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

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

HP-ThP-1 Femtosecond Laser Ablation (FESLA) XPS – A Novel XPS Depth Profiling Technique for Thin Films, Coatings and Multi-Layered Structures*, Mark Baker, S. Bacon, S. Sweeney,* University of Surrey, UK*; A. Bushell, T. Nunney, R. White,* ThermoFisher Scientific, UK

XPS depth profiling is a widely employed analytical technique to determine the chemical composition of thin films, coatings and multi-layered structures, due to its ease of quantification, good sensitivity and chemical state information. Since the introduction of XPS as a surface analytical technique more than 50 years ago, depth profiles have been performed using ion beam sputtering. However, many organic and inorganic materials suffer from ion beam damage, resulting in incorrect chemical compositions to be recorded during the depth profile. This problem has been resolved for most polymers through the use of argon gas cluster ion beams (GCIBs), but the use of GCIBs does not solve the issue for inorganics. A prototype XPS depth profiling instrument has been constructed which employs a femtosecond laser rather than an ion beam for XPS depth profiling purposes. This novel technique has shown the capability of eradicating chemical damage during XPS depth profiling for all initial inorganic, compound semiconductor and organic materials examined. The technique is also capable of profiling to much greater depths (10s - 100s microns) and is much faster than sputter XPS sputter depth profiling. FESLA XPS results will be shown for selected bulk, thin films and oxidised surfaces and the outlook for this new technique discussed.

HP-ThP-3 *in Situ* and Real-Time Measurements in Metallic Thin Film Research and Applications: The MISSTIC Experimental Setup*, Ramiro Zapata,* Laboratoire Surface du Verre et Interfaces UMR 125 / Institut des Nanosciences de Paris UMR 7588, France*; R. Lazzari,* Institut des Nanosciences de Paris UMR 7588, France*; H. Montigaud, M. Balestrieri, I. Gozhyk,* Laboratoire Surface du Verre et Interfaces UMR 125, France

Magnetron sputtering deposition is one of the main PVD deposition techniques, for a wide range of materials ranging from metals to semiconductors and insulators. Current research efforts in thin film growth and characterization are often hindered by extraneous interferences and impurities, stemming from film surface contact with the atmosphere between the film elaboration and *ex situ* characterization steps.

In order to overcome these challenges, the **MISSTIC** (Multilayers and Interfaces Sputtered-deposition on STructured substrates and In-situ Characterization) vacuum experimental setup was developed. This setup (Fig-A) is composed of a deposition chamber and an analysis chamber, connected via a load-lock mechanism through which samples can be transferred under vacuum conditions. This internal sample transfer between chambers avoids contact with the atmosphere, thereby avoiding interfering phenomena such as film ageing and adsorbed species from air. As such, by eliminating the need for capping (protective) layers on top of the deposited metallic films, *in situ* X-Ray Photoemission Spectroscopy (XPS) in the analysis chamber can characterize the deposited film surface chemistry, without any depth profiling necessary. Sample annealing under vacuum, with an electron beam setup located in the same chamber, can even be used for studying elemental diffusion in thin film stacks. Finally, surface characterizationusing *in situ* Low Energy Electron Diffraction (LEED) is used for the study of crystallized surfaces, and for studying thin film epitaxial growth – such as for the case of Ag film sputtering on ZnO underlayers.

Real-time characterization techniques are another kind of measurement, present in the **MISSTIC** deposition chamber. These measurements are carried out during film deposition, and allow for the detection of different stages of film growth: they include Surface Differential Reflectance Spectroscopy (SDRS), film electrical resistance, and a new method for film mechanical stress measurements (PReMC, Refs[1,2]. For the study of Ag film growth on silica substrates during magnetron sputtering deposition, real-time measurements allow for the detection of the nucleation, growth, coalescence, percolation, and continuous film formation threshold thicknesses. Combinations of these techniques are used for studying the effects of different parameters of the sputtering deposition process, on the Ag thin film growth mechanism.

Ref1: Sergey Grachev et al 2022 Nanotechnology 33 185701

Ref2: Quentin Hérault et al. Acta Materialia 221 (2021) 117385

HP-ThP-4 Ultrasonic Contact Impedance Measurements at Nanometer Scale*, Jurgis Daugela,* Johns Hopkins University, USA*; A. Daugela,* Nanometronix LLC, USA

Active ultrasonic microhardness aka Ultrasonic Contact Impedance (UCI) testers have been around since 1970s.While UCI microhardness testers relied on microscale contact elastic deformation, this technique, *at the nanoscale*, has a new application in the area of multi-cycling nanofatigue monitoring [1, 2]. A theoretical contact mechanical impedance model was explored during design stage in order to match impedances of ultrasonic tip/resonator and contacting surface.The contacting surface impedance consists of the contact compliance term since reactive terms are insignificant at the nano scale. The resulting operational mechanical impedance functions were employed in design optimization of the ultrasonic tip.

With the newly developed instrumentation such as the ultrasonic nanoindentation tip integrated into a nanoindentor that localizes nanonometer range displacements, millions of precisely placed loading cycles can be delivered within seconds.Thin film interface breakthrough induced nanoindentation displacement excursion and simultaneously monitored ultrasonic signals indicate fatigue failure and provide the number of failure cycles.

An experimental ultrasonic nanoindentation tip operated at 272kHz is delivering approximately 4.5 million cycles till 80nm thick SiC film interface fracture.It had to be pointed out that ultrasonically induced nanofatigue cycles reasonably agree with Ratcheting and Mason-Coffin fatigue models.

References:

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

HP-ThP-5 A Direct Correlation between Structural and Morphological Defects of Tio_2 Thin Films on Fto Substrates and Photovoltaic Performance of Planar Perovskite Solar Cells*, Mario Alejandro Millan Franco,* IER-UNAM, Mexico

Titanium oxide (TiO2) is often deposited on conductive fluorine doped tin oxide (FTO), followed by a thermal annealing to obtain anatase phase for planar perovskite solar cells (p-PSCs). Although high annealing temperature is desirable to increase the crystallinity of TiO2, morphological changes are induced in both TiO2 and FTO. In this work, structural and morphological changes in thermally annealed (400 - 550°C) FTO, TiO2 and TiO2/FTO system are identified and semi-quantified by X-ray diffraction, scanning electron and atomic force microscopy. 400 °C annealed TiO2 show the lowest crystallinity and the highest dislocation density, resulting in the lowest efficient p-PSCs. Conversely, 550 °C annealed TiO2 exhibits the highest crystallinity and lowest dislocation density, but the FTO film undergo an increase of surface roughness by more than 25%. Additionally, the 550 °C annealed TiO2 coatings on FTO show the highest concentration of surface ruptures and the largest exposed FTO substrate area. Such morphological defect concentration originates a larger direct contact of FTO and the perovskite film. TiO2 thin films annealed at 450 or 500 °C show a compromising between the crystalline structure and defect density, giving a better photovoltaic performance of p-PSCs prepared under ambient conditions with a conversion efficiency of 16.3%.

HP-ThP-6 In-Situ Stress Evolution in Sputtered Metal Alloy Films*, Vania Jiao, C. Appleget, C. Panetta, K. Folgner, J. Barrie,* The Aerospace Corporation, USA

Space-based optical glass sensors are sensitive to the harsh radiation of Earth's Van Allen belts, and one approach to protect these sensors is by using thick optical coatings. However, thick films of radiation absorbing materials, such as silver or gold, often exhibit increased surface roughness compared to the thin films used for high reflectivity mirrors. This surface roughness degrades the desired reflectivity and increases the optical scatter as film thickness increases. Alloying Ag with Al is an approach towards improving the surface roughness of these thick optical films, but alloying can lead to high residual stresses. These residual stresses are compositionally dependent and can be detrimental to surface figure and film adhesion. In this work, in-situ stress of sputtered AgAl alloy thick optical films (≈1 µm thickness) was monitored to better understand stress evolution. Films of varying composition were deposited on pre-

characterized Si substrates via RF magnetron sputtering to investigate the interplay of alloy content on microstructure, stress, and optical performance. For the AgAl alloys, the focus was on compositions within the intermetallic region, as this has been shown to yield films with greatly improved optical properties. All AgAl thick films showed improved surface roughness and scatter performance compared to their thick undoped Ag counterparts. In-situ stress measurements for all compositions revealed compressive films, developing into a more compressive state with increasing thickness. However, ex-situ stress measurements revealed films with tensile residual stresses. Monitoring the film stress post-deposition and during venting showed that the films underwent a stress reversal as they cooled. Various venting conditions were explored to further investigate this phenomenon.

HP-ThP-7 Characterising Thin Films Using Hard X-Ray Angle Resolved XPS*,*
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High-energy X-ray photoelectron spectroscopy has been used to determine the structure and chemical nature of HfOx thin-films deposited on Alumina substrates.

Shrinking device dimensions has increased the use of atomic layer deposition (ALD) due to the need for increased uniformity and control of layer thickness. The ability to deposit high dielectric constant (high-k) films via ALD has allowed for their widespread use in a swath of optical, optoelectronic, and electronic devices.

Using standard Al Kα excited XPS allowed determination of film thicknesses up to 7nm however beyond this it was not possible to accurately quantify the Si 2p peak from the substrate. Ag Lα excitation results in electrons of higher KE for the same photoemission peak. This increases the over-layer effective attenuation length which in real terms means the sampling depth increases by approximately a factor of two.

Here we use high-energy Ag XPS (Ag Lα radiation - 2984eV) in a conventional angle-resolved XPS (ARXPS) experiment. The ARXPS data is analysed using algorithms linked with physical data parameters based on thermodynamic models, maximising the entropy to find a solution of best fit [1] and generate a reconstructed depth profile over the greater sampling depth provided by the higher energy excitation source.This approach allows the non-destructive elucidation of the structure of ALD thin films of hafnia, alumina and a combination of the two not possible with the conventional Al Kα excitation source. The use of the higher photon energy excitation source mitigates the need for destructive depth profiling using Ar-ion beams to remove material with the risk of ion beam induced chemical changes.

We conclude with calculation of film thickness, the chemistry at the interfaces and the usefulness of Ag Lα excited XPS for such applications.

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HP-ThP-8 The Anisotropic Behavior of Super-Hard TiB_2 Films Studied by Synchrotron Nano-Diffraction*,*
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For hexagonal structured materials, anisotropic properties are well known due to their specific lattice distortion with respect to basal and prismatic planes. In the case of magnetron sputtered transition metal diborides direction-dependent hardness was reported for WB_{2-z}, ZrB_2, as well as for TiB_2 [1-3]. In more detail, the anisotropic behaviour of hexagonal AlB_2 structured diborides is explained by a more difficult dislocation movement due to energetically less preferred slip systems. For TiB_{2+z} it was shown that a preferred crystal growth in 0001 direction predominates super-hardness (> 40 GPa) over any stoichiometry variations [3,4]. Furthermore, the growth orientation of TiB_{2+z} is highly dependent on process parameters, especially the pressure, which was suggested by Neidhardt et al. [5] and experimentally confirmed in a recent publication [3].

For state-of-the art protective coatings not only a high hardness is beneficial, but also specifically low residual stress states are preferred. By varying the pressure during the growth of TiB_{2+x} coatings, the mechanical properties have been tailored by structural adaptions throughout the film cross-section. In addition, the incorporation of metallic Ti interlayers is an interesting tool for stress management within these films. To study the progression of the stress sates as well as orientation relations throughout the film cross-section, X-ray nano-diffraction synchrotron experiments (beamline P03 at PETRA III) have been performed. Furthermore, the structure-mechanical properties were described by a broad set of characterization techniques such as SEM, Nanoindentation, or micro-mechanical testing techniques.

Keywords: Transition Metal Diborides, Anisotropy, Residual Stresses, Synchrotron Investigations, PVD

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