues by fitting interatomic potential in a general nonlinear atomic cluster expansion (ACE) form [2] to this material system using an active learning approach to sample the amorphous configuration space and the D-optimality criterion and MaxVol algorithm to efficiently construct the training set [3]. The potential was trained for the W content between 10 and 60 at. % and C:B ratios between 4:1 and 1:4. Subsequently, we employed a melt & quench procedure to generate amorphous structural models containing more than 10000 atoms which yielded an isotropic mechanical response and revealed trends with respect to the system composition, density and quenching rates. The thus obtained values of Young's modulus were successfully validated against experimental data.

[1] S. Mirzaei et al., Surface and Coatings Technology 383, 125274 (2020).
[2] Y. Lysogorskiy et al., npj Computational Materials 7, (2021).
[3] Y. Lysogorskiy et al., Physical Review Materials 7, (2023).

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 3-4 - Session CM2-1-MoA

Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes I

Moderators: Thomas Edwards, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland, **Olivier Pierron**, Georgia Institute of Technology, USA

1:40pm **CM2-1-MoA-1 Micromechanics During Hydrogen Charging and the Study of Hydrogen Barrier Coatings***, Maria Jazmin Duarte (j.duarte@mpie.de), H. Gopalan, J. Rao, C. Scheu, G. Dehm,* Max-Planck Institut für Eisenforschung GmbH, Germany **INVITED**

Understanding the effects of hydrogen in materials became a pressing topic with the imminent shift towards green technologies, and the use of hydrogen as energy carrier. It is expected that the use of hydrogen will increase in all industries, together with the need for safe transport and storage and consequently the development of new materials and technologies to cope with it. A critical challenge is hydrogen-induced damage, or hydrogen embrittlement, that can cause the sudden failure materials. Hydrogen barrier coatings represent, in this regard, an appealing option to prevent and/or slow down the hydrogen ingress into structural alloys that are susceptible to embrittlement.

To characterize hydrogen and its effects in materials, at the relevant small-scale dimensions where embrittlement initiates, is a substantial yet demanding task. Current studies on hydrogen effects are in their majority limited to post-mortem probes and ex-situ charging, which neglect diffusible hydrogen, its migration and desorption at the analysis time. To rise above these constraints, we designed a novel “back-side” charging approach, to perform micromechanical testing during hydrogen charging [1]. Hydrogen is generated electrochemically at the back-side and diffuses towards the testing (front-side) surface. This unique method allows differentiating between the effects of trapped and mobile hydrogen, and performing well controlled measurements with different hydrogen levels monitored over time to consider hydrogen absorption, diffusion and release.

Using this new method, we unraveled dynamic effects of hydrogen on the mechanical properties of bulk alloys [2], and recently, we successfully applied it to study of hydrogen barrier coatings [3,4]. In this talk, I will present an overview of the technique, together with the case study of an Al_2O_3 hydrogen barrier coating. The hydrogen diffusion on Al_2O_3, ~9 orders of magnitude slower with respect to the used substrate, was measured by Kelvin probe. The mechanical stability of the coating was tested by nanoindentation and nanoscratching during hydrogen loading. The accumulation of hydrogen at the substrate-coating interface reduces the critical load required for cracking and leads to local delamination. Mechanical tests were complemented by atom probe tomography, confirming the presence of hydrogen close to the substrate/coating interface, and transmission electron microscopy, revealing the underlying microstructural changes.

[1] M.J. Duarte, et al., J. Mat. Sci. 56 (2021) 8732.

[2] J. Rao, et al., Mater. Des. 232 (2023) 112143.

[3] M. Wetegrove, et al., Hydrogen 4(2) (2023) 307.

[4] S.W Hieke, et al., Adv. Eng. Mater. (2023), *Accepted*.

2:20pm **CM2-1-MoA-3 The Micromechanical Behavior of Magnetron Sputtered TiN/Nb Multilayers***, S. Kagerer, N. Koutná,* Institute of Materials Science and Technology, TU Wien, Austria*; L. Zauner,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; T. Wójcik,* Institute of Materials Science and Technology, TU Wien, Austria*; G. Habler,* Department of Lithospheric Research, University of Vienna, Austria*; P. Polcik, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; O. Hunold,* Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; **Rainer Hahn (rainer.hahn@tuwien.ac.at),*** Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Damage tolerance is a prerequisite for using protective coatings in components subject to long-term stress. Physical Vapor Deposition offers possibilities in coating architectures using combinations of ductile and hard materials, even on the nm scale. However, ductility through dislocation motion is often suppressed on the micro-scale due to geometric limitations, resulting in unusually brittle behavior. In this work, we show a linear dependence between the necessary shear stress for dislocation motion in Nb layers and the overall plastic behavior of micropillar samples.

Computational pre-screening identifies fcc-TiN/bcc-Nb as a promising system providing stable, sharp, and strong interfaces with essentially different elastic moduli. Using a TiN compound target enables a sharp interface without nitrogen cross-contamination. Layer variation and changing the TiN to Nb ratio offer insights into the small-scale plastic behavior using the micropillar compression test. These show a fluent transition from ductile deformation for thick Nb layers to a brittle behavior similar to monolithic TiN upon decreasing the Nb layer thickness.

Combining micromechanical data with TEM analysis of fractured micropillars, we correlate these observations with increased stresses necessary for dislocation motion within the confined layer slip model. Furthermore, we will show the results of unique experiments combining micromechanics with synchrotron nanodiffraction to understand the stress situation in a pillar and describe deformation mechanisms.

2:40pm **CM2-1-MoA-4 Deformation Behaviour and Plasticity in FCC-BCC High Entropy Alloy Nanolaminate Structures***, S. Tsianikas,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; C. Tian,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland*; C. Guerra-Nuñez,* Swiss Cluster AG, Thun, Switzerland*; J. Michler, X. Maeder, **Amit Sharma (amit.sharma@empa.ch),*** EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland

In recent years, metal multilayer composites have been the focus of research due to their exceptional mechanical properties. Recent experimental [1-3], theoretical, and modeling [4]studies on multilayers have indicated that the enhancement of both strength and ductility is related both to the structure and properties of the interfaces between the layers, as well as the thicknesses and properties of the individual layers [5]. In spite of the ample literature available on pure metallic nanolaminate structures, the experimental data on compositionally complex alloy multilayers is rather missing.

In this context, here we present recent experimental data on the fabrication and mechanical behavior of nanolaminate FCC-BCC high entropy alloy thin films with interlayer thicknesses 50 nm. The alternating FCC-BCC layers are separated by atomic layer deposition of 2 nm amorphous Al2O3 layer without breaking the vacuumin a new Cluster System combining both ALD and PVD in the same equipment (Swiss Cluster AG). As a model system, FCC-NiCoCrFe and BCC- NiCoCrFe-Al (with Al ~10 at. %) layers with a total thickness of 3 microns is deposited on Si (100) substrate by magnetron sputtering and subsequently tested by micro compression and nanoindentation experiments. The mechanical response of the multi-layered structures is also compared with FCC-BCC multilayer without ALD and single-layer FCC and BCC counterparts. The uniformity in composition and microstructure of interlayers is confirmed by performing S/TEM imaging along the cross-section samples prepared by FIB using a standard liftout procedure. The microcompression experimental results on micro-pillars show a clear effect of interfaces and interlayer size effect on the mechanical response of nanolaminates at different strain rates. The post-mortem electron microscopy investigation provides insight into deformation mechanisms and deformation-induced phase transformations in the individual layers. This first study on multilayer film of two HEA’s will help fundamental studies on high entropy alloys and transformative to other complex systems.

1. S.J. Zheng, I.J. Beyerlein, J. Wang, J.S. Carpenter, W.Z. Han, N.A. Mara, Acta Materialia, 60 (2012) 5858-5866.

2. N.A. Mara, I.J. Beyerlein, J.S. Carpenter, J. Wang, JOM, 64 (2012) 1218-1226.

3. N. Li, N.A. Mara, J. Wang, P. Dickerson, J.Y. Huang, A. Misra, Scripta Materialia, 67 (2012) 479-482.

4. J. Wang, K. Kang, R.F. Zhang, S.J. Zheng, I.J. Beyerlein, N.A. Mara, JOM, 64 (2012) 1208-1217.

5. N. Mara, I. Beyerlein, J Mater Sci, 49 (2014) 6497-6516.

3:00pm **CM2-1-MoA-5 Characterisation of Hydrogen in Coatings and Thin Films Using Atom Probe and TDMS***, Peter Felfer (peter.felfer@fau.de),* Friedrich-Alexander University, Germany **INVITED**

In the transition to hydrogen as a future energy vector, thin films and coatings play a crucial role. Prominent current applications are coatings for

bipolar plates in fuel cells and electrolyzers. In the future, many more applications are likely, such as diffusion barrier and hard coatings on high-strength or wear exposed components such as valves and hydrogen injectors. This is because many base materials of hard coatings have very low hydrogen diffusion coefficients. However, real hard coatings are not single crystals and thus a much better understanding of the interaction of hydrogen with real hard coatings is required. Especially interactions between hydrogen and crystal defects are important as they carry permeation and trigger failures.

To understand these interactions, we are developing new nanoscale characterisation methods. These include the development of an special atom probe with ultra-low hydrogen background for nanoscale imaging and a similar thermal desorption system for analysis of mobile and trapped hydrogen. Both of these systems are based on titanium ultra-high vacuum chambers, drastically reducing the amount of background hydrogen in the vacuum. As a result, very little to no spurious hydrogen appears in the analyses. For the titanium atom probe, this has been demonstrated in voltage pulsing already. This method of analysis is however not suitable for coatings. A laser for the analysis of non-conductive materials such as thin films and coatings is currently being fitted. This unlocks the ability to quantitatively image hydrogen in thin films at the nanoscale and thus shed light on the prermeation mechanisms and interactions with crystal defects. First results will be shown in the talk. In parallel, we are testing the titanium thermal desorption system on thin films, to complement the nanoscale imaging of the atom probe with qualitative and eventually quantitative results on the amounts of mobile and trapped hydrogen in thin films.

4:00pm **CM2-1-MoA-8 Analysis of Stress Field in Nickel Borides Layer Produced by Vickers Indentation Tests in Cross Section: Finite Element Method***, **T. N. Cabrera-Yacuta (tcabreray1800@alumno.ipn.mx)**, G. Rodríguez-Castro, A. Meneses-Amador, I. Arzate-Vázquez,* Instituto Politécnico Nacional, Mexico*; O. Morales-Contreras,* Universidad Autónoma de Baja California, Mexico*; I. Campos-Silva, M. Melo-Pérez,* Instituto Politécnico Nacional, Mexico

This research studies numerically the stress fields formed in layers of nickel borides generated by Vickers indentations in cross section at different distances from the layer/substrate interface. Three powder-pack boriding conditions at 850, 900 and 950 °C for 2, 4 and 6 h, respectively, were applied to Inconel 718 for the formation of nickel borides. By means of X-ray diffraction, the Ni_4B_3, Ni_2B, Ni_3B phases were identified. In addition, a hardness range between 23.8 and 26 GPa was determined by Berkovich instrumented indentation, while 280 to 380 GPa for Young's modulus. The stress fields were analyzed by the finite element method using an explicit dynamic analysis. The numerical model is constituted by a Vickers indenter as a discrete and rigid body and by a 3D deformable solid defined through sections. As the layer thickness increases, the system is less sensitive to applied loads and the magnitude of stress fields decreases. Simulation results show that the maximum principal stresses cause cracking in the layer and that the shear stresses are not high enough to cause its delamination. The thicker layer/substrate system offers a higher resistance to cracking formed at 950 °C for 6h.

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 3-4 - Session CM2-2-TuM

Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes II: Fracture and Fatigue

Moderator: Matteo Ghidelli, CNRS, France

8:40am **CM2-2-TuM-3 Approaches for Circumventing FIB Artefacts in Small Scale Fracture Testing**, ***Eloho Okotete (eloho.okotete@kit.edu)***, *S. Lee, S. Brinckmann, C. Kirchlechner,* Karlsruhe Institute of Technology, Germany

Miniaturization has resulted in the production of small components ranging from a few nanometres to a few hundred micrometres, which are used in both consumer and industrial applications. To measure the fracture properties of thin films and interfaces at these length scales, geometries fabricated by Focused Ion Beam (FIB) are currently used. However, this method of milling can introduce impurities at the notch, which may affect the reliability of fracture measurements. To minimize the role of artefacts in small scale fracture studies, stable crack growth geometries are used, through which a sharp crack can be grown from a FIB notch. Another way to reduce the effects of FIB damage on test samples is by using inert notching ions.

In this talk, various methods to reduce FIB artefacts' role are presented systematically. In the first part, we discuss the study of fracture in single crystalline silicon notched with an inert ion source using a bridge notched single cantilever beam geometry that has recently been reported to demonstrate crack arrest. Furthermore, we use a new stable crack growth geometry to measure the fracture toughness of the hard-coating substrate interface [2]. The results indicate that cantilevers with deep notches and thin material bridges exhibit crack arrest, and the fracture toughness of cantilevers falls within the expected range for single crystalline silicon. In the new geometry, it is seen that the crack driving force decreases with crack extension in the geometry, preventing catastrophic failure. As a result, a natural crack is formed from the FIB notch, and final fracture occurs after the crack has grown beyond the region of the FIB milled notch. This reduces the influence of FIB-induced artefacts such as residual stresses due to ion implantation, finite notch radius, crystalline defects, and redeposition on the fracture toughness of materials tested at small length scales.

[1] Y. Zhang, M. Bartosik, S. Brinckmann, S. Lee, C. Kirchlechner, Direct observation of crack arrest after bridge notch failure: A strategy to increase statistics and reduce FIB-artifacts in micro-cantilever testing, Materials & Design 233 (2023) 112188.

[2] E. Okotete, S. Brinckmann, S. Lee, C. Kirchlechner, How to avoid FIB-milling artefacts in micro fracture? A new geometry for interface fracture, Materials & Design 233 (2023) 112134.

9:00am **CM2-2-TuM-4 Influence of Annealing-Induced Substrate Element Diffusion on the Microstructure and Mechanical Properties of TiN/TiCN Coatings Synthesized using Chemical Vapor Deposition**, ***Fabian Konstantiniuk (fabian.konstantiniuk@unileoben.ac.at)***, *M. Schiester,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; M. Tkadletz,* Department of Materials Science, Montanuniversität Leoben, Austria*; C. Czettl,* CERATIZIT Austria GmbH, Austria*; N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria

TiN/TiCN deposited by chemical vapor deposition (CVD) is widely used as hard coating system for cemented carbide cutting tools, typically under an Al_2O_3 top layer. During the deposition of the Al_2O_3 top layer, the underlying TiN and TiCN layers are exposed to high temperatures. Therefore, the present study focuses on the influence of this Al_2O_3 deposition step, which is mimicked by a vacuum-annealing treatment, on the microstructure and mechanical properties of the TiN/TiCN coating. By applying advanced characterization techniques such as scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), atom probe tomography (APT), and micro-mechanical bending tests on both, as-deposited and annealed coatings, changes in the microstructure and mechanical properties were studied. It was found that W and Co diffusion takes place along the TiN and TiCN grain boundaries from the substrate into the coating. While the hardness, Young's modulus, and fracture toughness remained unaffected by the annealing treatment, a significant decrease of the fracture stress with increasing annealing time was observed.

9:20am **CM2-2-TuM-5 Mechanical Properties of Thin Films Deposited by HiPIMS onto Flexible Substrates**, ***Tereza Kosutova (tereza.kosutova@angstrom.uu.se)***, Uppsala University, Department of Electrical Engineering, Sweden*; M. Tavares da Costa,* Karlstad University, Sweden*; K. Gamstedt,* Uppsala University, Department of Materials Science and Engineering, Sweden*; D. Drozdenko,* Charles University, Czechia*; T. Kubart,* Uppsala University, Department of Electrical Engineering, Sweden

Our study focuses on the strength and ductility of thin films deposited by magnetron sputtering on flexible substrates. Although thin films are widely used in surface engineering, their application on foils brings new requirements on the mechanical properties of the coating material as well as the substrate-coating interface. Here, we aim on the determination of mechanical properties of thin films deposited by dc and high power impulse magnetron sputtering (HiPIMS). The main goal is to identify deposition conditions that ensure good adhesion and ductility of the layers and therefore facilitate applications of coated metal foils.

In-situ testing in an SEM is used to quantify the film cracking during tensile loading and thus analyse the distribution of fracture strain and interfacial shear strength of the coating material. This technique is complemented by the strain field analysis of the substrate foils determined by digital image correlation to identify defects that could induce stress concentration and premature failure. Thin films of copper, titanium and amorphous carbon are evaluated as examples with different intrinsic ductility. Furthermore, the effect of interlayers was investigated. The behaviour of the films deposited on two different foils of aluminium and PET is compared.

To identify the impact of different deposition parameters, we analysed a series of samples deposited using different values of the duty cycle and the substrate bias. The results are correlated to the morphology, microstructure and chemical composition analysed mainly by SEM, XRD and EDX techniques. Whereas the copper exhibits high ductility and a good adhesion can be achieved with an ion assistance, the fracture behaviour of the titanium is dependent on the growth conditions.

9:40am **CM2-2-TuM-6 Fatigue-Induced Abnormal Grain Growth in Metallic Thin Films**, *Q. Li,* Georgia Institute of Technology, USA*; A. Barrios,* Colorado School of Mines, USA*; Y. Yang,* Georgia Institute of Technology, USA*; M. Jain,* Sandia National Laboratories, USA*; Y. Liu,* Georgia Institute of Technology, USA*; B. Boyce,* Sandia National Laboratories, USA*; T. Zhu,* ***Olivier Pierron (olivier.pierron@me.gatech.edu)***, Georgia Institute of Technology, USA

This presentation describes a microelectromechanical system (MEMS) based setup to investigate grain growth in ultrafine grained and nanocrystalline metallic thin films under high/very high cycle loading conditions (i.e., up to 10^9 cycles). The advantage of the technique is that it can test different metals (fcc, bcc, different textures) under identical loading conditions. The governing hypothesis is that abnormal grain growth occurs under this loading regime, and that the family of growing grains is mainly dictated by elastic anisotropy. Our preliminary results on Au and Al thin films are compared to our previous work on ultrafine grained Ni. Abnormal grain growth in Au is observed, as in Ni, however, the orientation of the growing grains is different for Au and Ni, given the difference in initial texture. The experimental results can be compared to micromechanics analyses and phase-field modeling, in order to better understand the origins of the thermodynamic driving force.

10:00am **CM2-2-TuM-7 Nanoscale Fatigue Measurements on Diamond-Like Carbon Coatings**, ***Joshua Vetter (joshua.vetter@de.bosch.com)***, *M. Günther, P. Hofmann, S. Grosse,* Robert Bosch GmbH, Germany*; S. Schmauder,* University of Stuttgart, Germany

Diamond-like carbon (DLC) coatings are frequently used to improve wear performance of technical components in tribological systems. Appropriate fatigue properties of the coating system are fundamental to ensure the functionality. The mechanical failure of the coating can lead to spallation and delamination processes already through further low external stresses and hence to total component failure. Therefore, precise measurements are mandatory. Established analysis like the Rockwell test according to DIN 4856 as well as scratch tests are performed with a single overload above the critical strength of the DLC coating disregarding real operating conditions and failure mechanisms e.g. fatigue through cyclic loads. In our study, we performed cyclic nanoscale fatigue measurements of DLC coatings to consider application-related stresses. The coating systems were deposited by PVD and PACVD techniques varying e.g. the thicknesses of the functional and support layer systems. Cyclic nanoindentation measurements with spherical diamond indenters were performed to evaluate the fatigue behaviour. We have shown that promising results can

be obtained from this type of measurements. Suitable test parameters were defined to investigate a wide range of different coating systems within a few hours by adjusting static force and force amplitude. Effects of different coating designs, layer thicknesses and mechanical properties (e.g. indentation hardness, indentation modulus, residual stress and yield strength) of the DLC layer could be evaluated. The critical stress for various DLC layer thickness was evaluated with a FEM simulation and compared to the results obtained from the fatigue measurements. With this, essential adjustments of the mechanical properties of the DLC layer were found to increase the fatigue limit. Furthermore, the effect of an additional pre-treatment by annealing under elevated temperatures from 250 °C up to 450 °C was investigated. The results of the nanoscale fatigue test provide information on previously unknown effects that could not be detected with nanoindentation hardness tests. For various DLC systems the thermal degradation under application related stresses could be shown. Our new measurement technique reveals that previous measurements e.g. adhesion measurement results from typical single overload or hardness measurements tests are not conclusive enough to consider application-related load spectra and that cyclic loads are necessary to guarantee the requested operation condition testing environment. Hence the developed fatigue test allows us to adapt the coating systems to the requirements of the real components.

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 5-6 - Session CM4-2-TuM

Simulations, Machine Learning and Data Science for Materials Design and Discovery II

Moderators: Po-Liang Liu, National Chung Hsing University, Taiwan , **Ferenc Tasnadi**, Linköping University, Sweden

8:00am **CM4-2-TuM-1 DFT + ML + Calphad: From Qualitative to Quantitative Phase Stability Predictions***, Moritz to Baben (mtb@gtt-technologies.de), P. Keuter, C. Früh, B. Reis, F. Tang,* GTT-Technologies, Germany **INVITED**

Today, phase stability predictions using quantum mechanical calculations can be considered state-of-the-art for metallurgical coatings and thin films. However, these predictions are usually qualitative in nature, partly because of missing data and partly because the processes are complex and not in thermodynamic equilibrium.

Here, it is shown how

(I) data gaps concerning phase stability can be closed by a the combination of 0 K DFT calculations, machine learning to cheaply extend the data validity to relevant temperatures and Calphad methodology to describe phase stability of solid solutions and thus solid-gas equilibria.

(II) phase stability data can then be used to make quantitative predictions for magnetron sputtering, i.e. a process that is usually considered to be far from equilibrium, using the para-equilibrium approach (nitrogen stoichiometry of TiAlN, to Baben et al., MRL 5 (2017) 158) or using a small process model based on the Hertz-Knudsen equation (stoichiometry of Mg-Ca Thin Films, Keuter et al, Materials 16 (2023) 2417).

8:40am **CM4-2-TuM-3 Cu-Zr-Al Thin Film Metallic Glasses in a Wide Range of Compositions and Growth Conditions***, Jiri Houska (jhouska@kfy.zcu.cz), P. Zeman,* University of West Bohemia, Czechia

Cu-Zr-Al thin film metallic glasses are investigated by a combination of simulations of their atom–by-atom growth with magnetron sputtering. We fulfill all requirements which maximize the usefulness of the results: mutual support of calculated and experimental data, simulation algorithm which exactly reproduces what is happening in the experiment, wide compositional range (from pure Cu to pure Zr and from [Al] = 0% to 20%), wide range of growth conditions (energy of arriving atoms, temperature, growth template). We focus on the homogeneity, densification, short-range order (bonding preferences and coordination numbers), medium-range order (common neighbor and network ring statistics) and functional properties. Special attention is paid to the key building blocks of Cu-Zr-Al: not only icosahedral clusters (12 vertices) but also newly identified supraicosahedral clusters (16 vertices).

First, we identify crystalline Zr-rich compositions (on any growth template) and Cu-rich compositions (with a strong effect of growth template), and glasses (as homogeneous as what result from a random distribution of atoms) at [Cu] = 20% to 80-85%. Increasing [Cu] in the glassy compositions leads to increasing coordination of both Cu and Zr, packing factor and icosahedron-like medium-range order. Second, increasing [Al] in glassy $Cu_{0.46}Zr_{0.54-x}Al_x$ preserves the homogeneity (at a very low preference to form Al-Al bonds) and once again leads to increasing coordination of all elements, packing factor and concentration of icosahedral clusters (around smaller Cu and Al) and supraicosahedral clusters (around larger Zr). All of that is achievable at low energy delivered into the growing films, while delivering too much energy (by energetic bombardment or by ohmic heating) may be even harmful.

While the atomic-scale simulations provide a lot of information not accessible experimentally, they are correlated with and explain experimental data including increasing hardness, Young's modulus, glass transition temperature and crystallization temperature with increasing [Cu]/[Zr] and [Al]/[Zr]. Collectively, the results [1,2] are important for understanding the structures and properties of this class of metallic glasses, and for optimizing their compositions and pathways for their preparation.

[1] J. Houska, P. Machanova, M. Zitek, P. Zeman, J. Alloys Compd. 828, 154433 (2020)

[2] J. Houska, P. Zeman, Comp. Mater. Sci. 222, 112104 (2023)

9:00am **CM4-2-TuM-4 Transformation Plasticity and Fracture in MB_2 (M=Ti, Ta, W, Re) Diborides via Ab-Initio and Machine-Learning-Potential Molecular Dynamics***, Shuyao Lin (shuyao.lin@tuwien.ac.at),* TU Wien, Institute of Materials Science and Technology, Austria*; T. Leiner,* Montanuniversität Leoben, Leoben, Austria*; Z. Chen,* Austrian Academy of Sciences, Austria*; R. Janknecht,* TU Wien, Institute of Materials Science and Technology, Austria*; F. Tasnadi,* Linköping University, Sweden*; Z. Zhang,* Austrian Academy of Sciences, Austria*; L. Hultman,* Linköping University, Sweden*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Holec,* Montanuniversitat Leoben, Austria*; D. Sangiovanni,* Linköping University, Sweden*; N. Koutná,* TU Wien, Institute of Materials Science and Technology, Austria

In this contribution we employ ab-initio molecular dynamics (AIMD) and machine learned interatomic potential molecular dynamics (ML-MD) simulations to elucidate trends and typical patterns in the mechanical response of transition metal diborides. Four representative diboride systems, MB_2, are selected, with M from the group IV (Ti), V (Ta), VI (W), and VII (Re) of the periodic table. The AIMD simulations serve to find finite-temperature equilibrium lattice parameters of the chosen diborides and to estimate their tensile and shear response at the atomic scale. The thereby produced *ab initio* dataset is used to fit and validate machine-learning interatomic potentials for ML-MD (within the moment tensor potential, MTP, formalism), providing a basis to study deformation behavior at the nanoscale. By controlling the phase structure (the AlB_2, WB_2, and ReB_2-prototype phase), supercell size (few to dozens of nm^3), and imposing well-defined loading conditions (tensile or shear deformation with various loading directions and temperatures), our ML-MD simulations allow assessing similarities as well as fundamental differences between the studied diborides. Considering a nanoscale model with a pre-indent on the surface, we go one step further and discuss ML-MD predictive power and limitations in the light of experimental results for an indented TiB_2 thin film.

9:20am **CM4-2-TuM-5 Fracture Toughness: Atomistic Understanding of Directional and Temperature Dependence for the case of $Ti_{1-x}Al_xN_y$***, Davide Sangiovanni (davide.sangiovanni@liu.se),* Linköping University, Sweden

The fracture toughness (K_{Ic}) of single-crystal lattices and interface structures is a physical property that depends on temperature and crystallographic orientation. For ceramic thin films, experimental characterization of K_{Ic} is complicated by the presence of grain boundaries or structural inhomogeneities. Narrow scatter among measured K_{Ic} values (1-to-5 MPa $\sqrt{m}$), combined to relatively large statistical uncertainties (±1 MPa $\sqrt{m}$), vanifies attempts to rank different hard ceramics according to their effective fracture resistance.

Taking B1-structure $Ti_{1-x}Al_xN_y$ as representative ceramic systems, I present results of atomistic fracture-mechanics simulations carried out at different temperatures (*T*) and for diverse crystallographic orientations of the fracture plane (hkl) / crack front [h'k'l']. The approach — based on K-controlled *nanoscale* loading, implemented with anisotropic *T*-dependent elastic responses **[1]** — can reliably forecast *observable* mechanical responses.

Direct atomistic observations of localized transformation-induced or slip-induced plasticity in flawed $Ti_{1-x}Al_xN_y$ lattices allow understanding and quantifying the impact of small-scale yielding on K_{Ic} and fracture strength

values calculated as a function of *T* and (hkl)[h'k'l']. Moreover, the simulation results evidence limits of Griffith (^{G}) and Rice (^{R}) criteria for predictions of stress intensities that lead to brittle-fracture (K_{Ic}^{G}) and dislocation emission (K_{Ie}^{R}). Alternative descriptors — based on properties evaluated by homogeneous deformation of defect-free crystals **[1,2]** — are proposed as convenient means to rapidly screen mechanical strength, tendency to undergo plastic deformation, and fracture resistance at any temperature of interest.

The talk will also briefly cover our recent developments in machine-learning interatomic potentials for cutting-edge description of materials subject to deformation at realistic conditions **[3]** and *ab initio* database of ceramic properties computed from 0 K to elevated temperatures **[4]**.

[1] Physical Review Materials (2023) https://doi.org/10.1103/PhysRevMaterials.7.103601
[2] Science Advances (2023) https://doi.org./10.1126/sciadv.adi2960
[3] Preprint (2023) https://doi.org/10.48550/arXiv.2309.00996
[4] npj Computational Materials (2022) https://doi.org/10.1038/s41524-022-00698-7

9:40am **CM4-2-TuM-6 Exploring Surface Energy and Work Function Changes in ZnGa2O4(111) via Ab Initio Studies***, **Po-Liang Liu (pliu@dragon.nchu.edu.tw)**, Y. Lin,* National Chung Hsing University, Taiwan

The metal oxide semiconductor gas sensor holds promise as the primary component for environmental monitoring within artificial intelligence-based systems designed for household and industrial gas detection. The fabrication of ZnGa2O4 thin films has been advanced due to their capacity to operate within sensor temperature ranges and discern the composition and concentration of mixed gases. The n-type semiconductor nature of ZnGa2O4 enables the detection of NO2 and H2S molecules. This semiconductor exhibits rapid and robust sensing responses along with high signal intensity towards NO2 and H2S, thereby anticipating an enhancement in sensor operational efficiency, particularly in terms of elevated temperature utilization. Hence, this study employs ab initio calculations based on the density functional theory to determine the surface energy of ZnGa2O4(111). The analysis reveals that the ZnGa2O4(111) surface comprises Ga, Zn, and O elements. Findings indicate that the surface energy for Zn-Ga-O-, O-, and Ga-terminated ZnGa2O4(111) range between 0.0516 to 0.2335 eV/Å2, 0.0516 to 0.7789 eV/Å2, and 0.0464 to 0.5918 eV/Å2, respectively. The Ga-terminated ZnGa2O4 has the lowest surface energy of 0.0464 eV/Å2 in a Ga-rich environment, showing the Ga-terminated ZnGa2O4(111) is the most favorable surface. The work function change of Zn-Ga-O-, O-, and Ga-terminated ZnGa2O4(111) are 3.70 eV, 0.48 eV, and 6.35 eV, respectively. This highlights that the Ga surface atoms demonstrate a maximum work function change, consistent with previously experimental observations

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 3-4 - Session CM1-2-TuA

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

Moderators: Naureen Ghafoor, Linköping University, Sweden, **Michael Tkadletz**, Montanuniversität Leoben, Austria

1:40pm **CM1-2-TuA-1 Structural Evolution of Nanoparticles Under Realistic ConditionsObserved with Bragg Coherent X-Ray Imaging*, Marie-Ingrid Richard (marie-ingrid.richard@cea.fr),*** CEA Grenoble, France **INVITED**

The advent of the new 4th generation x-ray light sources represents an unprecedented opportunity to conduct *in situ* and *operando* studies on the structure of nanoparticles in reactive liquid or gas environments. In this talk, I will illustrate how Bragg coherent x-ray imaging [1] allows to image in three dimensions (3D) and at the nanoscale the strain and defect dynamics inside nanoparticles as well as their refaceting during catalytic reactions [2–4]. As an example, we successfully mapped the lattice displacement and strain of a Pt nanoparticle in electrochemical environment (see Figure 1). Our results reveal that the strain is heterogeneously distributed between highly- and weakly-coordinated surface atoms, and propagates from the surface to the bulk of the Pt nanoparticle as (bi)sulphates anions adsorb on the surface [5].

We will also discuss the possibility to measure particles as small as 20 nm [6] and to enable high-resolution and high-energy imaging with Bragg coherent x-ray diffraction at 4th generation x-ray light sources [7]. Finally, I will highlight the potential of machine learning to predict characteristic structural features in nanocrystals just from their 3D Bragg coherent diffraction patterns [7].

We acknowledge funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No. 818823).

[1] I. Robinson and R. Harder, *Coherent X-Ray Diffraction Imaging of Strain at the Nanoscale*, Nat. Mater. **8**, 291 (2009).

[2] J. Carnis, L. Gao, S. Fernández, G. Chahine, T. U. Schülli, S. Labat, E. J. M. Hensen, O. Thomas, J. P. Hofmann, and M.-I. Richard, *Facet-Dependent Strain Determination in Electrochemically Synthetized Platinum Model Catalytic Nanoparticles*, Small Weinh. Bergstr. Ger. e2007702 (2021).

[3] J. Carnis et al., *Twin Boundary Migration in an Individual Platinum Nanocrystal during Catalytic CO Oxidation*, Nat. Commun. **12**, 5385 (2021).

[4] M. Dupraz et al., *Imaging the Facet Surface Strain State of Supported Multi-Faceted Pt Nanoparticles during Reaction*, Nat. Commun. **13**, 1 (2022).

[5] C. Atlan et al., *Imaging the Strain Evolution of a Platinum Nanoparticle under Electrochemical Control*, Nat. Mater. **22**, 6 (2023).

[6] M.-I. Richard et al., *Bragg Coherent Diffraction Imaging of Single 20 Nm Pt Particles at the ID01-EBS Beamline of ESRF*, J. Appl. Crystallogr. **55**, 621 (2022).

[7] M.-I. Richard et al., *Taking Bragg Coherent Diffraction Imaging to Higher Energies at Fourth Generation Synchrotrons: Nanoscale Characterization*, ACS Appl. Nano Mater. **6**, 10246 (2023).

[8] B. Lim et al., *A Convolutional Neural Network for Defect Classification in Bragg Coherent X-Ray Diffraction*, Npj Comput. Mater. **7**, 1 (2021).

2:20pm **CM1-2-TuA-3 Grain Boundary Segregation/Complexions in MT-CVD Ti(C,N) Thin Hard Coatings Analyzed by Nano-SIMS and Atom Probe Tomography*, Idriss El Azhari (idriss.elazhari@uni-saarland.de),*** *J. Barrirero,* Saarland University, Germany*; N. Valle,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; J. García,* Sandvik Coromant, Sweden*; C. Pauly, F. Soldera,* Saarland University, Germany*; L. Llanes,* Universitat Politècnica de Catalunya, Spain*; F. Mücklich,* Saarland University, Germany

Ti(C,N) is one of the most utilized thin hard coatings in metal-cutting industry in the last twenty years. In prior works, the authors carried out multi-scale testing and characterization experiments in which industrial cutting inserts coated with Ti(C,N) wear resistant hard coatings are contrasted to Zr(C,N) coated counterparts. The purpose was to comprehend the influence of the coating's microstructural features **on the deformation behavior of each coating and the corresponding impact on the entire coated cutting tool system**. The investigation showcased that the more compatible coefficient of thermal expansion of Zr(C,N) with the substrate, the better cohesive strength at the grain boundaries and the plastic deformation were found to assign to the Zr(C,N) coated hardmetal improved structural integrity and fracture toughness in comparison to Ti(C,N) [1,2].

In this work, the focus is shifted toward Ti(C,N) to understand the correlation between deposition temperature and its impact on the microstructural features and segregation/complexions at the grain boundaries. For this purpose Ti(C,N) was deposited on a WC-Co substrate at two different temperatures (885°C and 930°C) using a moderate temperature CVD process (MT-CVD). Electron Backscatter Diffraction (EBSD) is used to examine microstructures. High-resolution secondary ion mass spectrometry imaging (nano-SIMS) and atom probe tomography (APT) were combined to investigate compositional variations inside single crystals and segregation at the grain boundaries. It is shown that segregation of chlorine at the grain boundaries is affecting not only the grain size of the columnar crystals, but texture and crystal shapes are indeed affected and modified as the chlorine concentration is decreasing with increasing temperature deposition. Methods to tailor the microstructure of these compounds are discussed and suggested.

Bilbliography

[1]I. El Azhari, J. Barrirero, J. García, F. Soldera, L. Llanes, F. Mücklich, Atom Probe Tomography investigations on grain boundary segregation in polycrystalline Ti(C,N) and Zr(C,N) CVD coatings, Scripta Materialia. 162 (2019) 335–340. https://doi.org/10.1016/j.scriptamat.2018.11.041.

[2]I. El Azhari, J. Barrirero, N. Valle, J. García, L. von Fieandt, M. Engstler, F. Soldera, L. Llanes, F. Mücklich, Impact of temperature on chlorine contamination and segregation for Ti(C,N) CVD thin hard coating studied by nano-SIMS and atom probe tomography, Scripta Materialia. 208 (2022) 114321. https://doi.org/10.1016/j.scriptamat.2021.114321.

4:00pm **CM1-2-TuA-8 *In situ* Studies of Nucleation and Growth by High Energy X-Ray Scattering*, Jens Birch (jens.birch@liu.se),*** *N. Ghafoor, F. Eriksson,* Linköping University, Sweden*; S. Stendahl,* Uppsala University, Sweden*; S. Dorri, S. Nayak,* Linköping University, Sweden*; L. Rogström,* Uppsala University, Sweden **INVITED**

The understanding of the formation of nanoscale structures and their properties, requires time-resolved analytical tools able to probe into the nano realm. High energy (HE) X-rays, with wavelengths in the 0.01-10 nm range, provided by state-of-the-art synchrotrons feature four synergetic properties: High penetration depth, small scattering angles, very low beam divergence, and high intensity. This makes it easy to design in situ sample environments for experiments providing a large amount data using a sub-µm probe size, at a high rate data acquisition. Thus, HE X-rays lend themselves well for *in situ* and *operando* time-resolved experiments to shed light onto elusive nanoscale phenomena. A purposefully designed UHV-based deposition system for time-resolved *in situ* studies of thin film nucleation and growth processes is presented with examples ranging from high precision nm-period multilayer neutron mirrors to wear-resistant coatings, grown by magnetron sputtering and cathodic arc deposition at the High Energy Materials Science beamline P07 at PETRA III in Hamburg.

In situ time-resolved HE XRD,was used to study microstructural evolution of Ni/Ti:B_4C multilayer neutron mirrors in real time. Combining incorporation of $^{11}B_4C$ with temporally modulated ion-assistance during deposition, it was possible to achieve amorphous layers with interface widths s=4 Å (a reduction from 7 Å for state-of-the-art). The neutron reflectivity was observed to increase by 43%, implying up to 10x higher neutron throughput and a significantly increased neutron wavelength range for future neutron guides.

Another example is *in situ* characterization of epilayer strain evolution during magnetron sputter epitaxy of single crystal 6 nm-bilayer periodic superlattices of$CrB_{1.7}/TiB_{3.3}(0001)/Al_2O_3(0001)$. XRD revealed a rapid initial relaxation of superlattice-substrate misfit strain, from -0.067%, in the first bilayer period to -0.0013 % during growth of the 2nd bilayer. This observation precludes substrate misfit strain as driving force for an observed B segregation to tissue phases extending transversely through several bilayer periods.

Phase stability during cathodic arc as well as magnetron syntheses of polycrystalline TiAlN tool coatings were studied. The precipitation sequence and size evolutions of metastable cubic Ti-rich TiAlN nanocrystallites (responsible for hardening) and Al-rich wurtzite phase (causing over-hardening) could be followed in detail.

The improved prospects for future availability of the *in situ* deposition system upon installation of a large 1500 kg capability hexapod at the Swedish Materials Science beamline P21 will be presented.

4:40pm **CM1-2-TuA-10 Multidimensional Elemental and Molecular Analysis for Surface & Interface Studies***, **Kayvon Savadkouei (kayvon.savadkouei@horiba.com)***, HORIBA, USA*; P. Chapon, A. Stankova,* HORIBA, France

Surface and Interface corrosion studies require the use of complementary analytical techniques as each instrumentation provides results based on the interaction of the investigated material with a probing medium [1].

Obtaining elemental and molecular information for different probing size and depth are especially crucial.

HORIBA offers a Platform with multiple instruments able to tackle these complex analytical challenges.

Glow Discharge relies on plasma to sputter a representative area of a material and provides fast elemental depth profile with nanometer resolution [2].

Coupling GD and Raman microscopy allows us to obtain molecular information at various depths with micrometer lateral resolution [3,4].

Applying the GD software ideal to follow transient signals to a simultaneous ICP instrument coupled with an electrochemical cell (AESEC technique) offers deep insight on dissolution mechanisms and metallic surfaces performances [5].

We will illustrate the benefit of this Surface Platform for Elemental and Molecular Analysis with selected results on metallic parts for high temperature fuel cells, hard facing materials in Na fast reactors, perovskite solar cells, hydratation of anodic films and DCL coatings on bipolar plates.

References:

1. Compendium of Surface & Interface Analysis, Springer
2. Review: What Can Glow Discharge Optical Emission Spectroscopy (GD-OES) Technique Tell Us about Perovskite Solar Cells? Small Methods 2022, 2200633
3. Raman and glow discharge optical emission spectroscopy studies on structure and anion incorporation properties of a hydrated alumina film on aluminum. Applied Surface Science 592 (2022) 153321
4. Advances in RF Glow Discharge Optical Emission Spectrometry Characterization of Intrinsic and Boron-Doped Diamond Coatings. https://doi.org/10.1021/acsami.1c20785
5. Transient stainless-steel dissolution and its consequences on ex-situ bipolar plate testing procedure. International journal of hydrogen energy 45 (2020) 984-995

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 1-2 - Session CM3-1-ThA

Accelerated Thin Film Development: High-throughput Synthesis, Automated Characterization, and Data Analysis I

Moderators: Davi Marcelo Febba, NREL, USA, **Sebastian Siol**, Empa, Switzerland, **Andriy Zakutayev**, NREL, USA

1:40pm **CM3-1-ThA-2 Collaborative Intelligence in Thin Film Research for Clean Energy Technologies*, Shijing Sun (shijing@uw.edu),*** University of Washington, USA **INVITED**

Addressing global environmental challenges, particularly in the realm of energy storage and conversion, necessitates innovative approaches. In this context, artificial intelligence (AI) has emerged as a transformative tool, catalyzing the discovery of new materials. However, the practical application of computational models in laboratory settings presents distinct challenges. This talk will explore the evolving role of AI in scientific research, focusing on its capacity to enhance rather than replace human expertise. This synergy paves the way for advanced collaborative efforts in the development and analysis of thin films.

Drawing from my experience as both an experimentalist and a materials data scientist in academic and industrial settings, I will showcase data-driven approaches that accelerate the formulation of precursors for solution-processed thin films. Additionally, I will delve into how AI-assisted image characterisation can effectively detect imperfections and establish crucial structure-property correlations. These advancements are particularly significant in the pursuit of clean energy solutions, demonstrating the integral role of AI in accelerating scientific innovation in thin film technology.

2:20pm **CM3-1-ThA-4 Discovery and Design of a New Functional Amorphous Nitride: Y-W-N*, Oleksandr Pshyk (oleksandr.pshyk@empa.ch),*** *S. Zhuk, J. Patidar, A. Wieczorek,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; A. Sharma, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; C. Cancellieri,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; V. Stevanovic,* Colorado School of Mines, USA*; S. Siol,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Amorphous thin films are employed in many applications and offer unique characteristics, which are not observed in their crystalline counterparts.

We present the discovery and design of amorphous Y-W-N ceramic thin films. We performed an exploratory synthesis and high-throughput characterization of $Y_{1-x}W_xN$ thin films. The compositions are performed using combinatorial, reactive radio-frequency magnetron co-sputtering of Y and W targets in Ar/N_2 atmosphere, resulting in materials libraries with orthogonal composition and deposition temperature gradients. This allows for a rapid screening of the synthesis phase space. A composition window within $0.1 \leq x \leq 0.85$ is covered, whereas the substrate temperature (T_s) is varied from 80 °C up to 600 °C. High-throughput screening of the composition and structure of the libraries by means of XRF and XRD reveals a wide composition range of $0.2 \leq x \leq 0.6$ where thin films grow with an amorphous structure without precipitation. Moreover, the amorphous structure shows remarkable temperature stability of up to 600 °C. Optical properties mapping using an automated high-throughput UV−vis photo-spectroscopy system suggests a band gap of >2.5 eV and confirms the phase purity showing only negligible sub band gap absorption. The band gap can be tuned by varying the cation composition, whereas the highest absorption onset for $Y_{1-x}W_xN$ thin films is found for Y-rich samples with x=0.3 implying an optical band gap of ~3.3 eV. Mechanical properties mapping using an automated nano-indentation system shows that the hardness of $Y_{1-x}W_xN$ thin films with $0.3 \leq x \leq 0.5$ doesn't change significantly as a function of T_s and the highest hardness of 9.45±0.05 GPa is found for samples with x=0.5 while the increase of Y concentration deteriorates hardness down to 8.45±0.06 GPa for films with x=0.3. A representative pair of amorphous $Y_{1-x}W_xN$ thin films with x=0.3 and 0.5 are selected for a detailed study. A thorough structural and compositional analysis of the latter films by means of high-resolution TEM reveals a homogeneous amorphous structure of the films with no signs of elemental segregations or crystallization. To comprehend the application potential of these materials, a comprehensive study of a wide range of functional and physical properties is performed including a set of optical and dielectric constants, diffusion barrier performance, oxidation resistance, and thermal stability. Experimental findings are corroborated by theoretical calculations for a better understanding of a complex relationship between the elemental composition of amorphous $Y_{1-x}W_xN$ thin films and their physical and functional properties.

2:40pm **CM3-1-ThA-5 Deposition of Highly Crystalline AlScN Films Using Synchronized HiPIMS – From Combinatorial Screening to Piezoelectric Devices*, Jyotish Patidar (jyotish.patidar@empa.ch),*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; S. Bette,* aixACCT Systems GmbH, Germany*; O. Pshyk, K. Thorwarth,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; R. Kessels,* aixACCT Systems GmbH, Germany*; S. Siol,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Piezoelectric thin films are crucial for many technologies, in particular for RF components for telecommunication. Wurtzite Aluminum Nitride (w-AlN) is one of the most widely used material for these types of applications. Recently, Aluminium Scandium Nitride (AlScN), is becoming more popular due to its increased piezoelectric coefficient. Highly crystalline and textured thin films are essential for high-performing piezoelectric devices. In our prior work, we demonstrated that metal-ion synchronized HiPIMS (MIS-HiPIMS) with moderate substrate bias potentials can offer key advantages in the deposition of these materials.[1] Here we explore how these concepts can be applied to AlScN films.

In AlScN films, high Sc concentrations enhance the piezoelectric response by softening of the phonon modes. However, high Sc content can also lead to structural frustration and precipitation of cubic ScN (c-ScN). Investigating the Sc non-equilibrium solubility and structural evolution upon scandium alloying is experimentally involved and thus rarely discussed. In our work, we employ a combinatorial approach for an accelerated estimation of the solubility limits and optimization of film's properties, for varying synthesis environments. We investigate different synthesis routes by hybrid co-sputtering of Al/Sc in a reactive environment through a combination of direct current magnetron sputtering (DCMS) and HiPIMS processes, along with different biasing strategies.

The combinatorial screening reveals a striking correlation between the ion kinetic energy and non-equilibrium Sc solubility. In addition, certain deposition modes prove to be more resilient against structural frustration than others. Particularly, a reduction of misaligned grains is observed with the application of a negative substrate bias potential. Based on the results from the screening, uniform $Al_{0.8}Sc_{0.2}N$ thin films were deposited on Ti/Pt contacts, for each synthesis strategy. Detailed characterization of these films show that based on the chosen synthesis modes, the stress state can be tailored from -1.5 to 1.5 GPa. On the other hand, measurements of the piezoelectric coefficient $d_{33,f}$ show a performance comparable to the current state-of-the-art.

The results of this study showcase how high-throughput experiments can facilitate the development of complex sputter processes but also highlight the potential of synchronized HiPIMS processes for the deposition of piezoelectric thin films and other defect-sensitive materials.

[1] Patidar, Jyotish, et al., Surface and Coatings Technology (2023), 129719.

3:00pm **CM3-1-ThA-6 Advancing Metallic Glasses for Biomedical Applications: A Comprehensive Study on CuAgZr Alloys Using Combinatorial Synthesis, High-Throughput Characterization, and Machine Learning*, Krzysztof Wieczerzak (krzysztof.wieczerzak@gmail.com),*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory of Mechanics of Materials and Nanostructures, Switzerland

This work presents a study on CuAgZr metallic glasses (MGs), highlighting their potential in biomedical applications due to their exceptional strength, corrosion resistance, and antibacterial properties. Our research employs a novel approach combining combinatorial synthesis, high-throughput characterization, and machine learning to explore the mechanical properties of these alloys. We introduce the material library of CuAgZr alloys produced using direct current magnetron sputtering (DCMS) and employ advanced characterization methods to assess their composition, structure, and mechanical properties. A key finding of our study is the significant influence of high oxygen content in Cu-rich regions, a result of post-deposition oxidation, on the mechanical behavior of these alloys. This insight is pivotal in understanding the role of oxygen in synthesized alloys and its correlation with the growth mechanism and chemical composition. The introduction of the "Scanning Indenter" device in our study marks a significant technological advancement, enabling the automatic mapping of full wafers and integration of various characterization techniques like X-ray

fluorescence (XRF) X-ray diffraction (XRD), and nanoindentation. This facilitates a multimodal dataset creation, enhancing our understanding of material properties. Our findings also reveal the critical impact of nanoscale structural features on plastic yielding and flow in these alloys, with a notable correlation between atomic size mismatch, oxygen content, and hardness. Furthermore, we demonstrate the efficacy of machine learning, particularly the multi-layer perceptron (MLP) algorithm, in predicting the hardness of untested alloys, offering valuable insights for future research. This study not only sheds light on the mechanical properties of CuAgZr MGs but also underscores the potential of integrating combinatorial synthesis, high-throughput characterization, and machine learning for the development of new metallic glasses with enhanced strength and economic feasibility.

4:00pm **CM3-1-ThA-9 Accelerating Materials Discovery by Combining Combinatorial Synthesis of Thin-Film Libraries, High-Throughput Characterization and Data Science***, Alfred Ludwig (alfred.ludwig@rub.de),* Ruhr University Bochum, Germany **INVITED**

Discovery of new materials is a key challenge in materials science: e.g., new materials for sustainable production/storage/conversion of energy carriers are necessary to improve existing and to enable future energy systems. Efficient methods for discovery and optimization of new materials are necessary: Thin-film combinatorial materials science (1) is presented as an effective means to produce large datasets on new materials. This approach is useful for validation of theoretical predictions (e.g., from high-throughput computations), and production of large, consistent and complete experimental datasets which can be used for materials informatics. The approach comprises fabrication and processing of thin-film materials libraries by combinatorial sputter deposition processes and optional post-deposition treatments, followed by the high-throughput characterization of the different thin-film samples contained in these libraries, and finally the organization of the acquired multi-dimensional data in adequate databases as well their effective computational analysis and visualization. The importance of defining adequate screening parameters and according designs of materials libraries is addressed. High-throughput material characterization methods are automated, fast, and mostly non-destructive: examples are EDX, XPS and RBS for composition, XRD for crystal structure, high-throughput test stands for temperature-dependent resistance (phase transformation), magnetic, optical and mechanical properties as well as scanning droplet cells for (photo)electrochemical properties screening. Results for up to quinary systems are visualized in the form of composition-processing-structure-function diagrams, interlinking compositional data with structural and functional properties. The talk will cover and discuss examples of combinatorial discoveries and development of new materials in different materials classes and forms (films, nanoparticles) with a focus on compositionally complex materials. Furthermore, a new approach to accelerate atomic-scale measurements for complex alloys is presented as well as applications of materials informatics to accelerate and improve the materials discovery process.

4:40pm **CM3-1-ThA-11 Autonomous Sputter Synthesis and Data Management for Nitride Thin Films***, Davi Febba (davimarcelo.febba@nrel.gov), K. Talley, K. Johnson, S. Schaefer, S. Bauers, J. Mangum, R. Smaha, A. Zakutayev,* National Renewable Energy Laboratory, USA

Autonomous experimentation has emerged as an efficient approach to accelerate the pace of materials discovery. Although instruments for autonomous synthesis have become popular in molecule and polymer science, solution processing of hybrid materials, and nanoparticles, examples of autonomous tools for physical vapor deposition are scarce yet important for the semiconductor industry.

Moreover, sputtering reactors usually available in the market can be challenging to incorporate into an autonomous workflow, mainly due to the lack of comprehensive programming support. This makes it difficult to interface the instruments with optimization and active learning routines, common to an autonomous setup. To overcome these limitations, we recently designed and built a highly automated co-sputtering reactor featuring extensive programming capabilities and support for server-client interactions with other programming languages [1].

Furthermore, this high vacuum instrument is equipped with four cathodes, each with a dedicated channel for plasma monitoring via optical emission spectroscopy. It allows the exploration of a wide substrate temperature range, from cryogenic temperatures up to 1000 °C, in addition to RF and DC substrate biasing. Additional capabilities include real-time deposition data logging of sputtering parameters (such as power, voltage, pressure, gas flow), control of gas distribution to individual targets, time-sequenced shutters, and turbo gate position. All of these enable the user to execute complex programmable synthesis recipes.

In this presentation, we will discuss the details of this unique sputtering instrument and its integration with Python routines, resulting in an autonomous workflow for the synthesis of nitride thin films with controlled composition [1]. Moreover, we will also outline the integration of the time-series data automatically generated by this sputtering instrument with the research data infrastructure (RDI) [2]. NREL's RDI catalogs experimental data from inorganic thin films experiments at NREL and enables the High-Throughput Experimental Materials Database (HTEM-DB) (https://htem.nrel.gov/) [3], which stores information about synthesis conditions, chemical composition, crystal structure, and optoelectronic properties of materials.

[1] APL Mater 11, 071119, 2023

[2] Patterns, 2, 100373, 2021

[3] Scientific Data 5, 180053, 2018

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Golden State Ballroom - Session CM-ThP

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films (Symposium CM) Poster Session

CM-ThP-1 Localized Surface Plasmon Resonance of Silver Nanoparticle Thin Films on Moissanite: Simulation, Fabrication, and Characterization, ***Tsung-Jen Wu (d09224004@ntu.edu.tw)***, *S. Song, W. Chen,* National Taiwan University, Taiwan*; W. Lin,* National Taiwan University of Science and Technology, Taiwan*; M. Phan,* National Taiwan University, Taiwan*; S. Tseng,* National Synchrotron Radiation Research Center, Taiwan

The fabrication and characterization of silver nanoparticle (Ag NPs) thin films on a moissanite (silicon carbide) substrate and their inherent localized surface plasmon resonance (LSPR) properties were investigated in this study. The preliminary phase of this investigation employed Finite-Difference Time-Domain (FDTD) simulations to anticipate the LSPR effects and the resultant hue of the films. The size of the silver nanoparticles was maintained within a range of 10-25 nm, producing a greenish yellow hue attributed to the LSPR effect.

Two methods were harnessed to produce these size-specific Ag NP films. The first approach involved a dual-target co-sputtering technique utilizing silver and silicon dioxide. It prompted the spontaneous formation of Ag NPs, leading to a visible coloration due to the LSPR effect. The other method involved a single-target sputtering of silver, followed by an annealing process to foster the emergence of Ag NPs, yielding a characteristic color induced by the LSPR effect.

CM-ThP-2 Greybox-Models to Describe the Wear Behavior of Coated Cutting Tools, *K. Bobzin, C. Kalscheuer,* ***Nina Stachowski (stachowski@iot.rwth-aachen.de)***, Surface Engineering Institute (IOT) - RWTH Aachen University, Germany

The real application behavior of coated carbide tools can neither be satisfactorily measured, nor described within existing models with the current state of research. The wear development, beginning tool failure as well as the remaining tool life cannot be accurately identified or predicted. This inhibits the knowledge-based qualification of coated tools for more efficient cutting processes. In the current state of research, the tribological system of machining must be evaluated and repeatedly analyzed for every small change in the cutting condition. This is despite the fact that both involved disciplines of production and material engineering have already detailed whitebox models. However, not all available data from both disciplines can be integrated into these models.The main objective is therefore to combine the existing whitebox models with new data driven blackbox models in greybox models. These new greybox models are used to determine the temporal changes of the tools in use, which cannot be described in purely deterministic terms, right up to the end of their service life. Further developments in machining, material and coating technology enable the evolution of new methods for analyzing and simulating the wear behavior of coated cutting tools. This includes the investigation of time- and temperature-dependent coating properties such as indentation modulus, indentation hardness, thermal diffusivity and surface roughness with increasing cutting time. Such changes have not been considered in simulation models up to now. However, by taking such data into account, the description of the wear behavior can be probably significantly more accurate. Another key factor within the SPP 2402 is the data storage as well as the comparison of measurement methods. This enables a better estimation of quality within all participating consocial projects. The final greybox models allow the description of the time-dependent changes in the material properties and the stress collective during machining.

CM-ThP-3 Flow Curve Determination of TiAlSiN Coatings Using Nanoindentation and Iterative FEM Simulations, *K. Bobzin,* ***Christian Kalscheuer (kalscheuer@iot.rwth-aachen.de)***, *X. Liu,* Surface Engineering Institute - RWTH Aachen University, Germany

Physical vapor deposition (PVD) coatings are extensively employed to improve the service life of tools under high thermomechanical load in forming processes. The wear resistance of coatings is highly related to their mechanical properties, especially elastic and plastic properties that can be delineated by the flow curve. Consequently, the accurate determination of the flow curve holds paramount significance in the coating development process. While the elastic modulus can be easily measured using nanoindentation, other flow curve parameters are difficult to determine. The current analytical Juliano approach for determining the yield stress lacks precision and becomes challenging to use when the Juliano signal is not obvious, particularly evident in the investigated TiAlSiN coatings that exhibit minimal plastic behavior. Therefore, an easier and more precise flow curve determination method is required. In this study, flow curves of TiAlSiN coatings are determined combining nanoindentation and iterative finite element simulations (FEM). Initially, nanoindentation using a spherical indenter is performed accompanied by the measurement of time-load and time-displacement curves. Then the nanoindentation is simulated time-dissolved using FEM based on the load at each time step directly derived from the time-load curve. The flow curve parameters in FEM including the Young's Modulus E, yield stress Y, strain hardening coefficient B and strain hardening exponent n are iteratively adjusted by comparing the experimental and simulated time-displacement curves until a good match between two curves. Consequently, the flow curve can be obtained from the FEM model with the best match. The simulated time-displacement curves with physically reasonable flow curve parameters have a good agreement to the experimental time-displacement curves of various TiAlSiN coatings. The method uses FEM simulations to determine all flow curve parameters without measuring the Young's Modulus using nanoindentation and determining the yield stress using the Juliano approach.

CM-ThP-4 Material Property Distributions of Sputter-Deposited Thin Films on a Two-Dimensional Diagram with Incident Particle Energy and Substrate Temperature, ***Ichiro Ikeda (ichiro-ikeda@osakavacuum.co.jp)***, *K. Kuroshima,* Osaka Vacuum, Ltd., Japan*; Y. Gotoh,* Department of Electronic Science and Engineering, Kyoto University, Japan*; M. Iguchi, S. Sugimoto,* Osaka Vacuum, Ltd., Japan

Recently, we have confirmed that Anders' structure zone model (SZD)[1] is applicable to the case of conventional magnetron sputtering[2-3]. TheSZD shows the difference of the film structure on a two dimensional diagram with the normalized incident particle energy and normalized substrate temperature. Based on the fact that the properties of the films depend upon the film structure, we assumed that the distribution of mechanical or electrical property is also well expressed on this two-dimensional diagram. We named the diagram the material property diagram (MPD)[4].

In this study,we attempted to make MPDs ofelectrical conductivity and optical reflectancedistribution of Ti films. Titanium thin films were deposited under various deposition conditions. The deposition conditions were translated to the particle energy incident on a film surface using the computer simulation[2-3] to identify the deposition condition on MPD. From the accumulated data, we drew contour lines for each film property. As a result, it was confirmed that contour lines for electrical conductivity were arranged in parallel to ZONE border on SZD. The electrical conductivity is well explained by the SZD, reflecting the fact that film structure. On the other hand, the contour lines for the optical reflectance were not arranged in parallel to the ZONE border of the SZD. The optical reflectance has relationship different from the film structure. The film property will be well expressed on the MPD, and the diagram differs depending on the material and property itself. About the film property distribution, we confirmed little difference between equipments.

We made the simulation program calculating the sputtering condition from the requested film property value (ex. the conductivity) using the MPD on the assumption that the MPD does not depend on the sputtering condition and the equipment. We may be able toleave out the experience, the intuition or the test sputtering by the use of this program.

References

[1] K. Kuroshima et al., Annual Meeting of the Japan Society of Vacuum and Surface Science 2023,

Nagoya, October 31-November 2, 2023.

[2] K. Kuroshima et al., International Conference on Metallurgical Coatings & Thin Films 2024,

San Diego, May 19-24, 2024 (to be presented).

[3] A. Anders, Thin Solid Films, **518**, 4087 (2010).

[4] I. Ikeda et al., Annual Meeting of the Japan Society of Vacuum and Surface Science 2023,

Nagoya, October 31-November 2, 2023.

CM-ThP-5 AI-Enabled Construction and Prediction of Atomic Models for Thin-Film Heterostructures via Materials Genome Approach, ***Po-Liang Liu (pliu@dragon.nchu.edu.tw)***, *J. Dai,* National Chung Hsing University, Taiwan

Successful heteroepitaxial film growth enables the integration of heterogeneous films despite lattice mismatches. Exceptional heteroepitaxial films alleviate lattice mismatch stress and diminish material defect density, resulting in smoother surfaces and reduced deposition time for subsequent thin-film epitaxial growth. This study introduces a materials genome approach to predict heterostructures. Employing this novel method, we explore new thin-film heterostructures on flexible muscovite mica substrates. As flexible electronic devices rapidly advance, traditional epitaxial substrates are being supplanted by flexible alternatives, yielding substantial economic benefits. While polymers are commonly used for such devices, they suffer from poor thermal stability, low solvent resistance, and a low thermal expansion coefficient. Layered muscovite mica materials have emerged as a promising solution. Muscovite mica, with its two-dimensional layered structure, can be easily divided into flakes, offering mechanical flexibility, optical transparency, and high thermal stability. We have successfully developed a novel artificial intelligence-generated heterostructure for studying the GaN(001)/Muscovite(001) heterostructure. Our findings reveal that the GaN thin film, characterized by the gene T1, epitaxially grows on muscovite substrate models characterized by gene arrangements S1 and S3. The heterojunction demonstrates the potential to form 12 Ga-O bonds, with a calculated lowest interface energy of −1.21 eV/Å^2.

CM-ThP-8 In-Situ Characterization of the Crystallization Kinetics of Sputtered TiO_2 Thin Films, ***Daniel Félix Fernandes (daniel.f.fernandes@angstrom.uu.se)***, Department of Electrical Engineering, Division of Solid-State Electronics, The Ångström Laboratory, Uppsala University, SE-751 03 Uppsala, Sweden*; J. Hérnandez,* Madrid Institute for Advanced Studies in Nanoscience (IMDEA Nanoscience), Ciudad Universitaria de Cantoblanco, C/ Faraday 9, 28049 Madrid, Spain*; J. Martínez,* ALBA Synchrotron, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallés, Barcelona, Spain*; T. Kubart,* Department of Electrical Engineering, Division of Solid-State Electronics, The Ångström Laboratory, Uppsala University, SE-751 03 Uppsala, Sweden, Spain

Crystalline TiO_2 thin films are attractive owing to their photocatalytic, electronic, and optical properties.Anatase is the lower-temperature metastable phase of this material system and is the desired phase in many applications.While the phase formation can be controlled by both the deposition and post-depositionannealing temperatures, it is often desireable to reduce the overall thermal budget. Forthe large majority of cases, the employed temperaturesfor the crystallization of suchfilms areconsiderablyhigh, making it incompatiblewith heat-sensitive substrates.

In this study, the crystallization kinetics of TiO_2thin films during post-deposition annealing is investigated.These were grown by reactive magnetron sputtering at different temperatures and the kinetics assessedby in-situ Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS), with synchrotron radiation. The films were heated for 2 hours and, using an adapted Avrami model for phase change kinetics, the crystallization times were compared for three annealing temperatures: 225, 250 and 300°C. The growth conditions achieved in pulsed-DC (pdcMS) and High Power Impulse Magnetron Sputtering (HiPIMS) were investigated. For both techniques, the influence of the mode of reactive operation, the ionization of the sputtered flux and the deposition temperatures were studied.

All studied films were X-ray amorphous in their as-deposited state. However, the depositionconditions have a significant impact on the transformation kinetics. The results show that the deposition temperature is the single most influential parameter. While the reactive mode of operation also affected the transformation dynamics, HiPIMS was found to facilitate sthe crystallization compared to pdcMS films, and generally promoteda faster formation of the anatase phase. Additionally, from the GIWAXS experiments, a set of optimal growth conditions are identified for ex-situpost-deposition annealing. The optimized conditions were investigated for a 2 hour periodat 250°C. In all cases, anatase was achieved. Depending on the growth conditions, specific anatase planes were favored, as seen in GIXRD measurements.

CM-ThP-9 On the Utility of SiMTra Analysis for Forecasting Atomistics of Confocal Deposition of Bimetal Alloys, ***Kyle Dorman (krdorma@sandia.gov)***, *R. Kothari, N. Bianco, M. Kalaswad, C. Sobzcak, R. Dingreville, D. Adams,* Sandia National Laboratories, USA

Nanocrystalline thin films feature the potential for enhanced or altered material properties compared to their bulk single crystal counterparts. Assessing thermally stable binary metal systems that feature solute enrichment of grain boundaries (J.R. Trelewicz et al., PRB, 2009) for specific material properties, it is a complex task to survey the full compositional range. High-throughput methods of combinatorial sputtering (McGinn, ACS Comb. Sci., 2019) and complementary high-throughput automated data collection systems potentially permit swift accumulation of a large quantity of data on a broad selection of alloy compositions, if provided.

In this poster, we describe the application of the binary collision Monte Carlo program SiMTra (D. Depla et al., Thin Solid Films, 2012) to the challenge of efficient guidance of depositions to access a large range of compositions in a minimal set of depositions. A series of compositionally varied Cu-Ag and Ni-Pt bimetal alloy thin films were prepared by pulsed DC magnetron sputter deposition with varied sputter power and gun-tilt angle. SiMTra simulations provided estimates of film composition for the employed sputter chamber geometry and parameters involved with the simultaneous confocal sputter deposition of each pair of elements. The result is demonstrated with the near-full range of composition achieved, in only three depositions for Cu-Ag, onto 112 samples of 1 cm2 per 150 mm-diameter silicon wafer. The simulation results are presented in comparison to verifying Wavelength Dispersive Spectroscopy (WDS), to demonstrate the degree of accuracy with which SiMTra can specify the binary composition. Successful modeling of film compositions relied on the use of accurate global angular distributions of each elemental target which accounts for target erosion geometry, redeposition, material specific ejecta distributions, and sputter yield amplification with incidence angle following the method of Boydens et al. (Thin Solid Films, 2013). Additionally, we investigate the potential role of off-normal- vs. normal-oriented local ejecta distributions on final film composition by varying these orientations within separate simulations for comparison with WDS. Finally, we present other SiMTra outputs including the energy and incidence angle distributions of species arriving at the film growth surface, which are being used to optimize key film properties such as film hardness and resistivity.

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CM-ThP-10 Investigation of Lithium-Ion Battery Cathodes as a Function of Drying, ***Tatyana Kravchuk (tkravchu@ford.com)***, *S. Peczonczyk, T. Misovski, M. Trought, B. Emley, A. Straccia,* Ford Motor Company, USA

Studying the elemental distribution and morphology in Li-ion battery electrodes prepared under various drying conditions is crucial for comprehending the connection between processing conditions and battery performance. Efficiency in time, cost, and energy usage are common goals in large-scale battery manufacturing, and a deeper understanding of these connections can aid in the development of precise drying protocols for ensuring consistent and high-performance Li-ion batteries at a large scale.

This study describes an analysis performed using Time-of-Flight Secondary Ion Mass Spectroscopy on electrode coatings prepared under various drying conditions, including different temperatures of system components and airflow. The significance of sample preparation is underscored, with a discussion of various methods such as ion milling and microtoming. Subsequently, differences in element distribution and surface morphology between electrodes processed under different conditions are investigated. Experimental findings obtained via TOF-SIMS are compared to those obtained through other surface-sensitive techniques and to those predicted by computational simulation methods. Lastly, the implications of the results for manufacturing are deliberated.

CM-ThP-11 Actually Measuring Thin Film Elastic Constants by Combined X-ray Microdiffraction and Micromechanical Testing, ***Rebecca Janknecht (rebecca.janknecht@tuwien.ac.at)***, Institute of Materials Science and Technology, TU Wien, Austria; *R. Hahn,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *N. Koutná,* Institute of Materials Science and Technology, TU Wien, Austria; *J. Todt, M. Meindlhumer,* Department Materials Science, Montanuniversität Leoben, Austria; *A. Davydok,* Helmholtz-Zentrum Hereon, Institut für Werkstoffphysik, Germany; *P. Polcike, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany; *J. Keckes,* Department Materials Science, Montanuniversität Leoben, Austria; *H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

Direction-dependent X-ray Elastic Constants (XECs) measurements are far from routine and pose significant technical challenges. While nanoindentation offers insights into reduced Young's modulus, accessing direction-dependent XECs necessitates innovative methodologies due to inherent challenges compared to bulk materials (e.g., tensile testing). Although ab initio Density Functional Theory (DFT) calculations offer theoretical input, discrepancies persist between model systems and real-world properties, primarily due to a lack of available experimental data for newly emerging—and often chemically and structurally complex—material systems.

Our study addresses this gap by proposing a novel experimental approach to measure XECs, combining synchrotron microdiffraction and micropillar compression testing to investigate the in-situ stress-strain relation within TiN-based physical vapor deposited (PVD) thin films. Our investigation focuses on two individual ceramic TiBN coatings with boron contents up to 10 at.%, where linear elastic failure prevails. By employing in-situ uniaxial testing at P03 beamline of PETRA III synchrotron at DESY in Hamburg, Germany, we create a controlled environment for the determination of the stress in loading direction and strain in three directions to calculate orientation-dependent Poisson's ratios and Young's modulo, facilitating the calculation of XECs for crystal orientations 111, 200, and 220. By correlating our experimental results with ab initio calculations, our study provides a robust and new method for validating theoretical predictions and advancing thin film material testing and design.

CM-ThP-12 The Influence of Cantilever Geometry on the Measured Fracture Toughness of Hard Coatings, ***Rainer Hahn (rainer.hahn@tuwien.ac.at)***, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *S. Kolozsvari, P. Polcik,* Plansee Composite Materials GmbH, Germany; *C. Jerg,* Oerlikon Surface Solution AG, Liechtenstein; *H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Fracture toughness, K_{IC}, is an essential material property representing the resistance to crack propagation in the most prevalent opening mode. The fracture toughness should be correspondingly high to prevent premature failure of a material or a thin film with subsequent environmental exposure of the substrate. As a result, toughness is an important safety factor when designing protective coating materials exposed to mechanical loads. The fracture toughness of coatings is typically determined using micromechanical methods due to the small dimensions. The microcantilever bending test should be particularly mentioned here, as it determines the intrinsic K_{IC} without possible substrate influences.

This study investigated the influence of the cantilever geometry, particularly the distance between the point of force application and the position of the predefined crack. For this purpose, cathodic arc evaporated TiN was selected as a reference material, and a series of cantilevers were fabricated via focused ion beam (FIB) milling, and subsequently tested with an in-situ indentation stage within the SEM. The calculated fracture toughness was found to be dependent on the distance: as the distance increased, the values decrease to a subsequently constant K_{IC}. In summary, this study discusses failure sources for any over- and under-estimations due to geometrical aspects and provides guidelines for properly conducting and interpreting microcantilever bending tests estimating K_{IC}.

CM-ThP-13 e-Poster Presentation: Finite-Temperature Shear Deformation and Phase Transformations of Transition Metal Diborides MB_2 (M=Ti, Ta, W, Re) via Machine-Learning-Potential Molecular Dynamics, ***Shuyao Lin (shuyao.lin@tuwien.ac.at)***, TU Wien, Institute of Materials Science and Technology, Austria; *D. Holec,* Montanuniversität Leoben, Austria; *D. Sangiovanni, L. Hultman,* Linköping Univ., IFM, Thin Film Physics Div., Sweden; *P. Mayrhofer, N. Koutná,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal diborides (MB_2s) adopt three types of layered hexagonal structures (α, γ, ω) which are different stackings of the metallic sublattice, thus, may be inter-changeable by a displacive transformation. To test this hypothesis, we develop machine learning interatomic potentials (MLIPs) targeted to molecular dynamics simulations of finite-temperature tensile and shear deformation. The chosen material systems, MB_2, M=(Ti, Ta, W, Re), exemplify different energetic preference for the α, γ, ω phase polymorphs. Following the MLIP fitting procedure, a detail validation for atomic-to-nanoscale simulations is presented using a relevant ab initio dataset (including snapshots of ab initio molecular dynamics simulations on shear-induced phase transformation) as well as through the concept of the extrapolation grade. Consequently, the here-developed MLIPs are employed for room-temperature simulations of {0001}[$\overline{1}2\overline{1}$0] and {0001}[10$\overline{1}0]$ shear deformation with nanoscale-sized supercells. Our results reveal a significant impact of the phase prototypes on the shear strength, which is the highest for the energetically most favourable stackings. Shear-induced phase transformations are predicted for TiB_2 and TaB_2. The transformations can be aided by applying additional tensile or compressive strain along the hexagonal [0001] axis. For WB_2 and ReB_2, a nucleations of other defects (e.g. local amorphization or lattice rotation) is typically favoured over changes in the stacking sequence. Our comprehensive study provides insights into the phase-dependent mechanical properties of MB_2 and underscores the strength of machine-learning-potential molecular dynamics for understanding mechanical response of ceramic materials under application-relevant conditions.

CM-ThP-14 Angle-Resolved XPS Characterisation of Thin Films Using Hard X-Rays, ***Tom Swift (tswift@kratos.com)***, *J. Counsell,* Kratos Analytical Limited, UK; *C. Tupei, Y. Li,* Nanyang Technological University, Singapore

High-energy X-ray photoelectron spectroscopy (XPS) was employed to analyze the structure and chemical composition of HfOx thin films deposited on Alumina substrates. The ongoing trend of shrinking device dimensions has led to an increased use of atomic layer deposition (ALD) to enhance uniformity and control of layer thickness. ALD's capability to deposit high dielectric constant (high-k) films has facilitated its widespread application in optical, optoelectronic, and electronic devices.

Using standard Al Kα excited XPS enabled the determination of film thicknesses up to 7nm. However, accurate quantification of the Si 2p peak from the substrate became challenging beyond this thickness. Employing Ag Lα excitation resulted in electrons with higher kinetic energy for the same photoemission peak, effectively increasing the overlayer's attenuation length. In practical terms, this led to a roughly twofold increase in the sampling depth.

In this study, high-energy Ag XPS (Ag Lα radiation - 2984eV) was utilized in a conventional angle-resolved XPS (ARXPS) experiment. The ARXPS data was analyzed using algorithms connected with physical data parameters based on thermodynamic models, maximizing entropy to achieve the best-fit solution [1]. This process generated a reconstructed depth profile over a greater sampling depth provided by the higher energy excitation source. This approach allowed the non-destructive elucidation of the structure of ALD thin films of hafnia, alumina, and a combination of the two. Importantly, the use of the higher photon energy excitation source eliminated the need for destructive depth profiling using Ar-ion beams, reducing the risk of ion beam-induced chemical changes.

The focus of this investigation encompassed film thickness, chemistry at the interfaces, and the efficacy of Ag Lα-excited XPS for such applications.

[1] K. Macak, SIA 43(13) 2011

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 1-2 - Session CM3-2-FrM

Accelerated Thin Film Development: High-throughput Synthesis, Automated Characterization, and Data Analysis II

Moderators: Davi Marcelo Febba, NREL, USA, **Okeksandr Pshyk**, Empa, Switzerland, **Sebastian Siol**, Empa, Switzerland

8:20am **CM3-2-FrM-2 Combinatorial Synthesis and High-Throughput Characterization of Cu-Ag and Ni-Pt Thin Films Fabricated by Confocal Magnetron Sputter Deposition**, ***Kyle Dorman (krdorma@sandia.gov)***, *R. Kothari, N. Bianco, M. Kalaswad, C. Sobzcak, S. Desai, J. Custer, S. Addamane, M. Jain, F. DelRio, B. Boyce, R. Dingreville, D. Adams,* Sandia National Laboratories, USA

Nanocrystalline thin films feature the potential for enhanced or altered material properties compared to their bulk single crystal counterparts. While such possibilities are frequently limited by a lack of thermal stability, nanocrystalline thin films comprised of binary metal alloys such as $Pt_{0.9}Au_{0.1}$ have demonstrated greater resistance to annealing (P. Lu et al., Materialia, 2019) which is consistent with predicted thermodynamic preferences for a minority solute element to enrich and stabilize grain boundaries (J.R. Trelewicz et al., PRB, 2009). Recent studies on Pt-Au binary thin films have emphasized the role of grain boundary character in this solute stabilization (C. M. Barr et al., Nanoscale, 2021), and means of high-throughput combinatorial synthesis (McGinn, ACS Comb. Sci., 2019) have been developed to complement automated characterization and simulation capacity. To further develop understanding of the properties and synthesis of similar nanocrystalline binary metal systems, the suite of tools developed for Pt-Au analysis is now turned towards Cu-Ag and Ni-Pt combinations in search of optimized material properties and greater comprehension of nanocrystalline systems. Our study utilized simultaneous confocal sputter deposition of each pair of elements, with pulsed DC magnetron methods directing single element sources with a variety of approaches. The result, with the substrate fixed rather than rotated and the employment of photolithography, is a varied atomic composition across 112 samples on a single 150 mm diameter wafer. A series of such depositions, varying the gun-tilt angle and power at each cathode, allows swift examination of nearly the full range of alloy compositions. Wavelength Dispersive Spectroscopy, Atomic Force Microscopy, X-ray Diffraction, X-ray Reflectivity, sheet resistance, optical profilometry and nanoindentation were employed for high-throughput and fast-paced analysis. The binary collision Monte Carlo program SiMTra (D. Depla et al., Thin Solid Films, 2012) assisted with the deposition design to minimize the necessary quantity of sample batches, and enabled analysis of the energetic and compositional properties of the wafer at deposition with respect to the resultant hardness, modulus, film density, crystal texture, resistivity, and chemical stability for the case of tarnishing Cu-Ag combinations. The resulting correlations are examined with a goal of optimization of nanocrystalline material properties and identifying the corresponding fabrication conditions.

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8:40am **CM3-2-FrM-3 Combinatorial Screening of Al-Si-N-O Protective Coatings with Tunable Refractive Index**, ***Stefanie Frick (stefanie.frick@empa.ch)***, *A. Wieczorek, K. Thorwarth, O. Pshyk, J. Patidar, S. Siol,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Rising requirements of next-generation technologies lead to an increasing demand for multifunctional thin-film coatings. In order to accelerate the co-optimization of the functional properties of these coatings, combinatorial materials synthesis in combination with high-throughput automated characterization and data analysis is instrumental. The quarternary material system Al-Si-N-O is a promising candidate for protective optical coatings due to the hardness of its nanocomposite phase at low Si contents [1] and the tunability of the refractive index via the variation of the oxygen content [2]. In this work, thin film combinatorial libraries were deposited via reactive Hybrid Al-HiPIMS/Si-DCMS covering a significant fraction of the quarternary phase space by applying orthogonal anion- and cation gradients. Different approaches to obtain intentional oxygen gradients in combinatorial libraries, including varying localization of gas inlets as well as target configurations, will be addressed and the respective advantages and drawbacks will be discussed. Cation spreads mainly between 5 and 35 cation % Si were investigated as well as various oxygen contents depending on the respective anion gradient approach. Subsequently, the libraries were comprehensively characterized via automated mapping procedures with XPS, XRD, nanoindentation and UV-Vis spectroscopy. The latter allowed for automated refractive index determination employing the envelop method for transmission spectra according to Swanepoel [3]. The analysis of the data sets reveals the achievement of an indentation hardness of 20-24 GPa over a range of 10-35 cation % of Si corresponding to a refractive index of 2.03-2.05 in a pure nitride library. In addition, it is shown that the refractive index can be reduced down to 1.57-1.71 for a nearly pure oxide library and higher silicon contents (15-57 cation % Si) at the expense of hardness values of 7-9 GPa. The comprehensive combinatorial data sets allow for deeper insights in the composition-structure-property relationship in this complex material compared to experiments based on serial experimentation. Finally, the influence of the application of an RF bias at the insulating substrates, for an acceleration of the incident ions, on the film properties will be elaborated.

[1] A. Pélisson *et al.*, Surface and Coatings Technology, (2007), 202(4-7), 884-889.

[2] M. Fischer *et al.*, Science and Technology of Advanced Materials, (2019), 20(1), 1031-1042.

[3] R. Swanepoel *et al*, Journal of Physics E: Scientific Instruments, (1983), 16, 1214-1222.

9:00am **CM3-2-FrM-4 From Automated to Autonomous Thin Film Deposition Experiments**, ***Andriy Zakutayev (andriy.zakutayev@nrel.gov)***, NREL, USA **INVITED**

In this presentation, I will discuss recent progress towards demonstration of autonomous thin film deposition experiments in a highly automated combinatorial co-sputtering instrument at NREL. The autonomous operation will be demonstrated on the example of thin film reactively sputtered ternary nitride materials used for energy and electronic applications. A conceptual extension to other materials classes (e.g. oxides) ans other deposition methods (e.g. molecular beam epitaxy) will be discussed. A relation of autonomous deposition instruments to autonomous electrical characterization instruments, data processing pipelines, and high throughput computational reference data will be discussed.

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