Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room On Demand - Session H1

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

H1-1 INVITED TALK: Multimodal and *in situ* Electron Microscopy to Understand Local Deformation Mechanics*, Josh Kacher (josh.kacher@mse.gatech.edu)***, Georgia Institute of Technology, USA **INVITED**

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

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

H1-3 Development of In-situ Liquid Cell Transmission Electron Microscopy for Quantifying Temperature-Dependent Thin Film and Nanostructure Processing*, Serin Lee (serinlee@mit.edu)***,** Massachusetts Institute of Technology, USA*; N. Schneider,* Renata Global, USA*; J. Park,* Princeton University, USA*; S. Tan, F. Ross,* Massachusetts Institute of Technology, USA

Over the last several years, the technique of liquid cell TEM(LC-TEM) has been developed for imaging liquid samples in TEM with good spatial and temporal resolution. LC-TEM enables us to complete the triangle of structure-properties-processing of materials under controlled conditions of temperature, biasing, and liquid composition. Temperature control is particularly important as it is a key parameter in the operation of battery materials and the kinetics of electrochemical processes such as corrosion and etching, as well as being a useful variable in understanding the physics of nanostructure evolution. Here, we will discuss the effect of temperature on the evolution of dendrite formation from metal ions in solution, because this is a widely found morphology that has significant relevance to battery electrode stability and materials synthesis. First, we build a robust model to calculate the equilibrium concentration of chemical species in the liquid medium under electron beam irradiation as a function of temperature. The model includes the complete radiolysis reaction set for the full sent of chemical species in the initial solution. The model also includes the temperature-dependent radiolysis reaction parameters. We use Arrhenius behavior for the reaction rates and G values (rates of generation of the primary products due to beam irradiation). We use this model to predict how temperature affects the radiolysis-driven equilibrium concentrations of the species. Next, we expand the model so that it can be applied to understand temperature-dependent kinetics of nanostructure evolution, by considering the diffusion and depletion of precursors. This involves modification of the Stokes-Einstein equation with temperature-dependent viscosity to calculate the diffusion length. This complete model provides an opportunity to understand how radiolysis species behave at different temperatures under the combined effect of parameters such as the important experimentally controllable variables for liquid cell experiments: dose rate, initial concentration of the solution, pH, and aeration. We will show the results of testing this model by comparison of calculated results with experimental observations on nanoparticle generation from silver nitrate solution, dendrite growth trajectories, and the beam-induced etching and growth of metal thin films at different temperatures. We are excited by the opportunities presented by LC-TEM to develop and test a robust model that enables the temperature to be used quantitatively to probe the physics of nanostructure evolution and for a range of practical processing applications in energy storage, corrosion, and catalyst synthesis.

H1-4 UHV Specimen Transfer Systems for Analysis of Reactive Materials with Atom Probe Tomography*, Robert Ulfig (robert.ulfig@ametek.com)***,** *K. Rice, T. Prosa, D. Reinhard, J. Shepard,* CAMECA Instruments Inc., USA*; U. Maier,* Ferrovac GmbH, Switzerland

Atom Probe Tomography is the highest sensitivity 3D analytical technique with nanoscale spatial resolution and has been used to study a wide variety of materials. APT however analyzes small volumes and requires specialized specimen preparation resulting in very high surface to volume ratios. For a wide variety of microscopies and associated applications, changes related to exposed surfaces, or the bulk temperature history have little or no effect on the goal of the analysis, e.g. characterization of stainless steel grain size. For other studies, especially when using atom probe tomography, a carefully controlled environment (temperature, pressure, atmosphere, etc.) may be critical. For example:

– Rapid oxidizers (e.g. uranium, lithium)

– Surface contamination (e.g. catalysts)

– Characterization of hydrogen content in steels, semiconductors, etc.

– Analysis of “soft” materials potentially encased in vitreous ice (e.g. biological)

– Transport between various microscopic analysis/treatments (e.g. FIB-SEM, reaction chambers)

Due to growing interest in the above applications that require this capability, a UHV/Cryogenic transfer system has been developed based on a collaboration between the Max Plank Institute for Steel Research in Germany, CAMECA in the United States, and Ferrovac in Switzerland. The transfer design is based on the mobile UHV Suitcase from Ferrovac, customized to transfer samples held in a standard LEAP specimen carrier. This system can be fully integrated to a specially modified LEAP 5000 system’s hardware and software. Transfer can be completed in less than 1 minute to the LEAP or any system with a standard vacuum connection. This talk will describe the existing system and a new version of VCTM to FIB transfer system developed with cooperation from ThermoFisher Scientific for fast and easy transfer in/out of a standard FIB-SEM, to the LEAP, and to other systems such as reaction chambers.

H1-5 Cold Sprayed Cr-coating on Optimized ZIRLO™ Claddings: An Atom Probe Tomography Study of the Cr/Zr Interface and its Microstructural and Chemical Evolution after Autoclave Corrosion Testing*, Andrea Fazi (fazi@chalmers.se)***,** *H. Aboulfadl, H. Andrén, M. Thuvander,* Chalmers University of Technology, Gothenburg, Sweden

As-produced Cr-coated Optimized ZIRLO™ cladding material fabricated with the cold-spray deposition process is studied. Atom probe tomography is used to investigate the nature of the cold sprayed Cr-coating/Optimized ZIRLO™ bonding interface and the heat affected zone produced by the coating deposition on the Zr-substrate. A 10–20 nm thick intermixed bonding region is observed at the interface between coating and substrate. The chemical composition of this region suggests that this layer originated from a localized melting of a thin volume of the outermost former surface of the substrate. Chromium, diffusing from the coating into the Optimized ZIRLO™ substrate during the deposition process, is found segregating at grain boundaries at up to a few hundred nanometres distance from the interface. The same material is also analysed after autoclave corrosion testing to examine the microstructural and chemical evolution of the previously mentioned intermixed bonding region. Nucleation of $ZrCr_2$ intermetallic phase is discovered at the interface, inside the intermixed layer. Cr-rich regions are observed penetrating a few hundreds nanometres beyond the interface into the substrate, possibly along grain boundaries or sub-grain boundaries.

H1-6 INVITED TALK: Multicracking of Thin Films and Nanostructures on Stretchable Substrates; Impact on Magnetic Properties*, Damien Faurie (faurie@univ-paris13.fr),* *F. Zighem, S. Merabtine,* LSPM-CNRS, Université Paris13, France*; P. Lupo, A. Adeyeye,* National University of Singapore **INVITED**

Nanoscale systems fabricated on flexible or stretchable substrates are being studied more and more because of their ability to adapt to non-planar surfaces, particularly in confined environments. In addition, these systems have the advantage of being lighter and less expensive than their counterparts deposited on more conventional rigid substrates. In recent years, many magneto-electronic devices have been made on different polymer substrates. The ability of these magnetic thin films on polymer substrates to be folded or stretched is essential, but their use is still delicate, which is a brake on the industrialization of these systems.

The main issues are to understand how the applied strains to the flexible magnetic systems impact their magnetic properties. Obviously, when a thin film is deposited on a flexible substrate, it is usually submitted to high stresses due to the stretching or the curvature of the whole system and to the mechanical contrast between the film and the substrate. These stresses may have an important effect on the static and dynamic magnetic properties of thin films, especially on the resulting magnetic anisotropy. In particular, it is important that the large strains to which they are subject are not harmful to their functional properties. In fact, beyond the classical magnetoelastic effects observable at small strains, the phenomenon of multi-cracking and associated localized buckling observed for inorganic thin films on organic substrates tensily stressed lead to heterogenous strains must have effects on the magnetic properties. However, these are rarely discussed in the case of flexible magnetic systems, and have never been studied in depth.

In this work, we focused on experimentally identifying the cracking mechanisms for different magnetic alloys ($Co_{40}Fe_{40}B_{20}$, $Ni_{80}Fe_{20}$) deposited on Kapton® substrate. The phenomena of multicracking but also buckling of thin films have been studied. Thin films surface was probed by atomic force microscopy during *in situ* tensile tests to clearly identify these mechanisms. Subsequently, we have identified the effects of these irreversible phenomena on the magnetic properties of thin films (anisotropy and Gilbert damping coefficient).

References :

[1] S Merabtine, F Zighem, D Faurie, A Garcia-Sanchez, P Lupo, AO Adeyeye, Nano letters 18 (5), 3199-3202 (2018).

[2] S Merabtine, F Zighem, A Garcia-Sanchez, V Gunasekaran, M Belmeguenai, X Zhou, P Lupo, AO Adeyeye, D Faurie, Scientific reports 8 (1), 13695 (2018).

[3] D Faurie, F Zighem, P Godard, G Parry, T Sadat, D Thiaudière, P-O Renault, Acta Materialia 165, 177 (2019)

H1-9 Nano-scale Residual Stress Profiling in Ultra-thin Si_3N_4/ZnO Multilayer Stacks using FIB-DIC Method*, Marco Sebastiani (seba@uniroma3.it),* Roma TRE University, Italy

Silicon nitride (Si_3N_4) is commonly used in many optical applications because of its transparency over a wide spectral range from near-ultraviolet (UV) to the infrared (IR) region. One example is the low emissivity (Low-E) coatings, which are applied to large area architectural glazing to reduce heat losses from buildings. They combine high visible transparency with high reflectance in the far-infrared region. To achieve such combination of properties, Low-E coatings generally consist of dielectric/Ag/dielectric multi-layers stacks, where the thin (~ 10 nm) Ag layer reflects long wavelength IR back into the building while the dielectric layers both protect the Ag and act as an anti-reflective layer.

The architecture of the multi-layer stack influences its mechanical properties and it is strongly dependent on the residual stress distribution in the stack. Residual stress measurement by micro-ring core focused ion beam (FIB) milling at the surface offers lateral resolution better than 1 mm and provides information about the residual stress depth profiling with a resolution better than 50 nm. The method is suitable for both equi-biaxial and non-biaxial stress distribution and hence covers a large number of material systems. In this work, thin Si_3N_4/ZnO/Si_3N_4 stacks with varying thickness (100, 160 and 200 nm) were deposited by magnetron sputtering onto glass substrate and post deposition annealed at 650 °C for 12 minutes. Residual stress measurement by FIB-DIC revealed that the individual Si_3N_4 layers in the multi-layer stack are under different amount of compressive stresses. The magnitude of these stresses changes after the heat treatment cycle and provides useful insight into the multi-layer architecture. The results show that FIB-DIC is a reliable method for accurately probing the residual stresses with nanoscale resolution.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room On Demand - Session H2
Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes

H2-1 Advanced Characterization Techniques for Zinc Based Coatings on Steel Varying from Microstructure Investigation to Mechanical Testing*, Houssem Eddine Chaieb (houssem-eddine.chaieb@mines-paristech.fr),* Mines ParisTech, PSL Research University, Tunisia*; V. Maurel, K. Ammar, S. Forest, A. Koster,* Mines ParisTech, PSL Research University, France*; F. Nozahic, J. De Strycker,* ArcelorMittal Global R&D Gent, Belgium*; J. Mataigne,* ArcelorMittal Global R&D Maizières, France*; A. Tanguay,* LMS, Ecole Polytechnique, Paris-Saclay University, France*; E. Héripré,* MSSMat, CentraleSupélec, Paris-Saclay University, France

Zinc based coatings on steel are widely used in different fields ranging from construction to the automotive sector. The main quality of this type of coatings is their high resistance to corrosion. The addition of other alloying elements like aluminum and magnesium to the coating's composition enhances the corrosion resistance of the coatings and is associated with a modification of their mechanical properties.

The purpose of this work is to highlight some original characterization techniques that allowed to investigate the microstructure and the mechanical properties of some grades of Zn-Al-Mg coatings.

SEM observations, EBSD characterizations and FIB analyses were carried out both at deformed and non-deformed states. This allowed to diagnose the microstructural aspects of the coatings and to link them to the deformation and damage mechanisms. In-situ tensile tests and determination of strain fields were performed at different length scales. At a mesoscopic length scale, optical microscopy yields measurement of strain localization and associated failure probability down to a spatial resolution of about 100 µm, without any modification of the coating surface. Lithography technique was used within the SEM in-situ tensile test to deposit a double patterned gold grid on the coating's surface which allowed to capture strain at a global scale and at a finer scale, down to a spatial resolution below 2 µm. At this finer scale, detailed failure mechanisms have been analyzed through a direct comparison of local grain orientation, slip and twinning, and initiation of crack. The global scale was used to prescribe measured displacement field as a boundary condition for a Finite element analysis of the polycristal, including grain orientation and precise morphology of grain boundaries obtained by EBSD. The correlation between local straining and damage is finally discussed.

H2-2 Toward Novel Stretchable Electronics with Nanostructured Metallic Glass Films*, Matteo Ghidelli (m.ghidelli@mpie.de),* Max-Planck-Institut für Eisenforschung GmbH, Germany*; H. Idrissi,* Université Catholique de Louvain, Belgium*; A. Orekhov,* University of Antwerp, Belgium*; J. Raskin,* Université Catholique de Louvain, Belgium*; J. Park,* Yonsei University, Republic of Korea*; A. Li Bassi,* Politecnico di Milano, Italy*; T. Pardoen,* Université Catholique de Louvain, Belgium

Thin film metallic glasses (TFMGs) are emerging materials characterized by outstanding combination of mechanical/electrical properties involving a yield strength close to the theoretical limit, large ductility (> 10%) [1] and metallic-like conductivity [2]. Nevertheless, the synthesis of advanced TFMGs with engineered microstructure and the understanding of their mechanical/electrical properties is barely tackled, requiring the development of novel synthesis strategies and cutting-edge techniques for submicrometer scale characterization.

Here, we report the use of Pulsed Laser Deposition (PLD) as a novel technique to synthetize nanostructured $Zr_{50}Cu_{50}$ (%at.) TFMGs. We show how the control of PLD process parameters (background gas pressure and laser fluence) enables to synthetize different film microstructures involving atom-by-atom or cluster-assembled growth, resulting in a variety of film structures including compact fully amorphous, amorphous nano-porous with large free volume interfaces, and amorphous embedded with nanocrystals. High-resolution TEM reveals a nano-laminated atomic structure characterized by alternated layers with different chemical enrichment and local atomic order.

This self-assembled nanoarchitecture is at the basis of unique mechanical properties including large elastic modulus (145 GPa) and hardness (10 GPa). Quantitative *in-situ* TEM tensile tests reveal that films have an outstanding yield strength (3 GPa) and ductility (> 9%) product which is significantly dependent on the microstructure with large/low plasticity and low/high yield strength obtained for nanogranular/compact metallic glass films. Finally, we developed a stretchable transparent electrode based on nanogranular TFMGs nanotrough network showing excellent stretchability (70%) and low sheet resistance (~3 Ω/sq) which is then integrated in wirelessly rechargeable transparent heater, demonstrating the potential of these films for novel stretchable electronic devices.

[1] M. Ghidelli, H. Idrissi, S. Gravier, J.-J. Blandin, J.-P. Raskin, D. Schryvers, T. Pardoen, Acta Mater. 2017, 131, 246-259.

[2] B. Wan An, E.-J. Gwak, K. Kim, Y.-C. Kim, J. Jang, J.-Y. Kim, J.-U. Park, Nano Lett. 2016, 16, 1, 471-478.

H2-3 Intrinsic Mechanical Properties of Moderate Temperature Processed Cvd Amorphous Silicon Oxide (SiO_2) and Oxynitride (SiO_xN_Y) Thin Films*,* ***Maxime Puyo (puyo@chimie.ups-tlse.fr)****, C. Lebesgue, K. Topka,* Université de Toulouse, France*; B. Diallo,* Univ. Orléans, France*; R. Laloo, V. Turq, H. Vergnes, D. Samelor, F. Senocq, B. Caussat,* Université de Toulouse, France*; N. Pellerin, C. Genevois,* Univ. Orléans, France*; C. Vahlas,* Université de Toulouse, France

Silicon oxides (SiO_x) and silicon oxynitrides (SiO_xN_Y) films are frequently encountered as protective coatings to isolate devices and surfaces from air or aggressive media[1]. Several studies highlight the influence of both the structure and the chemical composition of such materials on their properties. Young modulus (E) and hardness (H) values are notably linked to the nature and the density of the material network and are strongly impacted by changes in stoichiometry[2]. For coatings, such modifications can also affect the adhesion to the substrate[3]. Characterizing the above mechanical properties is of importance, since it allows to monitor subsequent film functional properties and performances as a function of the processing conditions.

Herein, we focus on sub-micrometer SiO_x and SiO_xN_Y thin films processed on Si wafers by state-of-the-art, scalable, thermal chemical vapor deposition (CVD) processes which are well adapted to coat thermosensitive substrates with complex 3D geometry.Oxidation by oxygen or ozone of tetraethyl orthosilicate (TEOS), eventually substituted with nitrogen-rich precursors, such as tris(dimethylsilyl)amine (TDMSA), for SiO_xN_Y films, has been utilized to achieve lower deposition temperature. Films stoichiometry and composition were characterized; hydration of the network spans from 4 to 20 at.%H depending on the precursors and processing conditions.

Mechanical characterization of such films can be highly challenging, especially in the cas of important E mismatch between the film and the substrate and for very thin layers[4]:depending on the penetration depth, the substrate mechanical properties are likely to affect the measurement, resulting in the characterization of a film-substrate system instead of the intrinsic film properties. Consequently, E and H have been evaluated by nanoindentation using Oliver and Pharr method and several models[5,6] proposed in the literature have been used to extract the intrinsic film properties E_f and H_f. For SiO_x films, the calculated value of E_f was around 45 GPa; which is consistent with that reported for hydrated SiO_x[2]. Investigation on SiO_xN_Y is underway with the aim of revealing how the intrinsic film properties evolve with the processing conditions due to influence of the latter on the film chemical composition and network structure.

[1] K. Bawane *et al.*, *Corros. Sci.*, **2020**, 166, 108429

[2] H. Mei *et al.*, *Acta Mater.*, **2019**, 178, 36

[3] D.S Wuu *et al.*, *Surf. Coat. Technol.*, **2005**, 197, 253

[4] A. Kumar and K. Zheng, *Int. J. Appl. Mech.*, **2010**, 2(1), 41

[5] M. Martyniuk *et al.*, *Proc. of SPIE*, **2005**, 5798, 216

[6] A.M. Korsunsky and A. Constantinescu, *Mater. Sci. Eng., A*, **2006**, 423, 28

H2-4 New Models and Advancement in Measuring the Elastic Behaviour of Thin Films using Impulse Excitation Technique*,* ***Akram Alhussein (akram.alhussein@utt.fr)****,* University of Technology of Troyes (UTT), France*; E. Zgheib,* University of Technology of Troyes (UTT) and Lebanese University (UL), France*; M. Slim,* University of Technology of Troyes (UTT), France*; K. Khalil,* Lebanese University, Lebanon*; M. François,* University of Technology of Troyes (UTT), France

The deposition of thin films is developed more and more to meet the industrial and society needs. Coatings present a great solution to protect a material and giving it multiple functionalities. The elasticity behavior of these films is the mean issue to be controlled in order to enhance their performance (e.g. hardness, wear resistance, oxidation resistance, etc.).

The goal of our research work is to develop a new methodology to measure the elastic constants of films using impulse excitation technique (IET). IET is based on the analysis of vibrational frequencies of an excited sample. Different films were deposited using magnetron sputtering technology. Mono and multi layer films, isotropic and anisotropic materials, were deposited on glass and steel substrates. The parameters influencing the elasticity of the coatings were identified. The error factors and the measure uncertainty were evaluated.

The methodology used is based on a multi-scale approach for mono and multilayer films. The correlation between microstructure, texture, and the properties of the coating was established after performing experiments (Film deposition, IET measurements, Nanoindentation, XRD, etc.) and analytical developing using Abaqus and Mathematica software. These analyses allowed us to develop new models to get Young's and shear moduli of films and understand the relationship between the deposition parameters, the physicochemical properties, the microstructures and the elastic constants of the materials [1-5].

Keywords: Coatings, Elastic constants, Multilayers, Anisotropy, Microstructure, Texture, Micromechanical models, Impulse Excitation Technique, Magnetron sputtering.

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References:

[1] E. Zgheib, A. Alhussein, M.F. Slim, K. Khalil, M. Francois, Elastic behavior of anisotropic coatings sputter-deposited at oblique incidence, International Journal of Mechanical Sciences (2020) 106050.

[2] M.F. Slim, A. Alhussein, E. Zgheib, M. François, Acta materialia 175 (2019) 348 – 360.

[3] E. Zgheib, A. Alhussein, M.F. Slim, K. Khalil, M. François, Mechanics of materials 137 (2019) 103143.

[4] M.F. Slim, A. Alhussein, F. Sanchette, B. Guelorget, M. François, Thin solid films 631 (2017) 172-179.

[5] M.F. Slim, A. Alhussein, A. Billard, F. Sanchette, M. François, Journal of Materials Research 32(3) (2017) 497-511.

H2-5 Influence of the Bonding Nature on the Fatigue Resistance of Cr-based Thin Films*,* ***Lukas Zauner (lukas.zauner@tuwien.ac.at)****, R. Hahn,* TU Wien, CDL-SEC, Austria*; M. Alfreider,* Montanuniversität Leoben, Department of Materials Science, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; D. Kiener,* Montanuniversität Leoben, Department of Materials Science, Austria*; H. Riedl,* TU Wien, CDL-SEC, Austria

Innovative coating materials and architectural concepts extending the fatigue-life of modern high-performance components throughout their operating spectrum by controlled, and hence predictable crack propagation are of major interest for various industrial fields. Consequently, a fundamental knowledge on the decisive failure criteria of PVD deposited coatings – generally associated with an intrinsic lack in ductility – under long-term mechanical and/or thermal loading is paramount in order to enhance the limited bulk material properties utilizing protective thin films. Literature reports on fatigue resistance, of especially hard ceramic coating materials [1] but also thin films in general, are relatively rare. Thus, an in-depth analysis of different coatings – meaning prevalent bonding states, *i.e.* altered ratio of ionic, covalent, and metallic bonds – with respect to fatigue phenomena (e.g. LCF, HCF, strain rates or extrusion formation) is of great interest.

Within this study we present a methodical approach towards a general understanding on the failure behaviour of PVD deposited thin films from

the aspect of the bonding structure between the atomic constituents making use of a model system containing Cr and Cr-based compounds, respectively. The DC magnetron sputtered thin films have been analysed with respect to phase formation, thermo-mechanical properties, and morphology by means of nanoindentation, X-ray diffraction, as well as electron imaging techniques. The influence of the stress state was quantified through high-temperature wafer-curvature measurements. Microcantilever tests were used to calculate the fracture toughness K_{IC} and the fracture stress σ_f by introducing a pre-notch as well as bending the cantilevers in the as received state, respectively. Low (LCF) and high cycle fatigue (HCF) tests of unstrained micro-cantilever geometries were subsequently performed under various loading conditions based on the critical stress intensities observed during quasi static tests. Through this comprehensive approach we are able to identify the most critical aspects with respect to fatigue life of different coating material classes.

References:

[1] X. Luo, B. Zhang, G. Zhang, Fatigue of metals at nanoscale: Metal thin films and conductive interconnects for flexible device application, Nano Materials Science. 1 (2019) 198–207.

H2-6 Development and Application of a Multifunctional Nanoindenter: Coupling to Electrical Measurements and Integration in-situ in a Scanning Electron Microscope*, Fabien Volpi (fabien.volpi@grenoble-inp.fr), *S. Comby-Dassonneville, C. Boujrouf, M. Verdier,* SIMaP – Univ. Grenoble Alpes, CNRS, SIMaP, France*; D. Pellerin,* CSI/Scientec, France

Nanoindentation is a well-known characterisation technique dedicated to local mechanical testing of materials at small scales. In the past decades, numerous efforts have been made to expand the capabilities of nanoindentation technique [1]: real-time electron imaging, coupling with multifunctional characterisation tools, high temperature measurements,...

The present submission reports the development of a home-made multifunctional characterisation device based on a commercial nanoindenter. This device combines mechanical to electrical characterisations, and can be integrated in-situ in a Scanning Electron Microscope (SEM):

1. Electrical characterisations cover both resistive and capacitive measurements.
2. In-situ SEM integration allows precise positioning of nanoindentation tests (precision better than 100nm) as well as the positioning of electrically-coupled indentation maps.

Selected applications will be shown:

1. Dielectric permittivity determination under mechanical load: an experimental procedure and a data-processing method have been set up to quantitatively extract the dielectric permittivity of insulating films from capacitive-nanoindentation (Fig.1) [2].
2. Leakage current through insulators under mechanical load: Insulating films are know to degrade when subjected to mechanical stresses. The present device allows the real-time monitoring of this insulation degradation. Leakage mechanisms with or without mechanical load will be discussed.
3. Multifunctional property mapping: The combined mapping of mechanical and electrical properties is also possible (Fig.2). An illustration will be shown on a multiphase alloy developed for its compromise between high tensile strength and high electrical conductivity.
4. Real-time monitoring of the contact area: a three-step procedure applied to resistive-nanoindentation has been developed to precisely monitor the tip-to-sample contact area. This approach is expected to be an experimental alternative to analytical models for contact area determination.

Prospects are numerous : capacitive-nanoindentation can fill a gap between quantitative characterisations at macro-scales and relative characterisations at nanoscale; leakage measurements under mechanical loads should help the understanding of oxide degradations; SEM-integration opens to multifunctional property mapping;...

References:

1. H. Nili, K. Kalantar-Zadeh, M. Bhaskaran, S. Sriram, Prog Mater Sci. 58 (2013).

2. S. Comby-Dassonneville, F. Volpi, M. Verdier, Sensors and Actuators A: Physical, 294, 185-193 (2019)

3. S. Comby-Dassonneville, F. Volpi, G. Parry, D. Pellerin, M. Verdier, MRS Communications, 9(3), 1008-1014 (2019)

H2-7 X-Ray Photoelectron Spectroscopy Analysis of Electronic Band Structure for MIM Capacitor Interfaces*, Son Hoang (son.hoang@emdgroup.com), *T. Ngo, E. Januar, M. McBriarty, A. Lee, C. Clavero,* Intermolecular Inc., a subsidiary of Merck KGaA, Germany

Metal-Insulator-Metal (MIM) capacitors play a crucial role in many applications including dynamic random access memories (DRAM), radiofrequency and analog circuits, and high power microprocessor units. For the DRAM applications, the understanding of the electronic band structure of the interface between the high-k dielectric and metal is crucial to design an effective strategy to control the leakage current. Future DRAM MIM capacitors aim at an increasingly thinner oxide layer with equivalent oxide thicknesses below 0.5 nm [1], posing challenges in probing interfacial properties using conventional metrology methods.

In this work, we report an entirely XPS-based workflow to determine the interfacial band structure of TiN/ZrO_2/TiN stacks. The TiN/ZrO /TiN stacks were deposited on Si substrates by magnetron sputtering of TiN and atomic layer deposition of ZrO_2. XPS is a surface-sensitive technique, probing only the top 6-10 nm of the material being analyzed. Conventionally, XPS is used to analyze the composition, chemical states, and valence band structures of materials. In our case, we also employ XPS to determine the work function of TiN via cut-off energy measurement and the bandgap of the ultrathin ZrO_2 layer via examining the onset of energy loss in O1s core-level spectra [2]. An electronic band model of the interface is proposed based on the combined analyses, allowing us to determine barrier height and providing insight into the potential leakage of the stack.

[1] S. Y. Lee et al., Appl. Phys. Lett. 105 (2014) 201603

[2] M. T. Nichols et al., J. Appl. Phys. 115 (2014) 094105

H2-8 INVITED TALK: Strength and Fracture Toughness at Elevated Temperature of Monolithic and Multilayered Hard Coatings*, Jon Molina-Aldareguia (jon.molina@imdea.org)*, IMDEA Materials Institute, Spain **INVITED**

Hard coatings for the cutting tool industry experience high temperatures under service conditions. However, the characterization of their mechanical properties relies traditionally on nanoindentation tests, commonly at room temperature. With the current development of novel nanomechanical testing techniques, in combination with FIB milling, it is now possible to test these materials under compression, tension and/or bending, and to determine their strength and toughness, even at elevated temperature. These novel testing methodologies open new opportunities to explore microstructural effects on the mechanical behavior of hard coatings. In particular, the use of controlled loading configurations at the micrometer scale allows elucidating anisotropic effects in strength and toughness of hard coatings, and to identify weak microstructural features that can compromise their mechanical response. The ultimate objective is to generate the knowledge required to design new coatings with superior strength and toughness. In this talk, examples of application of micropillar compression, cantilever bending, microtensile testing and micropillar splitting tests to understand the mechanical behavior of hard coatings will be shown. Examples will include monolithic and multilayered nitride coatings, as well as nanoscale multilayer systems, combining metallic and ceramic layers.

H2-10 The Spinodal Decomposition of Nanolamellar CVD $Ti_{1-x}Al_xN$ recorded by *in-situ* Scanning Transmission Electron Microscopy*, Christian Saringer (christian.saringer@unileoben.ac.at)*, *M. Tkadletz,* Montanuniversität Leoben, Austria*; I. Letofsky-Papst,* Institute of Electron Microscopy and Nanoanalysis, NAWI Graz, Graz University of Technology and Graz Centre for Electron Microscopy, Austria*; C. Czettl,* CERATIZIT Austria GmbH, Austria*; N. Schalk,* Montanuniversität Leoben, Austria

$Ti_{1-x}Al_xN$ deposited by chemical vapor deposition (CVD) exhibits an extraordinary microstructure consisting of alternating Al and Ti rich face centered cubic (fcc) lamellae with thicknesses in the range of only a few nanometers. This microstructure allows to stabilize the fcc modification of $Ti_{1-x}Al_xN$ up to exceptionally high Al contents above $x \approx 0.8$. Consequently, this leads to both, an increase of the onset temperature of spinodal decomposition as well as an enhanced oxidation resistance. In the present work we have used *in-situ* scanning transmission electron microscopy to track the spinodal decomposition of this nanolamellar material into fcc TiN and fcc AlN, as well as the subsequent formation of hexagonal wurtzitic

AlN. In order to achieve that, an electron transparent sample was annealed inside the microscope up to a temperature of 1200 °C. Images were simultaneously collected using annular dark field (ADF) and high angle annular dark field (HAADF) detectors. Stacking the recorded images reveals a clear picture of the microstructural evolution taking place, enabling the observation of the spinodal decomposition *in-situ* during its occurrence. It can be seen that up to 975 °C the microstructure remains stable and the lamellar structure is preserved. At 1000 °C the pronounced elemental contrast achieved with the HAADF detector revealed first signs of spinodal decomposition in the Ti rich lamellae, while the Al rich lamellae remain stable. The decomposition process is completed at approximately 1150 °C and the material has entirely lost its lamellar structure. This is followed by a quick phase transformation and the formation of wurtzitic AlN, which is clearly visible from the recorded ADF images. Although the spinodal decomposition in $Ti_{1-x}Al_xN$ has been extensively investigated, the novel approach of recording the microstructural evolution using *in-situ* scanning transmission electron microscopy is able to shed new light on this and potentially on similar small scale processes.

H2-11 Improving the High Temperature Hardness of Nanocrystalline Copper through Tungsten Nanoparticles*, N. Rohbeck, T. Edwards, E. Huszár, L. Pethö,* ***Xavier Maeder (xavier.maeder@empa.ch)****, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The hardness of copper (Cu) can be greatly improved by a refined microstructure consisting of nano-sized grains. So far the application of such nano-grained Cu has been inhibited by its inability to withstand elevated temperatures and even at room temperature spontaneous abnormal grain growth has been observed.

Here, we show that the hardness of nano-grained Cu can be retained by incorporating about 1 vol% of tungsten (W) nanoparticles. Therefore, thin film Cu was synthesised by physical vapour deposition (PVD) inside a custom-built deposition chamber that had been modified to allow for concurrent co-deposition of W nanoparticles. *In situ* high temperature indentation measurements were performed up to a maximum of 400°C.

By comparing the hardness evolution with temperature of the Cu film containing W nanoparticles with the pure Cu sample, differences in the deformation mechanism become apparent. In the as deposited state both samples exhibited an identical hardness of 3.2 GPa and when the temperature increased the hardness decreased by equal amounts in both films. From 200°C onwards, however, the drop in hardness was notably sharper in the pure Cu film. After cool down, the hardness was found to be reduced by 50% in the pure Cu, whereas the Cu-W nanoparticle sample had retained more than 90% of its initial hardness value.

Subsequent TEM imaging showed that the W nanoparticles with a diameter of 4 nm were randomly distributed within the Cu matrix at an average spacing of 9 nm. The microstructure consisting of columnar grains with a high density of nanotwins was not changed after the thermal exposure. The pure copper films showed larger grains and exhibited a completely changed texture. Here we could prove that by incorporating as little as 1 vol% of second phase particles in nanocrystalline copper, the microstructure can be stabilised even at high temperatures leading to an improved hardness.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room On Demand - Session H3

Characterization of Coatings and Small Volumes in Harsh Environments

H3-1 INVITED TALK: Investigating Plasticity Effects on Failure and Fracture at the Microscale*,* ***Nathan Mara (mara@umn.edu)****, K. Schmalbach,* University of Minnesota, USA*; R. Ramachandramoorthy, J. Michler,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; W. Gerberich,* University of Minnesota, USA **INVITED**

Due to pronounced effects of sample size on the measured mechanical response, a major challenge persists in correlating microscale measurements to macroscale measurements, especially for ductility and fracture. For brittle materials with small plastic zone size relative to the sample size (e.g., Si), micro cantilever and 3-point bending have shown promising results. However, for semi-brittle (e.g., W) materials, the plastic zone size becomes comparable to the sample dimension and thus the conventional analysis methods based on linear-elastic and elastic-plastic fracture mechanics prove difficult or impossible to apply. We intend to address the challenges of diminished sample size inherent to evaluating fracture behavior at the microscale through investigation of the Ductile-to-Brittle Transition (DBT) in materials such as Si, SiC, and W. By using the DBT as our benchmark to bulk fracture behavior, we present an investigation of the interplay of sample size with the onset of increasing plasticity with temperature on fracture behavior. Trends in activation parameters will be discussed in terms of changes in dislocation-based mechanisms as a function of test temperature, strain rate, and loading state, and used to predict fracture behavior based on an analytical model.

H3-3 High Temperature Erosion Performance Evaluation of Advanced Materials*,* ***Debdutt Patro (debdutt.p@ducom.com)****, S. Josyula, H. Prasanna,* Ducom Instruments, India*; F. Alemano, D. Veeregowda,* Ducom Instruments, Europe

High temperature erosion testing at temperatures exceeding 600°C involves simultaneous erosion-oxidation interactions that can affect the interpretation of the erosion rates reported from such experiments. Ducom high temperature air jet erosion tester was used to conduct erosion tests at 1000°C on both alumina ceramic and Inconel 600 superalloy using alumina as an erodent. Erosion tests were conducted on as-received samples as well as pre-conditioned samples. Gravimetric and profilometric analysis was conducted after the test to obtain erosion rates and volumetric loss and SEM was conducted on the scar to identify the damage mechanisms. The magnitude of oxidative weight gain was found to be comparable to erosion related weight loss. Observed erosion rates were different for as-received and pre-conditioned samples with the pre-conditioned samples showing better repeatability. The high temperature erosion rates of IN 600 vs. alumina tested at different angles and SEM images indicate characteristic ductile and brittle erosion behavior respectively. The study highlights the importance of pre-conditioning of samples on (a) accurate erosion performance assessment of materials and (b) repeatability during high temperature erosion testing of materials.

H3-4 Characterization of Selective Solar Absorbing Coatings Under Operating Conditions*, C. D'Alessandro,* ***Antonio Caldarelli (antonio.caldarelli@na.isasi.cnr.it)****, D. De Maio, E. Gaudino,* UniNA and CNR - ISASI, Italy*; M. Musto,* UniNa - Univeristà degli Studi di Napoli "Federico II", Italy*; D. De Luca,* UniNA and CNR - ISASI, Italy*; E. Di Gennaro,* UniNa - Università degli Studi di Napoli "Federico II", Italy*; R. Russo,* CNR - ISASI, Italy

Thermal energy is an important fraction of the worldwide energy that is annually demanded, and it mainly used to produce industrial process heat, such as high pressure steam. Evacuated flat collectors, thanks to the high vacuum insulation, can respond to the mid-temperature (100 °C – 250 °C) heat request without concentration. The Selective Solar Absorber (SSA) is the key component of the solar collector: it should efficientlyconvert the incident solar irradiation into heat for the transfer fluid. Thanks to the high-vacuum insulation, the thermal radiation is the main loss mechanism that limits the panel efficiency. Solar absorptance and thermal emittance of the SSA are the radiative properties that, in first approximation, define the overall efficiency of the evacuated panel. Typically their evaluation is made at ambient temperatureand comes from optical analysis, such as FT-IR Spectroscopy and Optical Reflection Spectroscopy. Unfortunately at the operating temperature,the radiative properties can differ from the optical analysis performed at room temperature..In this work we describe a calorimetric emissiometer and the related procedure aimed at measuring the spectrally averaged absorptivity and thermal emittance under operating conditions (direct illumination and high vacuum insulation). The presented system has been validated with a commercial absorber under SUN and LED illumination. It has been used to perform calorimetric tests of novel SSAs designed to work at different operating temperatures [1] and other innovative absorbers. We will present the temperature dependence of radiative properties for several SSAs obtained using different substrates and different multilayer structures.

The system can detect variation in absorpted or emitted power of the order of 1% and it is a powerful tool to measure the SSA properties as function of temperature. It can be also adopted to perform thermal stress tests, i.e. keeping the SSA at a temperature higher than the stagnation temperature under the Sun irradiation by using a well calibrated LED system[2]. This allowsto estimate the possible coating degradation over the lifetime of the collector.

[1] D. Demaio et al . *"Multilayer design and deposition for efficient thermal energy conversion in high vacuum flat solar thermal panels"*submitted to this conference

[2] D' Alessandro, C. et al *"Low Cost High Intensity LED Illumination Device for High Uniformity Laboratory Purposes"*Preprints 2020, 2020060322 (doi: 10.20944/preprints202006.0322.v1).

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room On Demand - Session HP

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

HP-1 Expanding the Information and Increasing the Reliability of XPS Analysis*, Donald Baer (don.baer@pnnl.gov),* Pacific Northwest National Laboratory, USA*; K. Artyushkova,* Physical Electronics, USA*; C. Easton,* CSIRO, Australia*; M. Engelhard,* Pacific Northwest National Laboratory, USA*; A. Shard,* National Physical Laboratory, UK

Because of the importance of surfaces, interfaces, and thin films in many areas of science and technology, use of X-ray Photoelectron Spectroscopy (XPS) has grown exponentially for the past two decades. One impact of this rapid increase is that many analysts have limited experience or detailed knowledge of the method. This has led to two interrelated issues. First there is an increase of inaccurate or incorrect analyses of XPS data reported in journal publications. An examination of six months of XPS data in three quality journals indicated that 30% of the reported analyses had significant misleading errors and another 30% had the potential to significantly impact the conclusions. The error rate was even greater for papers reporting fitting of spectra. The second challenge is that much of the data analysis is conducted in the most simplistic manner and does not take full advantage of the information that XPS can provide regarding layered structures, including thickness determination and uniformity. Multiple efforts are needed, some underway, to address these two challenges. Raising community awareness of the issues and opportunities is a critical first step. The error rate assessment also identified the types of errors occurring, providing analysts with information of common problems. A survey of AVS members indicated that guides, tutorials, protocols, and standards could help the community. To that end, a collection of XPS guides and introductions to various aspects of XPS has been prepared and published in Journal of Vacuum Science and Technology A. These papers address a range of topics required for quality XPS including preparation and planning, instrument setup and data collection, quantitative data analysis and curve fitting and depth information. These papers both provide guidance for minimizing errors and suggest the full range of information that might be extracted. Guides aimed at the use of XPS for specific systems such as polymers, catalysts, nanoparticles, and epitaxial films provide application specific guidance extending beyond the most common analysis approaches. Increasingly XPS analyses may involve modeling of signals expected from complex surface structures, including ultrathin films, epitaxial layers, and nanoparticles using programs such as SESSA, Multiquant and QUASES. Other pathways to advancing XPS include using high energy X-rays (HAXPES), an expanding range of environmental conditions (NAP-XPS), reporting data according to the FAIR data principles, the development of expert systems that codify and apply the hundreds of years of XPS experience, and the application of AI for enhancing data analysis and recognizing faulty data.

HP-2 Electric Field Strength-Dependent Accuracy of TiAlN Thin Film Composition Measurements by Laser-Assisted Atom Probe Tomography*, Marcus Hans (hans@mch.rwth-aachen.de),* *J. Schneider,* RWTH Aachen University, Germany

Accurate quantification of absolute concentrations represents a major challenge for atom probe tomography (APT) since the field evaporation process is affected significantly by the measurement parameters. In the present work we investigate systematically the effect of laser pulse parameters on the accuracy of laser-assisted APT for a TiAlN thin film previously quantified by ion beam analysis, combining Rutherford backscattering spectrometry and time-of-flight elastic recoil detection analysis. The electric field strength is estimated from the Al^{2+}/Al^{+} charge state ratio for all systematically varied measurement parameters. Subsequently, the absolute concentrations from laser-assisted APT are compared to ion beam analysis data. An increase of the electric field strength from approximately 25 to 28 V nm^{-1} improves the accuracy of absolute concentrations measured by laser-assisted APT from 11.4 to 4.1 at.% for N, from 8.8 to 3.0 at.% for Al and from 2.8 to 0.9 at.% for Ti. Our data emphasize that the measurement accuracy of laser-assisted APT for TiAlN is governed by the electric field strength. It is shown that the smallest compositional discrepancies between ion beam analysis and APT are obtained for the maximum electric field strength of approximately 28 V nm^{-1} at 10 pJ laser pulse energy. This can be rationalized by considering the enhanced ionization of neutral fragments caused by the increased electric field strength.

HP-3 Integrated Atom Probe/tEBSD for Grain and Phase Boundary Analysis of Coatings and Thin Films*, Robert Ulfig (robert.ulfig@ametek.com),* *Y. Chen, K. Rice, T. Prosa,* CAMECA Instruments Inc., USA

Transmission EBSD mapping offers the ability to target site-specific grain or phase boundaries for Atom Probe Tomography (APT) analysis, and correlate boundary chemistries with grain misorientations. In this study we demonstrate that high-resolution transmission electron back scattering diffraction (tEBSD) maps can be acquired on needle-shaped APT specimens that consist of grains of size ranging from few hundred nanometers to few micrometers. The use of this correlative technique will be demonstrated with thermal barrier coatings (TBCs) used in turbine engines to operate at temperatures greater than the melting temperatures of engine components and consequently achieve better propulsive power performance and fuel efficiency. The general structure consists of three layers: a top is a coat made of yttrium-stabilized ZrO_2 (or YSZ), which has excellent thermal resistivity, a thermally grown oxide (TGO) scale, that consists of a-alumina grains, and a bond coat layer at the coating/substrate interface that improves adhesion of the ceramic layers on the superalloy substrate.

HP-4 Sub-50 nm X-ray Diffraction Reveals Nanoscale Residual Stress and Microstructure Distributions across the Cutting Edge Area of a TiN Coating on WC-Co*, Michael Meindlhumer (Michael.Meindlhumer@oeaw.ac.at),* *N. Jäger, S. Spor,* Montanuniversität Leoben, Austria*; M. Rosenthal,* ESRF Grenoble, France*; H. Hruby,* eifeler-Vacotec GmbH, Düsseldorf, Germany*; J. Keckes, C. Mitterer,* Montanuniversität Leoben, Leoben, Austria*; R. Daniel, J. Keckes, J. Todt,* Montanuniversität Leoben, Austria

The nanoscale microstructural and residual stress gradients across hard coatings on cutting tools are of high scientific and industrial interest. Here, cross-sectional X-ray nanodiffraction with a beam size of 35×25 nm² was used to retrieve structural and mechanical gradients in the cutting edge area of a ~2 µm thick TiN coating deposited by cathodic arc evaporation on a WC-Co substrate. Scanning small-angle X-ray scattering microscopy (SAXSM) is presented and utilized for the first time to investigate the nanoscale defect density in the cutting edge area. At the cutting edge, interface-like planar domains of high scattered intensity were indicated, while a gradual increase of the SAXS intensity at the rake face was correlated with pores found by scanning electron microscopy. Furthermore, the coating's <111> fibre texture axis orientation correlates with the substrate's surface normal, showing abrupt orientation changes across the former mentioned interface-like structures. The planar regions next to the edge exhibit gradual and constant stress profiles with anisotropic defect build-ups on the flank and rake faces, respectively. Directly at the edge, nonlinear lateral and cross-sectional compressive residual stress gradients ranging from ~0 to −3 GPa were observed, which together with the interface-like planar domains may represent a reliability issue during operation.

HP-5 e-Poster Presentation: Nanoindentation Analysis as a Two-Dimensional Tool for Mapping the Mechanical Properties of Complex Microstructures*, Nicholas Randall (nicholas.randall@alemnis.ch),* *J. Breguet,* Alemnis, Switzerland

Instrumented indentation (referred to as nanoindentation at low loads and low depths) has now become established for the single point characterization of hardness and elastic modulus of both bulk and coated materials. This makes it a very good technique for measuring mechanical properties of homogeneous materials. However, many composite materials comprise material phases that cannot be examined in bulk form ex-situ (e.g., carbides in a ferrous matrix, calcium silicate hydrates in cements, etc.). The requirement for in-situ analysis and characterization of chemically complex phases obviates conventional mechanical testing of large specimens representative of these material components. This paper will focus on new developments in the way that nanoindentation can be used as a two-dimensional mapping tool for examining the properties of constituent phases independently of each other. This approach relies on large arrays of nanoindentations (known as grid indentation) and statistical analysis of the resulting data.

HP-6 Microstructural Influences on the Fracture Properties of CrN Coatings*, Rainer Hahn (rainer.hahn@tuwien.ac.at)*, *S. Rosenecker,* CDL-SEC, TU Wien, Austria*; T. Wojcik,* TU Wien, Institute of Materials Science and Technology, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* TU Wien, CDL-SEC, 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 and aerospace industry. Besides TiN, CrN is one of the most used and best investigated hard coatings, preferably applied in conditions that require a low coefficient of friction. 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. In recent years, micromechanical testing methods have made it possible to measure and specifically improve precisely fracture toughness of thin film materials. There are various methods known for measuring K_{IC} obtaining all advantages and drawbacks, especially with respect to intrinsic material characteristics and accuracy.

In this contribution, we perform distinct micromechanical tests on cathodic arc evaporated CrN coatings. These coatings were deposited with different bias voltages and deposition temperatures in order to obtain a variation in both, microstructure (specifically crystallite size) and defect density. The importance of the microstructure on fracture characteristics has recently shown by Ast et al. for Ti-Al-N deposited by diverse PVD techniques [1]. However, a clear correlation between the column size and the density of column boundaries is still missing.

We found a significant influence of the residual stress state on the fracture properties of such hard coatings using the indentation fracture method. Furthermore, we used pillar splitting and cantilever bending tests to determine the intrinsic fracture toughness of our coatings with respect to the microstructure and defect density. These results were complemented by HR-TEM investigations together with x-ray diffraction studies, and nanoindentation tests.

References

[1] Ast J., et al., (2019). Fracture toughness determination of arc-PVD and HiPIMS hard coatings by micro-cantilever and pillar splitting tests.

HP-9 Thin Film Characterization Utilizing Broad Ion Beam Specimen Preparation and FESEM*, Natasha Erdman (erdman@jeol.com)*, *N. Inoue,* JEOL USA Inc, USA

Examination of materials cross sections often provides essential information about the crystal structure, layer or film thicknesses, existence of voids or cracks and other properties that might impact materials performance and reliability. Cross-sectional observation is especially essential in thin film technology, to examine layer thickness, deposition integrity (voids/adhesion), as well as film growth and crystallographic orientation. Currently various methods are used to prepare specimen cross sections for scanning electron microscope (SEM) observation. Mechanical methods of cutting and polishing are widely used, particularly for metallographic sample preparation. However, mechanical polishing presents several problems: a) in composite materials with different hardness values, the polished surface becomes uneven as the softer components are cut faster and more easily than the harder components; b) in soft materials, particles of hard abrasive can be buried in the material being polished; c) in materials with voids, the edges of the voids can stretch and deform; e) for metals, due to the strain caused by mechanical polishing on the polished surface, the information about the crystal structure by means of electron back-scatter diffraction (EBSD) becomes difficult or impossible to obtain; f) fine features like hairline cracks and small voids can get smeared shut and will not be recognized as such.

This paper presents utilization of broad ion beam instrument (JEOL CP polisher) for cross-sectional preparation of various thin film/substrate combinations. This table top instrument utilizes Ar ion beam to produce large area cross-sections of materials, with the ability to employ cryogenic (LN2) temperatures to address beam sensitive and eutectic metal systems. Moreover, the use of FE-SEM equipped with in-lens detectors and high sensitivity backscatter detecotr allows observation of the resulting samples to investigate nanoscale features, including voids, grain boundaries and layers. Additionally, EDS and EBSD can be utilized to provide additional characterization of the thin film specimens in terms of compositional variations and crystallographic orientation.

We will present examples of Zn thin films - depending on the film composition these may require cryogenic preparation to preserve film integrity. Additionally we would present examples of other materials - anodized films, evaporated metal thin films, solar films, etc.

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