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.

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H2-3 Intrinsic Mechanical Properties of Moderate Temperature Processed Cvd Amorphous Silicon Oxide (SiO_2) and Oxynitride (Si_OxN_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.

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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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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.

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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;...

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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.

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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.

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