Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 1-2 - Session CM1-1-ThM

Spatially-resolved and in situ Characterization of Thin Films, Coating and Engineered Surfaces I

Moderators: Barbara Putz, Empa Thun, Switzerland, **Aparna Saksena**, MPI für Eisenforschung GMBH, Germany

8:40am **CM1-1-ThM-3 Analysis of Deuterium by Atom Probe Tomography (Apt) - D in V Films and Fe/V Multi-Layered Films***, Ryota Gemma* ***[ryota.gemma@tokai.ac.jp]****,* Tokai University, Japan*; Talaat Al-Kassab, Astrid Pundt,* University of Göttingen, Germany **INVITED**

In this presentation, we will present the results of deuterium distribution and quantitative analysis by atom probe tomography (APT) in single-layered V or Fe/V multi-layered films. While V is a hydrogen-absorbing metal, Fe hardly dissolves hydrogen (H). Therefore, in Fe/V multi-layered films, almost all of the H atoms are supposed to be in the V layer, and the H distribution should show a clear contrast at the Fe/V interface. This is also the case for deuterium (D). D has a lower diffusion coefficient than H. Hence, a surface segregation of D during the APT analysis can be suppressed, enabling to visualize original D position in the host metal lattice. Furthermore, D can be distinguished from background hydrogen in the APT analysis chamber. By using a portable chamber to prevent the sample from being exposed to oxygen, we were able to measure the D concentration in V or Fe/V films over a wide concentration range. We compared the D concentration measured by APT with the compared with the results of measurements of the hydrogen concentration dependence of electromotive force (EMF) for similar samples, it was found that the average D concentration in the sample could be correctly evaluated using APT.

9:20am **CM1-1-ThM-5 Monitoring Thin Film Battery Electrodes via in-Situ/in-Operando Ellipsometry***, Máté Füredi* ***[mate.furedi@semilab.hu]****,* Semilab Semiconductor Physics Laboratory Co. Ltd., Hungary*; Jialin Gu, Adam Lovett,* University College London, UK*; Bálint Fodor, András Marton,* Semilab Semiconductor Physics Laboratory Co. Ltd., Hungary*; Stefan Guldin,* Technical University of Munich, Germany*; Thomas Miller,* University College London, UK

The electrochemical energy storage behavior of nano- and microscale (thin- and thick-film) electrodes displays unique characteristics that provide crucial insights into various charge storage mechanisms, essential for the optimal design of commercial battery applications. Additionally, these films are applicable for constructing microbatteries for miniature electronic devices (such as sensors). Critically, material chemistry, crystallinity, and nanostructure significantly influence active charge transfer mechanisms in these systems, generally classified as electrochemical double layer capacitive, pseudocapacitive, or battery-type behaviors. In lithium-ion batteries specifically, the charge storage mechanism involves the (de)/intercalation of lithium ions in active electrode materials, such as silicon, graphite, or transition-metal oxides.

By optically monitoring thin-film electrodes under electrochemical charge/discharge, a range of time-resolved structural data can be obtained. This work elaborates on this by integrating operando spectroscopic ellipsometric data acquisition. Ellipsometry, highly sensitive to thin films, offers an advantage by effectively excluding any electrolyte side-reactions from measurement, thus providing accurate, real-time data on the evolving structure of lithiated electrodes across charging states. Additionally, ellipsometry tracks thickness changes, enabling precise monitoring of degradation mechanisms.

This work demonstrates (on the example of transition-metal oxide thin-film electrodes) how ellipsometry can reveal intercalation processes, diffusion limitations, and pseudocapacitive contributions. This is further correlated with the complementing electrochemical data. The considerations of this work are furthermore broadly applicable to other thin-film electrode materials.

10:20am **CM1-1-ThM-8 RBS Study of PiTi and NiTi Multilayer Thin Film for Hydrogen Generation and Water Splitting***, Enos Nemukula,* University of Venda, South Africa*; Christopher Mtshali,* iThemba laboratoty, South Africa*;* ***Fhulufhelo Nemangwele [nemangwele@univen.ac.za]****,* University of Venda, South Africa

In this study, thin film samples of Pd-Ti and Ni-Ti systems were prepared using an electron beam evaporator under a vacuum pressure of 10^{-6} torr on Si<100>, borosilicate glass, and pure Ti substrates. The absorption of hydrogen, carbon, and oxygen into the thin films was followed by conducting an in-situ real-time Rutherford backscattering (RBS) investigation. RBS confirmed no spontaneous interdiffusion of atoms between the layers during the deposition. The layers were approximately $\sim 30\times10^{15}$ atoms/cm^2 (10 nm), and $\sim 433\times10^{15}$ atoms/cm^2 (150 nm) for Pd, and Ti layers in the Pd-Ti system, respectively while Ni layer was $\sim 31\times10^{15}$ atoms/cm^2 (10.3 nm). The in-situ real-time RBS was performed by linear temperature ramping from room temperature to a maximum temperature of 600 ^{o}C at a constant ramping rate of 7 ^{o}C per minute. The results showed an interfacial reaction, indicating an unstable system at higher temperatures. Elastic recoil detection analysis (ERDA) revealed an increase in hydrogen absorption of up to 5 at% from the residual gases inside the scattering chamber at a vacuum of 1×10^{-6} mbar. Increased oxygen peaks indicated enhanced absorption of this element from the residual gases inside the scattering chamber. These results suggest that this system has potential applications in hydrogen absorption.

10:40am **CM1-1-ThM-9 Exploring the Benefits of Automated, Redox Reactions in XPS Analysis***, James Lallo* ***[james.lallo@thermofisher.com]****,* Thermo Fisher Scientific, UK, USA*; Robin Simpson, Paul Mack, Tim Nunney,* Thermo Fisher Scientific, UK

This presentation investigates the benefits of automated, in-situ redox reactions for the purpose of producing well controlled oxide growth on the surface of various sample types. The driving force behind using such a procedure is in the potential for generating a sequence of spectra from a progressively chemically-modified surface to remove ambiguities that can lead to misinterpretation, thus aiding in faster understanding of the unmodified surface. Our study presents XPS results from coupled stepwise oxidation/reduction of surfaces, to aid in resolving such ambiguities across a wide array of materials. We use gas-phase oxidation agents to control the redox states of a specimen, leveraging the logarithmic growth of oxide thickness. This oxidation is implemented using vacuum ultraviolet light (VUV) and the generation of ozone and gas-phase hydroxide free radicals close to the surface of the specimens within the entry-lock of the Thermo Scientific Nexsa surface analysis instrument. This work focusses on the benefits of automating this process to ascertain the potential merits of including it into a standard operating procedure for XPS analysis.

11:00am **CM1-1-ThM-10 Hydrofluoric (HF) Acid Corrosion Study of Corrosion Resistant Alloys Used in Semi-Conductor Etching Process Equipment***, Donald Williams* ***[donald.williams@horiba.com]****, Kayvon Savadkouei, Brian Chung, Brad Drake, Patrick Lowery, Andrey Krayev, Eddy Robinson,* Horiba Instruments Inc., USA

Corrosion studies require the use of complementary analytical techniques, as each method provides results based on the interaction of the investigated material with a probing medium [1]. Obtaining elemental, molecular, and crystal/grain structure information at different spot sizes and probing depths is crucial, particularly for elements that are challenging to observe simultaneously, such as hydrogen and fluorine.

In this study, the dissolution of gaseous phase anhydrous hydrogen fluoride and diffusion of fluorine into various metal superalloys were monitored by analyzing changes in concentration, depth, and diffusion rate using Glow Discharge Optical Emission Spectroscopy (GD-OES). A representative area of ultra-high purity (UHP) 316L (composition compliant with SEMI standard F20) and Inconel® 600 alloys were rapidly sputtered to obtain fast elemental depth profiles with nanometer resolution [2].Atomic Force Microscopy (AFM) provides complementary data with relevance to corrosion studies, ranging from the subtle effects of surface passivation uniformity on the measured surface potential and conductivity of the material to the simple evolution of the surface topography with progression of corrosion (even in the earliest stages) [3].

The corrosion test samples are representative of alloys used in semiconductor manufacturing equipment, where improved alloy durability and the prevention of leaching of corrosion byproducts is critical. The goal is to understand the prevalent corrosion mechanisms in these common semiconductor alloys in order to find ways to increase equipment longevity and minimize contamination to the semiconductor manufacturing processes.

References:

1. Compendium of Surface & Interface Analysis, Springer
2. Review: What Can Glow Discharge Optical Emission Spectroscopy (GD-OES) Technique Tell Us about Perovskite Solar Cells? Small Methods 2022, 2200633
3. Review: Application of AFM-Based Techniques in Studies of Corrosion and Corrosion Inhibition of Metallic Alloys. Corrosion

and Materials Degradation 2020, 1, 345–372; doi:10.3390/cmd1030017

11:20am **CM1-1-ThM-11 Numerical Ellipsometry: Artificial Intelligence Based Real-Time, in Situ Process Control for Absorbing Metal Films Depositing on Known Transparent Substrates***, Frank Urban* ***[fk_urban@yahoo.com]****, David Barton,* Florida International University, USA

Ellipsometry can provide the optical properties and thickness of a thin film depositing on a known substrate, including transparent substrates, in real time using commercially available *in situ* instrumentation. The desired film parameters are related to visible light reflection measurements through Maxwells equations, wavelength, and geometry. A number of different methods have been developed for obtaining the desired parameters given a reflection or multiple reflections. One category of methods is iterative least squares curve fitting, frequently the Levenberg-Marquardt method. An emerging method is that of artificial intelligence (AI) employing artificial neural networks. One of the primary advantages of the AI method is speed. It can be a thousand times faster than the pre-existing curve fitting methods. The work here demonstrates the use of such an Artificial Intelligence method to enable real-time, *in situ* monitoring of thin film growth. Examples will be given using a single angle of incidence and three angles of incidence for comparison. Thin absorbing films (up to 45 nm) will be given using a multilayer perceptron configuration consisting of either 4 or 12 input and 4 output neurons with two hidden layers of 80 neurons each. Solutions are performed at each wavelength independently and do not rely on fitting functions. The design, training and use of a number of neural networks will be presented.

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