Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room San Diego - Session E2-2

Mechanical Properties and Adhesion

Moderators: Gerhard Dehm, Max-Planck Institut für Eisenforschung, Etienne Bousser, The University of Manchester, Fan-Bean Wu, National United University, Taiwan

8:00am **E2-2-1 Study of Bauschinger Effect in Ni Thin Metallic Films Submitted to Cyclic Deformation**, ***Pierre-Olivier Renault**, W He, P Godard, E Le Bourhis, P Goudeau,* Universite de Poitiers, France

The lifetime of flexible electronic devices is strongly dependent on their mechanical performance as they are submitted to complex thermo-mechanical cyclic loadings during service. As an elementary substructure inside such devices, metallic thin films are often supported by a polymer substrate.

A substantial amount of experimental work has shown that the plastic response of a thin metal film can be very different from that of its bulk counterpart. The yield stress, flow stress and hardening rate of thin films depend on film thickness. During cyclic deformation of a material, the plastic deformation in one direction can affect the plastic response in reverse direction; one consequence is the decrease of the yield strength of a metal when the direction of strain is changed, i.e. a reduced elastic limit at reversal straining. Such Bauschinger effects have been reported on different metallic thin films in the last ten years.

In this communication, an experimental method using uniaxial tensile testing is used to study the Bauschinger effect in thin metal films deposited on pre-stretched polyimide substrate. Thanks to our new pre-stretch setup based on previous work [1], the metallic thin films can be deformed alternatively from tension to compression within a strain domain of a few % (depending on the elastic range of the polymer substrate). The elastic intra-granular strain of polycrystalline thin films and true strain of substrates are measured in situ during tensile-compressive loading by X-ray diffraction (XRD) and digital image correlation (DIC) techniques. A complete strain transfer through the interface is observed in the elasto-plastic regime as the interface is strong enough thanks to the thin film elaboration PVD technique (namely ion beam sputtering) [2]. From lattice strain-true strain curves, the mechanical response of thin film/substrate set is analyzed in view of the complete loading history.

[1] Renault P.-O., Faurie D., Le Bourhis E., Geandier G., Drouet M., Thiaudiere D., Goudeau P., “Deposition of ultra-thin gold film on in situ loaded polymeric substrate for compression tests”, Materials Letters **73**, 99-102 (2012).

[2] Geandier G., Renault P.-O., Le Bourhis E., Goudeau Ph., Faurie D., Le Bourlot C., Djemia Ph., Castelnau O., Cherif S. M., Elastic-strain distribution in metallic film-polymer substrate composites, Applied Physics Letters 96, 041905 (2010).

8:20am **E2-2-2 Mo-Re Thin Films for Flexible Display Applications**, *F Hauser, T Jörg,* Montanuniversität Leoben, Austria*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; R Franz,* Montanuniversität Leoben, Austria*; H Köstenbauer, J Winkler,* Plansee SE, Austria*;* ***Christian Mitterer**,* Montanuniversität Leoben, Austria

Sputtered Mo films are nowadays widely used as thin films in flat panel display applications, e.g., for gate and source/drain electrodes or signal and data bus-lines. However, due to their brittleness, usability in future flexible displays is limited. In order to overcome this disadvantage, a strategy to improve the ductility of brittle Mo thin films by alloying with Re is explored within this work. A series of Mo-Re thin films with 50 nm thickness were grown on 50 µm thick polyimide substrates by magnetron co-sputter deposition from pure Mo and Re targets. Up to ~25 at.% Re, a solid solution with the body-centered cubic structure of Mo was obtained. In-situ characterization methods were applied to determine the electro-mechanical behavior of the films during deformation. Uniaxial tensile tests were performed under the light microscope to directly observe the fragmentation process and to determine the crack onset strain. In addition, the electro-mechanical response was evaluated by measuring the change in the electrical resistance during straining. After tensile straining, pure Mo thin films exhibited straight through-thickness cracks, which are usually observed for brittle films, while the Mo-Re films showed a wavy crack path, indicating a more ductile behavior. The addition of Re also has a significant effect on the electro-mechanical response of films, where the rise of the resistance indicated a crack onset strain three times higher than for pure Mo. In summary, alloying of Mo thin films with Re is a promising strategy to improve their ductility, which in turn can enable their utilization in flexible displays.

8:40am **E2-2-3 Rate Sensitive and Creep Behavior of Thin Metallic and Oxide Films: on Chip Testing and Activation Volume Analysis**, ***Thomas Pardoen**, G Lemoine, H Idrissi,* Université Catholique de Louvain, Belgium*; D Schryvers,* University of Antwerpen, Belgium*; M Ghidelli,* Université Catholique de Louvain, Belgium, Italy*; M Coulombier, R Vayrette, L Delannay,* Université Catholique de Louvain, Belgium*; S Gravier,* Grenoble INP, France*; J Raskin,* Université Catholique de Louvain, Belgium **INVITED**

Creep and viscoplastic deformation mechanisms are generally amplified in thin films compared to bulk systems due to various factors related to the dominance of the free surfaces and/or to the abundance of internal defects and interfaces. A series of experimental investigations on freestanding thin metallic, metallic glass and oxides films using an on chip uniaxial test method will be reviewed, focusing on the creep/relaxation behavior. The generic approach to tackle with thermally activated mechanisms through the activation volume mechanics framework is applied to rationalize the measurements. These measurements are supplemented by in or ex situ transmission electron microscopy analysis and micromechanical models to unravel the origin of the dominant deformation mechanisms in connection with the microstructure. The commonalities and specificities among these systems will be discussed. An important common characteristic is the improved ductility associated to a enhanced rate sensitivity.

9:20am **E2-2-5 Intrinsic Stresses - New Methods to Evaluate Them Using Enhancing Indentation Methods and New Models to Optimize Them**, ***Nick Bierwisch**, N Schwarzer,* SIO, Germany

In many d eposition processes intrinsic (or residual) stresses can't be avoided during the coating creation. Mostly because of bias or high deposition temperatures and the mismatch in the coefficients of thermal expansion for the various materials. The intrinsic stresses can have a big influence on the material behavior in contact situations.

In one way they can help fighting against your critical external loads and reducing the created stresses. On the other way they can also weaken the material compound when producing to much stresses in a weaker part of the system. Both sides can also have an effect on the adhesion strength between the different coatings. So gaining knowledge about these intrinsic stresses could help a lot in the field of modeling or simulating your worst case application scenarios.

This talk will show 2 new methods to evaluate the intrinsic stresses using extended indentation measurements and new mathematical models. One method applies a mixed load indentation by adding a lateral load component to the applied normal load. The other new measurement uses a reference probe with known intrinsic stresses. With this new measurement methods and new mathematical models the intrinsic stresses within your material can be evaluated.

The second part of the talk will focus on a new model, which allows you to optimize the intrinsic stress distribution to increase the performance in a given worst case application. Nowadays more and more production processes allow to steer the intrinsic stresses during the coating deposition process. This allows a new degree of freedom in the development process and can speedup the development. You can save a lot time because you don't need to search for new materials which also can improve the performance. So knowing how to build up the intrinsic stresses before the deposition process will speedup the development and optimization process of your new material compound a lot. You can save a lot of prototypes and therefore much development time and costs. This work is part of the EU project IStress [1] and within this project this model was implemented into the software package FilmDoctor [2]. It allows you to define your later application and the software will find an intrinsic stress distribution within your coatings which will decrease the resulting stresses in your worst case contact in your later application.

References:

[1] www.stm.uniroma3.it/iSTRESS

[2] [http://www.siomec.de/FilmDoctor]

9:40am **E2-2-6 Investigation of Buckling Driven Delamination of DLC Coatings for Evaluation of Adhesion Strength***, **Richard Braak**, U May, L Onuseit, G Repphun,* Robert Bosch GmbH, Diesel Systems, Germany*; M Guenther, J Emmerlich,* Robert Bosch GmbH, Germany*; C Schmid, K Durst,* Physical Metallurgy, TU Darmstadt, Germany

Diamond like carbon coatings (DLC) are widely used as wear-resistant coatings, e.g. in the automotive industry for Diesel injection systems. Their exceptional properties, as high hardness and high modulus are the result of the ion bombardment during the plasma coating process. In addition the thin films sustain substantial residual compressive stresses which can be a problem with respect to the adhesion: The in-plane compressive stress can lead to buckling driven delamination. It occurs in different shapes: Circular, straight-sided or worm-like blisters or even big-area delamination. The type of appearance is closely linked to the mode-dependent fracture toughness of the interface.

In the current work, ta-C coatings (tetragonal amorphous carbon) with different kinds of adhesion layer design are investigated. As the mechanical properties of the whole coating system do have influence on the buckling behavior, depth profiles of the layered structures are taken via nanoindentation on a small angle cross section (SACS). The intrinsic stresses are determined with two separate methods: The curvature test and via a focused ion beam (FIB) in combination with digital image correlation (DIC).

In the first part of the paper commonly used indentation and nanoscratch tests are discussed, the latter with constant and increasing load. The created damages are investigated thoroughly via SEM-imaging (Scanning Electron Microscopy). The findings lead to a novel adhesion test which is presented in the second part. A ranking of the adhesion strength of the different adhesion systems can be done with the suggested method. The ranking is used to show the range of application of the common scratch and indentation tests.

10:00am **E2-2-7 Characterization of Thin Films by Nanoindentation: Avoiding Mistakes during the Measurement and Data Analysis***, **Esteban Broitman**,* Engineering Consulting, Sweden

Nowadays, nanoindentation has become a routinely technique for the mechanical characterization of thin films and small-scale volumes. Thanks to the development of friendly analysis software and advances in high sensitive instrumentation, it feels like the measurement and calculation of hardness and elastic modulus can be done automatically by just *"the pushing of one button."* However, the consequences of the easy procedures have led many researchers to publish erroneous data [1].

In this paper, common mistakes in the measurement and data analysis during the nanoindentation of thin films will be critically reviewed, and the possible ways to correct them will be discussed: 1) the misuse of the 10%-thickness *"rule of tomb"* to avoid the effect of the substrates; 2) the lack of thermal drift correction in long-term duration experiments; 3) the wrong data conversion from Vickers microindentation to Berkovich nanoindentation; 4) the ignorance of pile-up effects; 5) the misinterpretation of indentation size effects at low penetrations; 6) the wrong determination of tip area functions; 7) the lack of load frame compliance correction during the characterization of very hard coatings; 8) the confusion of thermal drift with creep and viscoelastic effects; 9) the misinterpretation of pop-ins and pop-outs; 10) the preconceptions about a direct relationship between hardness and tip penetration; 11) the preconceptions about a direct relationship between elastic modulus and hardness; 12) the lack of considering surface roughness influence; 13) the possible change of surface mechanical properties during sample preparation; 14) the use of dirty or damaged tips; 15) the natural differences in the results when using spherical, cube-corner, or Berkovich indenters; 16) ignoring the influence of indentation loading rate; 17) the interpretation of elastic recovery in very elastic or very plastic films; 18) the confusion of load-penetration nanoindentation curves with stress-strain compression diagrams; 19) the difference in the results between load-controlled and depth-controlled indentations; and 20) the lack of knowledge about possible work/strain hardening effects or phase transformations during indentation.

The origins of the aforementioned mistakes will be elucidated from the lack of understanding on contacts mechanics theory, the limits and validation of Oliver and Pharr's method, and preconceptions transmitted from generation to generation of nanoindentater users. At the whole, it will be stressed that it is not enough to know *"how to push the button"* in order to measure the nanoscale mechanical properties of thin films.

[1] E. Broitman, Tribology Letters 65 (2017) 23.

10:20am **E2-2-8 Plasma Electrolytic Oxidation Coatings on AZ31 Magnesium Alloys with Si_3N_4 Nanoparticle Additives***, **YiYuan Lin**, J Lee, C Tseng,* Ming Chi University of Technology, Taiwan*; B Lou,* Chang Gung University, Taiwan

The magnesium AZ31 alloys have been used in a wide range of lightweight applications such as aerospace, automotive and personal computers due to its unique properties. However, high chemical reactivity, poor corrosion and wear resistance limit their widespread uses in many fields. The plasma electrolytic oxidation (PEO) process can produce protective oxide layer on the magnesium alloy to improve its mechanical property, wear resistance and corrosion resistance. In this work, the silicon nitride (Si_3N_4) nano particles were added into the electrolyte of PEO treatment on AZ31 alloy to improve the mechanical and anticorrosion properties of oxide coating. Surface and cross-sectional structure of the oxide layers was studied by scanning electron microscope (SEM). Energy dispersive spectrophotometry (EDS), X-ray diffraction (XRD) techniques were employed to determine the phase structure and chemical composition of the layers. The adhesion and mechanical properties of coating were analysis by scratch test, pin-on-disk wear test and hardness test, respectively. Potentiodynamic polarization tests were employed to investigate the electrochemical corrosion behavior of PEO treated AZ31 alloy. Effects of Si_3N_4 addition concentration on the microstructure, mechanical and anticorrosion properties were further discussed in this work.

10:40am **E2-2-9 Fractures, Wrinkles and Buckles in Brittle Multi-layers on Flexible Substrate***, **Davy Dalmas**,* Laboratoire de Tribologie et Dynamique des Système (LTDS), Ecole Centrale de Lyon, France*; I Ben Cheikh, G Parry, R Estevez,* SIMaP – Univ. Grenoble Alpes, CNRS, SIMaP, France

Polymer film coated with stacks of thin layers (metal, oxides or organic) are more and more used in many industrial applications such as flexible and opto microelectronics (screens, OLED, Photovoltaic applications...). Maintaining the mechanical stability of these coated systems requires both to control the cohesion of the coating and its adhesion to the substrate for various mechanical loadings. As the mechanical behaviour of these systems is highly dependent on both the properties of the substrate (modulus, thermal expansion coefficient, glass transition temperature ...), and of the coating (deposition conditions, the residual stresses,…), it is essential to develop dedicated characterization methods and idealized model experiments to understand the mechanical stability of those thin films deposited on flexible substrates.

In this Study, fracture propagation of TiO_2 and Ag layers of various thicknesses coated on a PET substrate is investigated during simple traction tests. During those tests, two phenomena can be observed. Firstly, at low strain, channel crack starts to appear in the coating. We show that the crack density undergoes a transition from a statistic failure distribution classically observed for brittle material and well-described by Weibull distribution to a deterministic sequence of failures set by the elastic mismatch between the film and the substrate. At high strain, the crack density saturates more rapidly than expected (i.e. for distance between two consecutive cracks one order of magnitude higher that he film thickness). Secondly, we observed a second transition from wrinkling to buckling of the coating in the transverse direction to Poisson effect. We show that the transition between those two phenomena is driven by the composition of the coating.

Finally, we propose a two-dimensional model of a film bonded to an elastic substrate to describe the evolution of crack density with the applied strain in the case of large elastic mismatch between the film and the substrate. We then extend this model to an elasto-plastic one in order to account for the plasticity in the substrate. This plasticity is experimentally evidenced by in-situ AFM imaging and numerical validation by FEM that both show the localisation of strain in the substrate during fracture process. We propose that this localisation is responsible of the early saturation of crack density observed at high strain.

11:00am **E2-2-10 Combined XPS and Adhesion Studies of Metal - Polymer Interfaces for Space Applications***, **Barbara Putz**,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Monanuniversität Leoben, Austria*; G Milassin, Y Butenko, C Semprimoschnig,* European Space Research and Technology Centre (ESTEC), The Netherlands*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Monanuniversität Leoben, Austria

Good adhesion of metal-polymer interfaces is crucial for the reliability of a vast number of high-tech and everyday applications, such as multilayer insulation for satellites as well as flexible and rigid microelectronic devices. Of special interest for space applications is how stable these interfaces are chemically and mechanically with respect to the extreme thermal cycling the devices undergo in operation. In low earth orbit a spacecraft typically encounters 6000 thermal cycles of +/- 100°C during one year in operation. In this study, mechanical adhesion measurements are combined with X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) in order to relate the interface strength to the interface chemistry and structure for the Aluminium-Polyimide (Al-PI) system. This material system is used as a multilayer insulator for satellites currently in orbit. The interfacial adhesion energy was measured using tensile induced delamination before and after a thermal cycling treatment of +/- 150^{o}C up to 200 thermal cycles. In order to assess the chemistry of the interface, an 180^o peel test was used to provide access to the metal side and the polymer side of the interface. Peeling allows the interface of interest to be evaluated without any additional etching or sputtering steps that would alter the interface chemistry. XPS survey scans and relevant high resolution core levels were recorded on both sides of the peeled interfaces to identify and understand relevant interfacial bonding and to distinguish between adhesive failure of the interface and cohesive failure in the substrate. TEM cross-sections were used to examine the interface structure as a function of thermal cycling and related to the mechanical adhesion measurements. It was determined that the Al-PI system initially has very good metal-polymer adhesion which does not degrade due to the thermal loads caused by the sun during orbit. The combination of mechanical adhesion measurements, structure and chemistry evaluation of the interfaces allows for an improved understanding of how thermal treatments can influence interfacial behaviour between metals and polymers. This new knowledge will help improve design and reliability of the materials used in space applications and can also provide vital information for flexible and rigid microelectronics used on earth.

11:20am **E2-2-11 Mapping Adhesion Energy of Tungsten Based Barrier Layers with Scratch Induced Buckling***, **Andreas Kleinbichler**, J Zechner,* KAI - Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Austria*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria

Diffusion barrier layers provide microelectronic devices with chemical and mechanical stability, thus ensuring the reliability during service. The barrier layer prevents the contamination of the conductive metallization due to Si diffusion in a certain temperature range while also acting as an adhesion layer to the underlying substrate providing mechanical stability. However, the interface adhesion may change due to temperature gradients present during sputter deposition and result in a radius dependent adhesion across the wafer. Tungsten-titanium (WTi) alloys have been demonstrated to be very important barrier materials in copper based microelectronic devices as they exhibit thermal stability up to 800°C and good adhesion behavior to silicon oxide substrates. The adhesion of WTi to Borophosphosilicate glass (BPSG) is of special interest in modern metal–oxide–semiconductor field-effect transistors (MOSFET) since the strength of this kind interface is usually weak. A reliable way of assessing the adhesion quantitatively is required to properly map the adhesion across the wafer surface and for the different temperatures the wafer is exposed to during the production process and later during its lifetime. The adhesion of a 300nm WTi film with an 800nm BPSG substrate on top of a 700µm Si wafer has been investigated using scratch testing. The scratches induce buckles in the film which are used to quantitatively calculate the film/substrate-adhesion and can easily be performed as a function of the position over the wafer. From the different positions a map of the adhesion energy of the WTi-BPSG interface can be constructed. The adhesion map will help identify areas on the wafer that might have been influenced by the thermal gradient present during production.

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