Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H1-1-MoM

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

Moderators: Grégory Abadias, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France, **Xavier Maeder**, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, **Michael Tkadletz**, Montanuniversität Leoben, Austria

10:00am **H1-1-MoM-1 In Situ Observations and Measurements of Plastic Deformation, Phase Transformations and Fracture With 4D-STEM***, **Andrew Minor (aminor@berkeley.edu)***, UC Berkeley and LBNL, USA **INVITED**

In situ TEM experiments are typically recorded either in real space or diffraction space. However, it would be ideal to have information from both for when transient events occur that cannot be repeated exactly (ie-defect generation or irreversible phase transformations). 4D-STEM can come close to providing simultaneous real-space imaging and diffraction analysis during *in situ* testing, making it possible to perform orientation and strain mapping and defect and phase identification via diffraction pattern analysis during in-situ deformation in a TEM. This talk will highlight recent *in situ* 4DSTEM nanomechanical deformation experiments that explore transient events where both information from diffraction space and real space are used. The diffraction patterns are used to identify different phases, defects, orientations and relative strain, while the images formed by using virtual apertures provide microstructural context for the analysis. Example experiments include defect generation and fracture in multi-principal element alloys and in situ heating and cooling of materials going through phase transformations.

10:40am **H1-1-MoM-3 Real-Time N_2-Mediated Growth Manipulation of Ultrathin Ag Layers***, **Gregory Abadias (gregory.abadias@univ-poitiers.fr)***, Institut PPrime - CNRS - ENSMA - Université de Poitiers, France*; A. Jamnig, D. Babonneau, A. Michel, Y. Robin,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; A. Resta, A. Vlad, A. Coati,* Synchrotron SOLEIL, France*; K. Sarakinos,* University of Helsinki, Finland*; B. Krause,* Karlsruhe Institute of Technology (KIT), Germany

Noble-metal ultrathin films, with nominal thickness smaller than ~15 nm, are ubiquitous in a wide range of plasmonic devices and other optoelectronic applications. Silver (Ag) layers have recently gained interest as alternative transparent conductive electrode (TCE) candidates for flexible photovoltaics to currently used indium tin oxide, which is inherently brittle and suffers from high cost and poor sustainability. However, Ag films obtained by conventional physical vapor deposition have the natural tendency to self-assemble into 3D agglomerates on weakly interacting substrates, resulting in the formation of rough surface profiles. Therefore, strategies to produce fully continuous, ultrathin and ultrasmooth Ag layers without compromising their electrical conductivity are needed. Among them, the use of gaseous additives, such as N_2 or O_2, appears as an efficient route to shift the continuous film formation thickness to lower values [1,2]. However, to understand the full evolutionary growth regime requires the implementation of *in situ* and real-time diagnostics.

In the present work, the impact of N_2 addition on the morphological and structural evolutions of ultrathin Ag layers is investigated by coupling complementary *in situ* and real-time diagnostics. Lab-scale studies include wafer curvature, surface differential reflectance spectroscopy and electrical resistivity to determine the morphological transition thicknesses (percolation and continuous formation thickness) [3] as a function of N_2 partial pressure. These are augmented by real-time X-ray synchrotron studies (SIXS beamline at SOLEIL) in which the diffraction and reflectivity signals are simultaneously recorded, together with stress evolution. This enable us to explore the influence of N_2 on island shape, texture and stress development, as well as relaxation mechanisms during growth interruptions.

1. Yun, J. *et al.* An unexpected surfactant role of immiscible nitrogen in the structural development of silver nanoparticles: An experimental and numerical investigation. *Nanoscale***12,** 1749–1758 (2020).

2. Jamnig, A. *et al.* 3D-to-2D Morphology Manipulation of Sputter-Deposited Nanoscale Silver Films on Weakly Interacting Substrates via Selective Nitrogen Deployment for Multifunctional Metal Contacts. *ACS Appl. Nano Mater.***3,** 4728–4738 (2020)

3. Colin, J. *et al.* In situ and real-time nanoscale monitoring of ultra-thin metal film growth using optical and electrical diagnostic tools. *Nanomaterials***10,** 2225 (2020)

11:00am **H1-1-MoM-4 Phase Transformation and Solid-State Dewetting of Precious Metal High Entropy Alloy Thin Films on a Sapphire Substrate***, **Xavier Maeder (xavier.maeder@empa.ch)**, A. Sharma, P. Schweizer, J. Michler,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The transition of thin films into isolated particles at a temperature below the melting point of the bulk material is known as solid-state dewetting. So far, most of the literature is limited to dewetting studies on pure metal and binary alloys thin films. The experimental data on dewetting of compositionally complex alloys is rather missing.This work studied the solid-state dewetting behavior of precious metal high entropy alloy thin film deposited on a (0001) single-crystalline sapphire substrate and annealed in a range of temperatures. The combination of dedicated imaging, composition mapping, and diffraction techniques is used to investigate the interplay of grain growth, phase transformations, and dewetting kinetics with the process of in-situ annealing in the TEM.Both X-ray diffraction and the transmission electron microscopy observations revealed the FCC (single-phase) →FCC1+FCC2 (double-phase)→FCC3 (single-phase) phase transformation sequence during annealing. In addition, ex-situ annealing experiments have been performed in the same temperature range to assess the film's dewetting and phase transformation kinetics quantitatively.

11:20am **H1-1-MoM-5 Investigation of Silicon Samples by the Emerging Picosecond Ultrasonics***, F. Faese, **Julien Michelon (jmichelon@neta-tech.com)**, X. Tridon,* Neta, France

With the constantly increasing needs in microelectronics, photovoltaic cells, and other high-tech components in specialized industries, characterizing the growth of epitaxial (epi) silicon on silicon or evaluating the quality of Si/Si bonding becomes more and more critical. For instance, managing the epi Si layer paved the way to new generations of devices such as the Metal Oxide Semiconductor devices (MOS, CMOS and MOSFET) [1] as well as high performance photovoltaic cells [2]. Therefore, in order to address these increasing needs, existing characterization tools provide constantly improved performances, and new characterization tools regularly emerge to provide a technological breakthrough that offers more challenging features.

Some of the existing characterization tools that meet the needs are destructive, such as Scanning and Transmission Electron Microscopy, or semi-destructive such as Secondary Ion Mass Spectrometry. Only a few characterization tools can measure the thickness of epi Si on Si and evaluate the quality of Si/Si bonding after the fabrication process and non-destructively. Among these techniques is the emerging Picosecond Ultrasonics (PU) [3]. This communication will present the principle of operation of this technique and describe some of the potentialities regarding the characterization of Si-based samples. First, we will see how PU can measure the thickness of a layer of epi Si on a Si substrate and describe the related advantages of this technique. Second, we will focus on Si/Si bonding applications with an illustration of PU possibilities to evaluate the quality of the silicon direct bonding.

[1] Skibitzki, Oliver. "Material Science for high performance SiGe HBTs: Solid-Phase Epitaxy and III-V/SiGe hybrid approaches." (2013).

[2] Hamon, Gwenaëlle, et al. "Plasma-enhanced chemical vapor deposition epitaxy of Si on GaAs for tunnel junction applications in tandem solar cells." Journal of Photonics for Energy 7.2 (2017): 022504.

[3] Thomsen, C., et al. "Coherent phonon generation and detection by picosecond light pulses." Physical review letters 53.10 (1984): 989.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H1-2-MoA
Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces II

Moderators: Grégory Abadias, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France, **Xavier Maeder**, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, **Michael Tkadletz**, Montanuniversität Leoben, Austria

1:40pm **H1-2-MoA-1 Decomposition of CrN Induced by Laser-Assisted Atom Probe Tomography**, ***Helene Waldl (helene.waldl@unileoben.ac.at)**, M. Schiester,* Montanuniversität Leoben, Austria*; M. Hans,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; N. Schalk, M. Tkadletz,* Montanuniversität Leoben, Austria

It is well known that measurement parameters can significantly influence the elemental composition determined by atom probe tomography (APT). Especially results obtained by laser-assisted APT show a strong dependence of the laser pulse energy on the apparent elemental composition. Within this study laser-assisted APT experiments were performed on $Cr_{0.51}N_{0.49}$ and thermally more stable $(Cr_{0.47}Al_{0.53})_{0.49}N_{0.51}$, applying two different laser wavelengths (i.e. 532 and 355 nm) and systematically varied laser pulse energies. The deduced elemental composition of CrN exhibited a strong increase of the Cr content, when the laser pulse energy was increased for both laser wavelengths. For low laser pulse energies Cr^{2+}, CrN^{+}, N^{2+}, N_2^{+}were identified, while the amount of detected Cr^{2+} ions increased and the amount of N^{2+} ions strongly decreased at higher laser pulse energies. Further, increased detection of more complex Cr containing ions such as Cr_2N^{2+} at the expense of CrN^{+} was observed at higher pulse energies. At the highest pulse energy levels used within this work the Cr content was > 80 at. %, dominated by the amount of detected Cr^{2+} ions. The change of the spectrum of the detected ions with increasing laser pulse energy led to the conclusion that high laser pulse energies initiate the thermal decomposition of CrN, consistent with the known thermal decomposition path into Cr_2N and subsequently into Cr and gaseous N. On the contrary, variation of the laser pulse energy for the thermally more stable CrAlN resulted only in a slight increase of Cr and a decrease of Al and N with increasing laser pulse energy and no change in the type of detected ions. In conclusion, within the present study the decomposition of a coating material with low thermal stability induced by laser-assisted APT was reported for the first time, emphasizing the importance of the selection of suitable measurement parameters for metastable materials, which are prone to thermal decomposition.

2:00pm **H1-2-MoA-2 Watching Matter Move: Observing in-situ Silver Intercalation in Real Time**, ***Falk Niefind (Falk.Niefind@nist.gov)**,* NIST-Gaithersburg, USA*; C. Dong, R. Maniyara, J. Robinson,* Pennsylvania State University, USA*; S. Pookpanratana,* NIST-Gaithersburg, USA

Collective electron oscillations, known as plasmons, respond strongly to electromagnetic radiation and their chemical environment.[1] Therefore, plasmonic materials have great potential in applications such as optoelectronic devices and sensors.[2] Thin silver (Ag) films are a particularly appealing plasmonic material, due to their low ohmic resistance. However, thin metallic films need to be shielded against unwanted environmental interactions to prevent degradation. One option is to intercalate the Ag atoms between an epitaxially grown graphene (EG, as a top layer) and silicon carbide (SiC).[3]

Here, we use photoemission electron microscopy (PEEM) to observe the Ag de- and re-intercalation process between EG and SiC during in-situ annealing directly in real time (~1 s resolution). PEEM is a surface-sensitive, full-field imaging technique that achieves nanometer-scale spatial resolution with topographic and electronic contrast. It's basic operating principle employs the imaging of electrons released from a sample surface via the photoelectric effect.

The samples were prepared by ex-situ confinement heteroepitaxy (CHet)[3] during which Ag atoms diffuse through plasma engineered defects of the top graphene layer towards the EG-SiC interface at ~900 °C. To our surprise, we found the intercalation process to be observable even at moderate temperatures (300 °C) until it eventually ceases, where additional heating will not drive the reaction forward. Kinetic analysis of the real space images indicated that the intercalation is probably defect mediated, as has been observed for the CHet process. In addition, we conducted scanning electron microscopy (SEM)-energy dispersive x-ray (EDX) analysis, atomic force microscopy (AFM) as well as x-ray photoelectron spectroscopy (XPS) to corroborate and aid in proposing a mechanism of our PEEM-based observations.

1. Z. M. A. El-Fattah et al., ACS Nano 13, 7771-7779 (2019).
2. A. S. Baburin, Optic. Mater. Expr. 9, 611-642 (2019).
3. N. Briggs et al., Nature Materials 19, 637-643 (2020).

2:20pm **H1-2-MoA-3 In-Situ Study of Plasma Surface Interaction Utilizing a Microplasma in a TEM**, ***Holger Kersten (kersten@physik.uni-kiel.de)**, L. Hansen, N. Kohlmann, U. Schuermann, L. Kienle,* Kiel University, Germany

The idea of in-situ investigation of a microplasma in a transmission electron microscope (TEM) was successfully demonstrated in 2013 for the first time [1]. Since then no attempts have been taken to observe the plasma surface interaction in real time. Various technical challenges, e.g. size limitations, gas sealing and handling of high voltages, have to be overcome to enable the in-situ TEM imaging.

A stable atmospheric pressure microplasma discharge was designed and studied ex-situ in advance to gain insight in the plasma surface interaction by several diagnostics [2]. For the experimental studies, a simple setup utilizing parallel plate electrodes with a 50-150 µm interelectrode distance divided by a Kapton spacer with a 1mm diameter hole as discharge region intended for in-situ TEM studies is used. The rather small setup operated in Ar or He, respectively, results in an atmospheric pressure DC normal glow discharge observed by I-V characteristics of the microplasma. Significant differences due to the working gas, electrode material and electrode distance have been found. Currents in the range of 0.5-3 mA resulted in electrode potentials of 140-190 V for most experimental conditions. Optical emission spectroscopy and imaging revealed stable plasma operation and enabled the determination of current densities (approx. 16 mA/mm^{2}for He, or 28 mA/mm^{2}for Ar) independent of the input current as the discharge channel grows in diameter. Sheath thicknesses in the range of a few µm have been calculated by the collision-dominated Child-Langmuir law and trends are confirmed by the optical imaging. Energy flux measurements revealed a pronounced effect of ions on the measurement process and resulted in high energy fluxes locally up to 275 W/cm^2. Effective secondary electron emission coefficients ranging from 1 to 1.6 depending on the discharge conditions have been determined based on the energy balance at the cathode.

Prototypes of the vacuum-proof microplasma cell have been build and preparations for the in-situ studies are successfully ongoing right now. In the present contribution the microplasma and its vacuum-proof encapsulation is addressed and a report on the current state of the in-situ experiments for surface modification will be given.

[1] K. Tai et al., Scientific Reports **3**(2013), 1325.

[2] L. Hansen et al., Plasma Sources Sci. Technol., 2022, accepted.

2:40pm **H1-2-MoA-4 Detection of Individual Nucleated Dislocation Slip Trace During *in Situ* TEM Tensile Testing by Advanced Image Analysis**, ***Xiaoqing Li (li_xiaoqing@berkeley.edu)**, A. Minor,* University of California at Berkeley, USA

Nucleation of crystalline defects such as dislocations lies at the heart of mechanical deformation. Here, we demonstrate a technique for observing the nucleation of individual dislocations during *in situ* transmission electron microscopy (TEM) tensile testing and measuring fundamental parameters relevant for plasticity from the individual events. Our method relies on systematic detection of dislocation slip traces with automated image analysis in an oriented single crystal Ni sample. In this work, a method for detecting a nucleated dislocation is presented and a quantitative approach is applied to extrapolate the energetic barriers for the nucleation of surface dislocations in pristine crystals.

The in-situ tensile test on a defect-scarce single crystal Nickel sample with stable plastic deformation consisting of single defect nucleation was performed on a push-to-pull device in a JEOL 3010 microscope. The load-displacement relation, along with simultaneous video of the deformation (24 frames/second) were recorded (Fig. 1). For a nucleated dislocation that quickly sweeps through a perfect crystal, only the dislocation 'slip trace lines' existed but difficult to be caught. In order to detect dislocation slip traces from dislocations moving at speeds higher than possible to detect directly, contract analysis of frames before and after an event was carried out (Fig. 2). By subtracting the brightness value of each pixel in each two consecutive frames, the dislocation slip trace line can be marked out. Also,

molecular dynamics (MD) simulation was performed to confirm the nucleation specific type of dislocation operating during the uniaxial loading condition. Using the identification of individual defect traces from *in situ* testing, a cumulative probabilistic function is applied to correlate the relationship between a dislocation nucleation event and the corresponding stress level (Fig. 3). Our analysis allows for the extrapolation of the activation parameters for individual dislocation nucleation events using the data on one sample in one tensile test. Precise and quantitative correlation of activation parameters for dislocation nucleation from *in situ* TEM nanomechanical testing can provide direct quantitative measurements useful for computational models of plasticity.

3:00pm **H1-2-MoA-5 Effect of Film Thickness and Trace Width on Electrical Conductivity of Stretchable Composite Inks Under Monotonic and Cyclic Tensile Loading***, Qiushi Li (gli75@gatech.edu), O. Pierron, A. Antoniou,* Georgia Institute of Technology, USA

Flexible and stretchable electronics devices often employ a conductive ink film to transmit electrical signal. As these devices are designed to perform electrically while undergoing large deformation, understanding the electrical conductivity of the ink film under deformation is essential for designing reliable devices. The current work studied the electrical performance of a conductive ink consisting of silver flakes embedded in a polyurethane binder and screen printed on a thermoplastic polyurethane substrate. The effect of ink film thickness (10, 20, 30 mm), differentiated by the number of printing passes and consequently the number of ink layers, for different film trace widths (from 0.25 to 2 mm) was investigated under both monotonic and cyclic tensile loading conditions up to 200% applied strain. *In-situ* experiments under confocal as well as scanning electron microscopes were also performed to examine the evolution of strain localization and damage for specimens with different ink film thicknesses and trace widths. The ink film thickness was found to have a significant impact on electrical performance for smaller trace widths in both the monotonic and cyclic loading cases, but as trace width increased the effect of film thickness was diminished. Based on these findings, a relationship between electrical performance and the geometric design parameters of ink film thickness and trace width was proposed.

3:20pm **H1-2-MoA-6 Exploring Diffusion and Segregation Phenomena on the Nano Scale by *in Situ* Tem Heating Studies (Virtual Presentation)***, Yolita Eggeler (yolita.eggeler@kit.edu),* Laboratory for Electron Microscopy, KIT, Germany **INVITED**

At high temperatures, local diffusion and segregation phenomena affect thermo-mechanical properties of high-performance alloys. This is fascinating from a fundamental point of view but also important in view of the exploitable service lives of high temperature components. Therefore, these processes need to be investigated using *in situ* analytical electron microscopy. This can be achieved by combining multiple heating/cooling steps in the transmission electron microscope (TEM). MEMS based heating chips are used to expose micro machined specimen with specific microstructures to well defined temperature intervals, during which local diffusion/segregation phenomena take place. After cooling energy dispersive X-ray spectroscopy (EDXS) detectors allow to capture elemental distributions maps. Maps which are taken after different accumulated exposure times allow to study the kinetics of nano scale diffusion and segregation phenomena. As one key element of the *in situ* study, two elements of the microstructure (a γ' phase particle and the adjacent γ channel) are used as an intrinsic nano-diffusion-couple (NDC). A thermodynamic equilibrium is established at one temperature followed by annealing at a different temperature. The kinetics in which the new equilibrium is reached is studied using STEM-EDXS. The NDC approach is not only well suited to study interdiffusion across interfaces in two phase model systems, as will be demonstrated in the first part of the study, where experimental results shed new light on the predictions of thermodynamic/kinetic modelling procedures. It also allows to study segregation phenomena to linear and planar defects in compositionally complex alloys, the second key topic which will be investigated. It will be shown that chemical segregation to planar defects can be interpreted as a local phase transformation. Kinetic results on how segregation proceeds will be presented. Special emphasis will be placed on discussing the potential and the limitations of this type of *in situ* investigations and areas in need of further work.

4:00pm **H1-2-MoA-8 *In-situ* Spectroscopic Ellipsometry Based Real-Time Growth Monitoring of Metal-Oxide Atomic Layer Deposition Processes***, Ufuk Kilic (UFUKKILIC@UNL.EDU), S. G. Kilic, M. Hilfiker, A. Mock, D. Sekora,* University of Nebraska-Lincoln, USA*; G. Melendez,* Polytechnic University of Puerto Rico*; N. Ianno, C. Argyropoulos, E. Schubert, M. Schubert,* University of Nebraska-Lincoln, USA

Within the last decade, Atomic Layer Deposition (ALD) of conformal metal-oxide ultra-thin films has provoked an unprecedented interest due to the materials' potential roles in several applications including on-chip photonic devices, ultra-fast switching systems, and next generation transistors [1]. While downsizing of material dimensions for devices applications is an ongoing demand from industry, the ultra-precise control of growth processes during the fabrication of complex systems is a requirement for advanced manufacturing technologies. The integration of spectroscopic ellipsometry (SE), an optical, contactless, and non-invasive technique, into ALD processes has been demonstrated as a powerful and widely-used tool for in-*situ* thin film growth monitoring [2].

In this study, we successfully optimized the oxygen plasma enhanced ALD growth for three different metal-oxides: ZnO, WO_3, and TiO_2, by employing $Zn(CH_3)_2$, $(tBuN)_2(Me_2N)_2W$, and $Ti(OC_3H_7)_4$ organometallic precursors, respectively. To analyze the *in-situ* SE data which were measured within and across multiple cycles during plasma-enhanced ALD of metal-oxide thin films, *a dynamic dual box model is proposed.* The model consists of five layers (substrate, mixed native oxide and roughness interface layer, metal oxide thin film layer, surface ligand layer, ambient) with two of them acting as dynamic parameters (metal oxide thin film layer thickness and surface ligand layer void fraction) to unravel in-cycle kinetics of the metal-oxide ALD growth process. *In-situ* SE data analysis revealed a dynamic surface roughening process with fast kinetics followed by subsequent roughness reduction with slow reaction kinetics upon cyclic exposure to precursor materials and plasma enhanced chemical surface reactions. The proposed dynamic dual box model may be generally applicable to monitor and control metal oxide growth during atomic layer deposition and can be further implemented for precise feedback control and real-time optimization of deposition parameters.

References:

[1] George, S. M., Chem. Rev. 110.1 (2009): 111-131.

[2] Kilic, U., et al.,J. Appl. Phys.*:1805.04171*(2018).

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H2-1-TuM

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

Moderators: James Gibson, RWTH Aachen University, Germany, **Olivier Pierron**, Georgia Institute of Technology, USA

8:00am **H2-1-TuM-1 Reflectance Anisotropy Spectroscopy and Microscopy for the Investigation of Ultrathin Films With Micron Resolution***, Ralph Spolenak (spolenak@mat.ethz.ch),* ETH Zurich, Switzerland **INVITED**

Raman microscopy is the lab-scale gold standard for resolving stress distributions at the micron length scale. Unfortunately, the Raman effect is limited to polarizable materials, which typically excludes metals, an important materials class for both optical and plasmonic applications. Reflectance anisotropy spectroscopy (RAS) is, as our group recently demonstrated, sensitive to the effect of elastic distortion on the band structure of metals and thus allows for the determination of elastic strain.

While this is already valuable as an averaging technique further insight in both the plastic and brittle behavior of metals can only be gained on the local scale. Consequently, this contribution focuses on the development of a broad band RAS microscope, with the challenges of the broadening of the incidence angle as well as the accessible wave length range.

Our group is proud to present first results on pattering induced strain fields in gold thin films, the analysis of strain-engineered semiconductor devices and the observation of single plasmonic dipoles.

8:40am **H2-1-TuM-3 Combinatorial Mechanical Microscopy Using Correlated Nanoindentation Mapping and EDX***, Jeffrey M. Wheeler (jeff.wheeler@femtotools.com),* FemtoTools AG, Switzerland

Mechanical microscopy is an emerging technique using high-speed nanoindentation to map the mechanical behavior and extract phase-level properties from complex microstructures with micron-scale lateral resolution. As such, it is a powerful technique for combinatorial materials science investigations on samples with compositional gradients, such as diffusion couples. In this work, correlated high-speed nanoindentation and energy-dispersive spectroscopy (EDX) were applied to investigate the Ni—Ta system. All seven phases in the system were clearly resolved in the resulting maps, and the mechanical properties and composition ranges for each phase were determined. Good agreement with *ab initio* calculations was generally observed with some exceptions, most notably $NiTa_2$. This was achieved using a simple correlation method utilizing directly overlaid data matrices to allow compositional labeling of mechanical data. This allowed easy data segmentation without requiring complicated statistical deconvolution methods. Without this correlative method, phase deconvolution of the Ni—Ta system would have been challenging due to several phases possessing adjacent compositions and mechanical properties. This demonstrates the potential of this new correlative approach for future investigations, particularly those involving complex microstructures and/or compositional variation.

9:00am **H2-1-TuM-4 Progress in the Development of High Strain Rate Nanoindentation Experiments***, Warren Oliver (warren.oliver@kla.com),* KLA Corporation, USA*; C. Walker, B. Hackett,* Texas A&M University, Department of Materials Science & Engineering, USA*; P. Sudharshan,* International Advanced Research Centre for Powder Metallurgy & New Materials (ARCI) , India*; G. Pharr,* Texas A&M University, USA

High strain rate mechanical testing using instrumented indentation has recently received considerable attention. High strain rates as high as 10^4 are achievable at reasonable indenter velocities (on the order of 0.5 m/s) because the sample size is small. An instrument capable of displacement measurements at rates as high as 1.25 Mhz with sub nanometer resolution and a time constant of 10 microseconds has been constructed. The system also incorporates mechanics that allow the load frame to have a stiffness as high as 90 MN/m making the associated correction very small. While the system directly measures the displacement signal needed accurately, measuring the loads exerted on the sample in sub millisecond experiments can be challenging. In some cases, the time constant of the loading system must be considered. In addition, the load can be dominated by inertial effects. Dynamic models used to describe the system will be considered. A number of approaches for calculating or measuring the loads exerted on the sample will be discussed. Preliminary data for fused silica and Aluminum will be presented.

9:20am **H2-1-TuM-5 Testing the Adhesion of a Sintered Ag Film on a Cu Substrate Using Laser Shocks***, Xavier Milhet (xavier.milhet@ensma.fr),* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; T. de Resseguier,* institut pprime - CNRS - ENSMA - Université de Poitiers, France*; A. Sghuri,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; L. Signor,* institut pprime - CNRS - ENSMA - Université de Poitiers, France

Silver (Ag) paste sintering, is now used for die bonding in the latest generation of power electronic modules. Since the processing conditions require low temperature, low stress and short time, the Ag joints exhibit a porous structure that evolves significantly when exposed to the operating temperatures (between 250C and 300C) [1,2]. In order to model the behavior and properties evolution, there is a need for a fine characterization of the joint itself as well as those of the interface, especially during aging. While the first point has now been relatively widely investigated [3-5], the information on the interface properties is still scarce. In this study, we have explored an alternative route to test the adhesion of the Ag film on a copper (Cu) substrate using laser driven shocks: a laser pulse is calibrated to induce tensile loading near the interface between the substrate and the film, and time-resolved velocity measurements complemented by post-recovery observations provide quantitative information on the adhesive strength. Although such highly dynamic load is somewhat far from the practical application, this method presents the advantage over other techniques to really focus on the interface properties. The results are used to explore the relationship between adhesion, aging and the underlying microstructure.

1- K.H. N'TSOUAGLO, X. MILHET, J. COLIN, L. SIGNOR, A. NAIT-ALI, J. CREUS, M. GUEGUEN, P. GADAUD, M. LEGROS, Advanced Engineering Materials, accepted 2021

2- X. MILHET, A. NAIT-ALI, D. TANDIANG, Y.J. LIU, D. VAN CAMPEN, V. CACCURI, M. LEGROS Acta Materialia 156 (2018) 310

3- J. CARR, X. MILHET, P. GADAUD, S. BOYER, G. THOMPSON, P.D. LEE Journal of Materials Processing Technology 225 (2015) 19

4 - X. MILHET, P. GADAUD, V. CACURRI, D. BERTHEAU, D. MELLIER, M. GERLAND Journal of Electronic Materials 44 (2015) 3948

5- V. CACCURI, X. MILHET, P. GADAUD, D. BERTHEAU, M. GERLANDJournal of Electronic Materials, 43 (2014) 4510

9:40am **H2-1-TuM-6 Transfer Learning in Characterization of Nanoindentation Induced Acoustic Events***, Antanas Daugela (antanas_daugela@hotmail.com),* Nanometronix LLC, USA*; J. Daugela,* Johns Hopkins University, USA

A passive monitoring of acoustic waves during nanoindentation has been attracting the attention of material scientists since the inception of nanomechanical test instruments. The conventional acoustic wave signal treatment via RMS or integrated energy values proved that quantitative acoustic wave properties correlate well with the local contact materials' phenomena such as yield point initiation for W(100) [1, 2], Sapphire [3], phase transformations on SMA, and differentiating of thin film fracture modes.A nanofatigue phenomenon can be observed on thin films by monitoring the resulting multi-cycle nanoindentation loading-unloading curves and post test imaging, which helps in identifying the materials' phenomena [4].However, the true potential of the acoustic characterization method is unleashed in the synergy between wavelet based acoustic signal decomposition and machine learning [5].

The Transfer Learning is a subclass of machine learning which utilizes existing Deep Learning Neural Networks [5].In this work, a Transfer Learning based signal classification of nanoindentation induced passive and active acoustic events is explored.Both passive and active acoustic monitoring can be conducted during nanoindentation with the integrated utrasonic tip.The proposed Transfer Learning technique yields a reliable classification of acoustic signatures on submicron thick coatings.

References:

1. A. Daugela et al, *Zeitschrift fur Metallkunde*, **92(9)**, p.1052-1056 (2001)

2. N. I. Tymiak et al, *Journal of Materials Research*, **18(4)** , p.1–13 (2003)

3. N.I. Tymiak et al, *Acta Materiallia*, **52** p.553-563 (2004)

4H. Kutomi et al, *Tribology International*, **36**, p.255-259 (2003)

5. A. Daugela et al, *Materials Science & Engineering A*, **800** 140273 (2021)

10:00am **H2-1-TuM-7 Nanoindentation Testing to Measure Surface Free Energy in Thin Films and Engineered Surfaces**, *M. Sebastiani,* Università degli studi Roma Tre, Italy*; P. Phani,* International Advanced Research Centre for Powder Metallurgy & New Materials (ARCI), India*; **Edoardo M. Rossi (edoardo.rossi@uniroma3.it)**,* Università degli studi Roma Tre, Italy*; R. Guillemet,* Thales Research & Technology, France*; W. Oliver,* Nanomechanics Inc., KLA Corporation, USA

The ability to engineer and control the Surface Free Energy (SFE) of functional materials is critical for a multitude of applications as this property represents a relevant design parameter for producing components with precisely controlled interfacial performances. The non-destructive measurement of SFE in nanopatterned superhydrophobic hard surfaces is a challenge in both research and industry since, in most cases, time-consuming contact angle measurements (CAMs) are not feasible. Nanoindentation testing can offer a possible contact-mechanics methodology that allows measurement of intrinsic surface properties [1]. In this sense, a novel method has been developed for the assessment of the adhesive interactions by carefully controlling environmental and instrumentation issues. A commercially available nanoindenter has been specifically modified to enable accurate measurement of the pull-off forces raising between the tip and the sample surface. A novel testing protocol implementing adhesion-accounting contact mechanics models [2] has been developed to leverage the new hardware capabilities.

A set of reference surfaces was selected for testing and validation: (i) highly energetic, new, and atomically flat surfaces from cleavage of the silicate sheet-based structure of muscovite mica; (ii) DSP germanium <100> crystals. The latter yielded the pristine substrates for the development of superhydrophobic surfaces, via both patterning and fluorinate silane coating. Those processes performances were independently studied and, ultimately, their interplayed role was investigated on both nanopatterned and silanized substrates. CAMs were performed on all the surfaces investigated to provide comparative results. The method is found to measure SFE over five orders of magnitude, covering hydrophilic to super-hydrophobic surfaces.

[1] F. M. Borodich et al. Proc. R. Soc. A. 464, 2759–2776 (2008).

[2] K. L. Johnson et al. J. Colloid Interface Sci. 192, 326–333 (1997).

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H3-TuA

Characterization of Coatings and Small Volumes in Harsh Environments

Moderators: Thomas Edwards, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland, **Peter Hosemann**, University of California, Berkeley, USA

2:20pm **H3-TuA-3 Stabilized Nanocrystalline Thin Films for Enhanced Thermal, Radiation, and Mechanical Performance**, ***Brad Boyce (blboyce@sandia.gov)***, Sandia National Laboratories, USA **INVITED**

Nanocrystalline thin films can be alloyed to promote thermal stability via solute segregation to grain boundaries.The segregation can impede boundary migration kinetically via solute drag or Zener pinning, or thermodynamically by reducing the boundary's energetic cost.In this study we examine a Pt-Au alloy where the Au has been shown to promote boundary stability upon annealing.Going beyond the thermal contribution, we explore the Pt-Au alloys performance under monotonic tension, fatigue loading, wear loading, and ion irradiation.In each of these cases, the presence of solute can provide synergistic benefits on material properties.However, there are cases where the solute is also detrimental; for example, an over abundance of Au at the grain boundaries can lead to an overall embrittlement and reduced ductility.Through a series of in-situ TEM, in-situ SEM, and ex-situ experiments, we explore the complex role of solute segregation on the thermal, mechanical, and radiation properties.Finally, we propose a chemical pathway to achieve gradient nanostructured metals via compositional tailoring.Unlike the existing plastic deformation methods, like surface mechanical attrition, the compositional tailoring can lead to a heterogeneous grain structure that is 'antifragile': naturally stabilized against further evolution.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

3:00pm **H3-TuA-5 Explaining How *H/E* Influences Coating System Wear Under Harsh Conditions - Insights from Elevated Temperature Nanoindentation, Scratch and Impact Tests**, ***Ben Beake (ben@micromaterials.co.uk)***, Micro Materials Ltd, UK

The ratio of hardness to elastic modulus (H/E) of coating systems and their wear resistance under harsh conditions has been explored. Small-scale tribo-testing at room and elevated temperature (to 600C) has been used to simplify the wear conditions, allowing the role of contact severity, length scale and damage tolerance to be studied to determine why coating optimisation strategies are effective and why they can fail.

Results show the importance of relatively low elastic modulus in reducing tensile stresses in sliding/abrasive contact. This is a key factor in why coating design for optimised H/E and resistance to plastic deformation, H3/E2, can be more effective than aiming for extremely high hardness.

The influence of substrate ductility and load support on the damage tolerance of the coating system in impact tests has been investigated by testing at different contact size (nano/micro/macro). The combination of a coating with moderate hardness, high plasticity index and a tough (i.e. damage tolerant) substrate can improve impact resistance.

The results of the small scale tests show that mechanical and microstructural factors should not be considered in isolation. The role of coating microstructural design in optimising the high temperature mechanical properties of coating systems and their performance in tribologically severe contact conditions such as high speed machining is highlighted.

4:00pm **H3-TuA-8 *In-Sem* Micromechanical Testing Up to 1000 °C of High Entropy Transition Metal Nitride Thin Films Alloyed With Al**, *A. Pshyk,* Linköping University, IFM, Sweden; ***Thomas Edwards (thomas.edwards@empa.ch)***, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *B. Bakhit,* Linköping University, IFM, Sweden; *M. Jain,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *P. Küttel,* Alemnis AG, Switzerland; *G. Greczynski, L. Hultmann,* Linköping University, IFM, Sweden; *J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Transition metal nitride (TMN) based thin films have a hugely diverse range of applications due to their unique properties including high hardness, thermal stability, high-temperature oxidation resistance and low coefficient of friction. Recently, high entropy transition metal nitrides (HENs) have proven to be among the most promising ways to advance TMN-based thin films. HENs have gained considerable interest in the scientific community, demonstrating a blend of properties often highly enhanced in comparison to their conventional TMN counterparts. Although the outstanding properties of HENs have been well demonstrated at room temperature, their thermal stability and related high temperature mechanical properties are rarely investigated: the question of their potential as high temperature structural materials remains open.

Here, we investigated the mechanical properties of different HENs at temperatures up to 1000 °C by micromechanical testing. Equimolar (TiHfNbVZr)N and (TiHfNbVZrTa)N thin films alloyed with different Al content were deposited using a novel hybrid method combining high-power impulse magnetron sputtering (HiPIMS) from an Al target with DC magnetron sputtering (DCMS) from high entropy alloy targets, i.e. equiatomic TiHfNbVZr and TiHfNbVZrTa targets, in which a negative substrate bias is synchronized with the Al-rich portion of the HiPIMS pulse. The elevated temperature performance of the HENs was evaluated using a state-of-the-art high-temperature micromechanical testing system to carry out micropillar compression. The tests were performed *in situ* in an SEM at 25, 500, 700, 800, 900 and 1000 °C under vacuum, allowing observation of the deformation mechanism changes at elevated temperature, and avoiding oxidation. This direct measurement of mechanical properties (strength, plasticity limit, stress-strain behaviour, brittle-to-ductile transition) of HENs at elevated temperatures was interpreted in relation to the microstructure, phase composition, lattice distortion and valance electron concentration of the HENs, as well as phase changes upon annealing, e.g. spinodal decomposition. Further high temperature notched microcantilever fracture toughness measurements are currently underway.

Experimental details such as indenter material selection and chemical reactivity are also discussed.

4:20pm **H3-TuA-9 Custom Cryo-Nanoindenter for in-Situ Investigations of the Brittle-to-Ductile Transition in a Scanning Electron Microscope**, ***Hendrik Holz (Hendrik.Holz@fau.de)***, *S. Gabel, B. Merle,* University Erlangen-Nuernberg, Germany

Hydrogen is a promising energy carrier, which however needs to be transported and stored at cryogenic temperatures. A more thorough understanding of the mechanical behaviour of structural materials and coatings at those low temperatures is crucial to ensure safe operations. While nanomechanical testing of materials at elevated temperatures has gained traction over the past few years, only a handful of nanoindentation systems are yet commercially available for operation below room temperature. In this work, we present a novel custom-built cryo-cooled in-situ nanoindenter, which is operated inside a scanning electron microscope. This nanoindenter is based on a commercial system from Femtotools, where we have added low-vibration gas flow cooling and temperature control. In this presentation, we will show first applications to the brittle-to-ductile transition of chromium. Chromium is commonly used as a coating on top of steel and is therefore a natural candidate material for liquid hydrogen tanks. Its suitability for cryogenic application is paramount.

4:40pm **H3-TuA-10 Development of a Novel High Strain Rate Nanoindenter for Small-Scale Mechanical Characterization Over a Wide Strain Rate Range**, ***Stefan Zeiler (stefan.sz.zeiler@fau.de)***, *H. Holz, B. Merle,* University Erlangen-Nuernberg, Germany

Understanding the changes in mechanical behavior at high deformation speeds and the influence of the microstructure are crucial steps to increase the damage tolerance of components that are exposed to impacts during their lifetime, e.g. safety-relevant components in cars and airplanes. Currently, there is a deficit in experimental techniques for probing the

mechanical behavior of coatings and small volumes at high strain rates. In this presentation, we will introduce a nanoindenter with enhanced electronic components, which was used to overcome the indentation strain rate limitation of conventional nanoindentation (ca. 0.1 s^{-1}). An intrinsically displacement-controlled piezo-actuator is operated in combination with a piezo-based load cell and a 1 MHz data acquisition system. Novel testing methods allow measurements with constant indentation strain rates up to ca. 10^4 s^{-1}. This presentation will focus on challenges with the experimental procedures and show first applications to superplastic alloys over several orders of magnitude of indentation strain rate.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H2-2-WeM

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

Moderators: James Gibson, RWTH Aachen University, Germany, **Olivier Pierron**, Georgia Institute of Technology, USA

9:40am **H2-2-WeM-6 Abnormal Grain Growth in Ultrafine Grained Ni Under High-Cycle Loading**, ***Olivier Pierron (olivier.pierron@me.gatech.edu)***, Georgia Institute of Technology, USA

Abnormal grain growth can occur in polycrystalline materials with only a fraction of grains growing drastically to consume other grains. Here we report abnormal grain growth in ultrafine grained metal in a rarely explored high-cycle loading regime at ambient temperature. Abnormal grain growth is observed in electroplated Ni microbeams with average initial grain sizes less than 640 nm under a large number of loading cycles (up to 10^9) with low strain amplitudes (< 0.3%). Such abnormal grain growth occurs predominantly in the family of grains whose <100>orientation is along the tensile/compressive loading direction. Micromechanics analysis suggests that the elastic anisotropy of grains dictates the thermodynamic driving force of abnormal grain growth, such that the lowest strain energy density of the <100>oriented grain family dominates grain growth. These results are compared to other recent investigations of cyclic-induced grain growth in metals. In order to establish the general applicability of abnormal grain growth in metals controlled by the elastic anisotropy of single-crystal grains, a high-throughput technique to perform systematic characterization of cycle-induced grain growth in ultrafine grained metallic films with varying degrees of elastic anisotropy is presented.

11:00am **H2-2-WeM-10 Superlattice Effect on the Mechanical Properties of Transition Metal Diboride Coatings**, ***Rainer Hahn (rainer.hahn@tuwien.ac.at)***, *A. Tymoszuk,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

PVD deposited superlattice structures enable the simultaneous enhancement of hardness and fracture toughness of thin ceramic coatings – evading the strength-ductility trade-off dilemma [1]. While a deeper understanding of this effect has been gained for transition metal nitrides (TMN) [2], hardly any knowledge is yet available for diborides (TMB_2). Here we show that superlattices can—similarly to the nitrides—increase both mechanical properties of diboride coatings. For this purpose, we developed non-reactively sputtered TiB_2/WB_2 and TiB_2/ZrB_2 superlattice coatings, the former is characterized by a high difference in shear modulus (ΔG ~112 GPa), and the latter features a high lattice mismatch (Δa ~0.14 Å) of the participating layer materials.

Nanoindentation, as well as in-situ microcantilever bending tests, yield a distinct increase in hardness (up to 45.5 ± 1.3 GPa) for the TiB_2/WB_2 system but no increase in fracture toughness. Contrary, TiB_2/ZrB_2 shows no increase in H, while K_{IC} increases by ~ 20% up to 3.70 ± 0.26 MPa·$m^{1/2}$. Similar behavior is observed for cube-corner-based fracture toughness evaluation, however, under the influence of corresponding residual compressive stresses. X-ray diffraction studies show a preferred (001) orientation for most of our coatings, the only exception thereby are the TiB_2/WB_2 superlattices with a bilayer period Λ > 9 nm, where we observe increasing (101) orientation with an increasing bilayer period. Furthermore, the number of satellite peaks and their intensity hints towards sharp interfaces, later confirmed by our HR-TEM studies. These results are discussed and complemented by an extensive literature review.

Keywords: Hard Coatings, Diborides, Physical Vapor Deposition, Micromechanical Testing, Fracture Toughness

[1] R. Hahn, M. Bartosik, R. Soler, C. Kirchlechner, G. Dehm, P.H. Mayrhofer, Scr. Mater. 124 (2016) 67–70.

[2] R. Hahn, N. Koutná, T. Wójcik, A. Davydok, S. Kolozsvári, C. Krywka, D. Holec, M. Bartosik, P.H. Mayrhofer, Commun. Mater. 2020 11 1 (2020) 1–11.

11:20am **H2-2-WeM-11 Fatigue Behavior of Gold Thin Films at Elevated Temperature Studied by Bulge Testing**, ***Anna Krapf (anna.krapf@fau.de)***, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

Microcomponents, such as microchips, actuators and sensors, are often based on metallic thin films that must endure cyclic thermomechanical loading during their lifetime. The mechanical properties of these thin films are usually different from bulk materials and so are their thermomechanical fatigue mechanisms. For this reason, an advanced bulge setup was used to cyclically load gold thin films of 150 nm thickness at temperatures in the range 25 °C – 100 °C. The stress-controlled experiments highlight the significance of the interface character for the fatigue lifetime. The presentation will discuss the fatigue properties and damage mechanisms of gold thin films – freestanding and with brittle sublayer - as a function of the microstructure, temperature and stress amplitude.

11:40am **H2-2-WeM-12 Tensegrity Metamaterials - Towards Failure Resistant Engineering Systems**, ***Jens Bauer (jens.bauer@uci.edu)***, University of California, Irvine, USA **INVITED**

Failure of materials and structures, including ductile metals, brittle ceramics, discrete foams and space-trusses, is typically preceded by highly localized deformation. Formation of shear bands and crack surfaces, and buckling of walls and struts thereby cause a chain reaction of locally confined damage events, while large parts of the system do not experience critical loads. In lightweight structures, localized deformation causes catastrophic failure, limiting application to small strain regimes. To ensure robustness under real-world non-linear loading scenarios, over-designed linear-elastic constructions are adopted.

Breaking with this established paradigm, we present three-dimensional (3D) tensegrity metamaterials which delocalize deformation, demonstrating a pathway towards superior, failure resistant load bearing systems. In a tensegrity system, isolated rigid compressive bars stretch a continuous mesh of tethers forming a free-standing lightweight, truss structure. We demonstrate that the unique isolation of compressive members in tensegrity systems suppresses the propagation of instable deformation mechanisms. This facilitates a delocalized deformation pattern, which is free from localized under- or over-use. As a result, tensegrity metamaterials possess unprecedented failure resistance, with up to 25-fold enhancement in deformability and orders of magnitude increased energy absorption capability without failure over same-strength state-of-the-art lattice architectures. These findings provide important groundwork for design of superior engineering systems, from reusable impact protection systems to adaptive load-bearing structures.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Golden State Ballroom - Session HP-ThP

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes (Symposium H) Poster Session

HP-ThP-1 e-Poster Presentation: Strategies for Increasing the Fracture Toughness of Hard Coatings Using CrN as a Role Model, ***Rainer Hahn (rainer.hahn@tuwien.ac.at)***, *S. Rosenecker, D. Forstner,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; T. Wojcik,* Institute of Materials Science and Technology, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Transition Metal Nitrides (TMN) are well known for their good mechanical stability, chemical inertness, as well as tribological properties. Hence, they successfully found application in the metal forming industry, and are in use as protective coatings in the automotive, aerospace, and energy industry. Besides TiN, CrN is one of the most applied and investigated hard coatings. A decisive disadvantage of these hard coatings, however, is their low fracture tolerance. Premature failure of the coating due to crack initiation and propagation leads to economic disadvantages or completely excludes an application for safety reasons.In recent years, micromechanical testing methods have made it possible to measure and specifically improve the fracture toughness of thin film materials [1]. This study focuses on microcantilever bending tests [2].

In this contribution we present three possible strategies for enhancing the fracture toughness of cathodic arc evaporated CrN coatings: toughening by grain refinement, multilayer toughening, and alloying approaches. While our first approach—grain refinement—did not lead to a significant toughness increase, we could observe an increase in fracture toughness and hardness for the other two strategies. Hereby, superlattice (multilayered) systems, CrN/TiN in our case, show the highest potential with an increase from 2.0 $MPa \cdot m^{1/2}$ and 20 GPa for pure CrN up to 3.7 $MPa \cdot m^{1/2}$ and 30 GPa respectively. Nonetheless, the alloying of Si (the maximum Si content was 10 at.%) to CrN as the second promising approach still yields an increase in toughness up to ~3.0 $MPa \cdot m^{1/2}$ and 28 GPa. Besides the mechanical characterization of our samples, we also performed extensive X-ray diffraction studies and high-resolution TEM studies to describe the structure and morphology.

Keywords: Hard Coatings, Physical Vapor Deposition, Micromechanical Testing, Fracture Toughness

References:

[1] B.N. Jaya, C. Kirchlechner, G. Dehm, J. Mater. Res. 30 (2015) 686–698.

[2] K. Matoy, H. Schönherr, T. Detzel, T. Schöberl, R. Pippan, C. Motz, G. Dehm, Thin Solid Films 518 (2009) 247–256.

HP-ThP-2 Insights on Fracture and Fatigue Mechanisms of Hard Protective Coatings, ***Lukas Zauner (lukas.zauner@tuwien.ac.at)***, *R. Hahn,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Tailoring the intrinsic fracture characteristics of hard protective coatings towards the fatigue properties of state-of-the-art bulk materials is paramount for the application of innovative coating materials extending the fatigue-life of high-performance components. Thus, an in-depth knowledge on the failure pathways of ceramic-based thin films – generally associated with lack in intrinsic ductility – but also coated components under long-term mechanical and/or thermal loading is essential to extend their lifetime. In consequence, understanding and implementing coating concepts that allow for a controlled, and hence predictable crack propagation throughout their operating spectrum are of major interest for various industrial applications. Despite recent advances [1], literature reports on the fatigue resistance of especially hard ceramic coatings, but also coated components in general, are relatively rare with a strong approach via macroscopic test facilities. Within this study we present a methodical approach to understand the failure behaviour on different length scales utilizing model systems (*i.e.*, Cr and Cr-based compounds) to consider the aspect of different bonding strengths and crystal structures, respectively. Using quasi-static and cyclic bending of pre-notched, unstrained micro-cantilever beams in conjunction with in-situ synchrotron X-ray diffraction the intrinsic fracture toughness (K_{IC}) as well as the critical failure aspects of thin films under various loading conditions are presented. Up to the high-cycle fatigue regime (*i.e.*, $N = 10^7$ cycles), the failure of monolithic sputter deposited PVD coatings is shown to be dominated by the inherent fracture resistance, irrespective of the bonding character. The recorded fatigue behaviour is further correlated with large-scale dynamic-mechanical analysis of coated Ti6Al4V platelets to step up in length scale and thus including residual stresses and changes in the elastic constants on the coating-substrate interface. The results are expected to provide key-insights into the underlying mechanisms promoting crack growth in PVD coated components.

[1] Bai, Yanyun, et al. "Stress-sensitive fatigue crack initiation mechanisms of coated titanium alloy." *Acta Materialia* 217 (2021): 117179.

HP-ThP-5 Acoustic Monitoring of Nanoindentation Induced Nanofatigue, ***Jurgis Daugela (jdaugel1@jhu.edu)***, Johns Hopkins University, USA*; A. Daugela,* Nanometronix LLC, USA

In the era of fast product development thin film engineers are looking for quick and efficient methods of characterization.Nanoindentation based multi-cycle loading offers an inside look into the real-time contact fracture dynamics [1]. A nanofatigue phenomenon can be observed on thin sub-micrometer films by monitoring the resulting multi-cycle nanoindentation loading-unloading curves, where post-test imaging helps identify a materials' behavior [2, 3].In addition, classical Mason-Coffin and racheting fatigue models derived for the nanoscale contact can be utilized in predictions and correlate well with experimentally obtained nanofatigue cycles.

A newly developed ultrasonic nanoindentation tip operates in the hundreds of kHz; therefore, it induces milions of load cycles within seconds.The resulting nanofatigue induces different thin film fracture modes such as radial, sink-in, and produce unique acoustic signatures.The ultrasonic nanoindentation tip monitors associated waveforms, which can provide an additional inside into the nanofatigue process dynamics via advanced acoustic waveform analysis.Following our previous study [4], acoustic waveforms were processed using a combination of wavelet based signal decomposition and Deep Learning. The proposed Deep Learning technique yields a reliable classification of acoustic signatures obtained during the fracturing of sub-micrometer thick coatings.

References:

1. B. D. Beake et al, *Materials Science & Engineering A*, 7**80** 139159 (2020)

2. H. Kutomi et al, *Tribology International*, **36**, p.255-259 (2003)

3. Y. Matsuda et al, Wear, **259**, p. 1497–1501 (2005)

4. A. Daugela, *Materials Science & Engineering A*, **800** 140273 (2021)

HP-ThP-6 Spotting the CSM Plasticity Error during Nanoindentation with Continuous Stiffness Measurements, *B. Merle,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; **Hendrik Holz (hendrik.holz@fau.de)***, University of Erlangen-Nuremberg (FAU), Germany

Dynamic nanoindentation is a popular method for continuously probing the mechanical properties of a coating as a function of depth. Here, it is shown that special caution must be exercised when testing materials with high modulus-to-hardness ratios (E/H) at fast loading rates, as the choice of harmonic parameters can result in a significant underestimation of the elastic modulus and overestimation of hardness.The errors are caused by the processing of elastic-plastic data by the lock-in amplifier in a technique initially designed to be applied to elastic deformation only. Intuitively, the higher the amount of plastic deformation within a cycle is, the larger the difference to the ideal condition is, and the higher the error is. The exact mechanisms leading to this error are discussed based on simulated CSM signals and experimental measurements.

HP-ThP-7 Advanced Characterisation in Amorphous Thin Films for Biomedical Applications, *M. Sebastiani,* ***Edoardo M. Rossi (edoardo.rossi@uniroma3.it)***, Università degli studi Roma Tre, Italy

One of the main goals of tissue engineering is the preparation of multifunctional biomaterials showing good mechanical properties, biocompatibility, and antibacterial activity simultaneously. Multi-element thin films are a new class of nano-engineered materials showing an

excellent combination of high-strength and biocompatibility. Additions of Au, Cu, Zn or Ag to Ti-based films can induce potential antibacterial behavior [1, 2]. In this framework, Ti-Cu and Ti-Cu-Ag thin films were deposited on silicon substrate by physical vapor deposition magnetron sputtering (MS-PVD), with the aim of obtaining concurrent biocompatibility and antibacterial properties with better mechanical properties. The produced films were characterized by X-ray diffraction (XRD), nanoindentation, atomic force microscopy (AFM), scratch adhesion and X-ray photoelectron spectroscopy (XPS), to investigate their structural, mechanical, and surface properties. The biocompatibility of thin films is investigated by fibroblasts MRC-5 cell lines. Finally, the antibacterial activity of these thin films against Pseudomonas aeruginosa (P. aeruginosa) and Staphylococcus aureus (S. aureus) is evaluated and correlated to the Ag contents. Ti-Cu thin films shows complete amorphous structure, but addition of silver changes the film structure to partially crystalline at 20% Ag and completely crystalline at 30% Ag. XPS spectroscopy shows titanium oxidized to Ti (IV), copper partially oxidized to Cu (II) and partially in metallic state while silver remains unoxidized. The observed surface chemistry can be a main explanation for the excellent combination between biocompatibility and antibacterial properties [3]. In fact, the formation of mixed copper and titanium oxide on the surface of Ti-Cu and Ti-Cu-Ag thin films induces high biocompatibility and remarkable antibacterial properties.

[1] L. Somlyai-Sipos, et. al., Appl. Surf. Sci. Chem. Soc. Rev. (2020), 553, 147494.

[2] W. Zhang, et. al., J. Mat. Sci. Technol. (2021), 88, 158.

[3] S. Rashid, et. al., Nanomaterials 2021, 11, 435.

HP-ThP-8 Capabilities of Time-of-Flight Low-Energy Ion Scattering Demonstrated on the Example of Surface Oxidation of Ti and Ti-Based Hard Coatings, ***Philipp M. Wolf (philipp.wolf@physics.uu.se)***,** Department of Physics and Astronomy, Uppsala University, Sweden*; D. Neuß,* Materials Chemistry, RWTH Aachen University, Germany*; T. Tran,* Department of Physics and Astronomy, Uppsala University, Sweden*; M. Hans, J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany*; D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden

Ion scattering methods, especially Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA), are well established methods allowing the study of composition and structure of materials with a nm resolution. Ever thinner films and the study of surfaces introduce the need for a sub-nm resolution, difficult to achieve with MeV ion methods like RBS and ERDA. Here, we present a time-of-flight low-energy ion scattering (ToF–LEIS) setup, offering resolutions down to a monolayer,[1] using the exemplary case of surface oxidation of pure Ti and Ti-based hard coatings like TiN and (Ti,Al)N. The employed ToF-LEIS setup, able of detecting both neutrals and ions, offers high surface sensitivity to study the structure and composition of the outermost atomic layers by using primary ions with energies of 1–10 keV.[2] A connected preparation chamber, including an ion sputter gun, a heating filament, a gas inlet system, an Auger electron spectrometer (AES), a low-energy electron diffraction setup and an e^-–beam evaporator enables the in situ preparation and study of surfaces exposed to stimuli like high temperatures or reactive gases. The possibility of studying initial modification steps at surfaces not only offers further insights into the behavior of the immediate surface region, but can also yield knowledge on the general behavior of material systems. Due to the low ion currents necessary, ToF-LEIS, like other ion scattering methods, can be considered as non-destructive.

We demonstrate the analytical power of our approach by studying the surface oxidation of in situ grown Ti as well as ex situ grown Ti, TiN and (Ti,Al)N prepared by sputter deposition. These systems were chosen to compare surfaces more prone to oxidation like pure Ti with surfaces that show a comparably increased stability towards oxidation like TiN and (Ti,Al)N. The films were exposed to O_2 at pressures of 1.0×10^{-6} and 1.0×10^{-5} mbar for up to 90 min with sample temperatures ranging from room temperature up to 850°C. As expected, the ex situ grown Ti-based hard coatings show a high resistance to further surface oxidation even at increased temperatures, while for pure Ti we were able to observe surface oxidation both in AES and ToF-LEIS measurements already when offering 1.0×10^{-6} mbar O_2 for 30 min at room temperature, further increasing with the amount of offered O_2. The presented results showcase the capability of our ToF-LEIS setup to study surfaces and ultrathin films and the effects external stimuli have on them.

[1]D. Primetzhofer et al., Appl. Phys. Lett., 92, 011929, 2009

[2]M. Draxler et al., Vacuum, 73, 39-45, 2004

Author Index

Bold page numbers indicate presenter