Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H1-2-MoA
Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces II

Moderators: Grégory Abadias, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France, **Xavier Maeder**, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, **Michael Tkadletz**, Montanuniversität Leoben, Austria

1:40pm **H1-2-MoA-1 Decomposition of CrN Induced by Laser-Assisted Atom Probe Tomography**, ***Helene Waldl (helene.waldl@unileoben.ac.at)***, *M. Schiester,* Montanuniversität Leoben, Austria*; M. Hans,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; N. Schalk, M. Tkadletz,* Montanuniversität Leoben, Austria

It is well known that measurement parameters can significantly influence the elemental composition determined by atom probe tomography (APT). Especially results obtained by laser-assisted APT show a strong dependence of the laser pulse energy on the apparent elemental composition. Within this study laser-assisted APT experiments were performed on $Cr_{0.51}N_{0.49}$ and thermally more stable $(Cr_{0.47}Al_{0.53})_{0.49}N_{0.51}$, applying two different laser wavelengths (i.e. 532 and 355 nm) and systematically varied laser pulse energies. The deduced elemental composition of CrN exhibited a strong increase of the Cr content, when the laser pulse energy was increased for both laser wavelengths. For low laser pulse energies Cr^{2+}, CrN^{+}, N^{2+}, N_2^{+}were identified, while the amount of detected Cr^{2+} ions increased and the amount of N^{2+} ions strongly decreased at higher laser pulse energies. Further, increased detection of more complex Cr containing ions such as Cr_2N^{2+} at the expense of CrN^{+} was observed at higher pulse energies. At the highest pulse energy levels used within this work the Cr content was > 80 at. %, dominated by the amount of detected Cr^{2+} ions. The change of the spectrum of the detected ions with increasing laser pulse energy led to the conclusion that high laser pulse energies initiate the thermal decomposition of CrN, consistent with the known thermal decomposition path into Cr_2N and subsequently into Cr and gaseous N. On the contrary, variation of the laser pulse energy for the thermally more stable CrAlN resulted only in a slight increase of Cr and a decrease of Al and N with increasing laser pulse energy and no change in the type of detected ions. In conclusion, within the present study the decomposition of a coating material with low thermal stability induced by laser-assisted APT was reported for the first time, emphasizing the importance of the selection of suitable measurement parameters for metastable materials, which are prone to thermal decomposition.

2:00pm **H1-2-MoA-2 Watching Matter Move: Observing in-situ Silver Intercalation in Real Time**, ***Falk Niefind (Falk.Niefind@nist.gov)***, NIST-Gaithersburg, USA*; C. Dong, R. Maniyara, J. Robinson,* Pennsylvania State University, USA*; S. Pookpanratana,* NIST-Gaithersburg, USA

Collective electron oscillations, known as plasmons, respond strongly to electromagnetic radiation and their chemical environment.[1] Therefore, plasmonic materials have great potential in applications such as optoelectronic devices and sensors.[2] Thin silver (Ag) films are a particularly appealing plasmonic material, due to their low ohmic resistance. However, thin metallic films need to be shielded against unwanted environmental interactions to prevent degradation. One option is to intercalate the Ag atoms between an epitaxially grown graphene (EG, as a top layer) and silicon carbide (SiC).[3]

Here, we use photoemission electron microscopy (PEEM) to observe the Ag de- and re-intercalation process between EG and SiC during in-situ annealing directly in real time (~1 s resolution). PEEM is a surface-sensitive, full-field imaging technique that achieves nanometer-scale spatial resolution with topographic and electronic contrast. It's basic operating principle employs the imaging of electrons released from a sample surface via the photoelectric effect.

The samples were prepared by ex-situ confinement heteroepitaxy (CHet)[3] during which Ag atoms diffuse through plasma engineered defects of the top graphene layer towards the EG-SiC interface at ~900 °C. To our surprise, we found the intercalation process to be observable even at moderate temperatures (300 °C) until it eventually ceases, where additional heating will not drive the reaction forward. Kinetic analysis of the real space images indicated that the intercalation is probably defect mediated, as has been observed for the CHet process. In addition, we conducted scanning electron microscopy (SEM)-energy dispersive x-ray (EDX) analysis, atomic force microscopy (AFM) as well as x-ray photoelectron spectroscopy (XPS) to corroborate and aid in proposing a mechanism of our PEEM-based observations.

1. Z. M. A. El-Fattah et al., ACS Nano 13, 7771-7779 (2019).
2. A. S. Baburin, Optic. Mater. Expr. 9, 611-642 (2019).
3. N. Briggs et al., Nature Materials 19, 637-643 (2020).

2:20pm **H1-2-MoA-3 In-Situ Study of Plasma Surface Interaction Utilizing a Microplasma in a TEM**, ***Holger Kersten (kersten@physik.uni-kiel.de)***, *L. Hansen, N. Kohlmann, U. Schuermann, L. Kienle,* Kiel University, Germany

The idea of in-situ investigation of a microplasma in a transmission electron microscope (TEM) was successfully demonstrated in 2013 for the first time [1]. Since then no attempts have been taken to observe the plasma surface interaction in real time. Various technical challenges, e.g. size limitations, gas sealing and handling of high voltages, have to be overcome to enable the in-situ TEM imaging.

A stable atmospheric pressure microplasma discharge was designed and studied ex-situ in advance to gain insight in the plasma surface interaction by several diagnostics [2]. For the experimental studies, a simple setup utilizing parallel plate electrodes with a 50-150 µm interelectrode distance divided by a Kapton spacer with a 1mm diameter hole as discharge region intended for in-situ TEM studies is used. The rather small setup operated in Ar or He, respectively, results in an atmospheric pressure DC normal glow discharge observed by I-V characteristics of the microplasma. Significant differences due to the working gas, electrode material and electrode distance have been found. Currents in the range of 0.5-3 mA resulted in electrode potentials of 140-190 V for most experimental conditions. Optical emission spectroscopy and imaging revealed stable plasma operation and enabled the determination of current densities (approx. 16 mA/mm^{2}for He, or 28 mA/mm^{2}for Ar) independent of the input current as the discharge channel grows in diameter. Sheath thicknesses in the range of a few µm have been calculated by the collision-dominated Child-Langmuir law and trends are confirmed by the optical imaging. Energy flux measurements revealed a pronounced effect of ions on the measurement process and resulted in high energy fluxes locally up to 275 W/cm^2. Effective secondary electron emission coefficients ranging from 1 to 1.6 depending on the discharge conditions have been determined based on the energy balance at the cathode.

Prototypes of the vacuum-proof microplasma cell have been build and preparations for the in-situ studies are successfully ongoing right now. In the present contribution the microplasma and its vacuum-proof encapsulation is addressed and a report on the current state of the in-situ experiments for surface modification will be given.

[1] K. Tai et al., Scientific Reports **3**(2013), 1325.

[2] L. Hansen et al., Plasma Sources Sci. Technol., 2022, accepted.

2:40pm **H1-2-MoA-4 Detection of Individual Nucleated Dislocation Slip Trace During *in Situ* TEM Tensile Testing by Advanced Image Analysis**, ***Xiaoqing Li (li_xiaoqing@berkeley.edu)***, *A. Minor,* University of California at Berkeley, USA

Nucleation of crystalline defects such as dislocations lies at the heart of mechanical deformation. Here, we demonstrate a technique for observing the nucleation of individual dislocations during *in situ* transmission electron microscopy (TEM) tensile testing and measuring fundamental parameters relevant for plasticity from the individual events. Our method relies on systematic detection of dislocation slip traces with automated image analysis in an oriented single crystal Ni sample. In this work, a method for detecting a nucleated dislocation is presented and a quantitative approach is applied to extrapolate the energetic barriers for the nucleation of surface dislocations in pristine crystals.

The in-situ tensile test on a defect-scarce single crystal Nickel sample with stable plastic deformation consisting of single defect nucleation was performed on a push-to-pull device in a JEOL 3010 microscope. The load-displacement relation, along with simultaneous video of the deformation (24 frames/second) were recorded (Fig. 1). For a nucleated dislocation that quickly sweeps through a perfect crystal, only the dislocation 'slip trace lines' existed but difficult to be caught. In order to detect dislocation slip traces from dislocations moving at speeds higher than possible to detect directly, contract analysis of frames before and after an event was carried out (Fig. 2). By subtracting the brightness value of each pixel in each two consecutive frames, the dislocation slip trace line can be marked out. Also,

molecular dynamics (MD) simulation was performed to confirm the nucleation specific type of dislocation operating during the uniaxial loading condition. Using the identification of individual defect traces from *in situ* testing, a cumulative probabilistic function is applied to correlate the relationship between a dislocation nucleation event and the corresponding stress level (Fig. 3). Our analysis allows for the extrapolation of the activation parameters for individual dislocation nucleation events using the data on one sample in one tensile test. Precise and quantitative correlation of activation parameters for dislocation nucleation from *in situ* TEM nanomechanical testing can provide direct quantitative measurements useful for computational models of plasticity.

3:00pm **H1-2-MoA-5 Effect of Film Thickness and Trace Width on Electrical Conductivity of Stretchable Composite Inks Under Monotonic and Cyclic Tensile Loading***, Qiushi Li (gli75@gatech.edu), O. Pierron, A. Antoniou,* Georgia Institute of Technology, USA

Flexible and stretchable electronics devices often employ a conductive ink film to transmit electrical signal. As these devices are designed to perform electrically while undergoing large deformation, understanding the electrical conductivity of the ink film under deformation is essential for designing reliable devices. The current work studied the electrical performance of a conductive ink consisting of silver flakes embedded in a polyurethane binder and screen printed on a thermoplastic polyurethane substrate. The effect of ink film thickness (10, 20, 30 mm), differentiated by the number of printing passes and consequently the number of ink layers, for different film trace widths (from 0.25 to 2 mm) was investigated under both monotonic and cyclic tensile loading conditions up to 200% applied strain. *In-situ* experiments under confocal as well as scanning electron microscopes were also performed to examine the evolution of strain localization and damage for specimens with different ink film thicknesses and trace widths. The ink film thickness was found to have a significant impact on electrical performance for smaller trace widths in both the monotonic and cyclic loading cases, but as trace width increased the effect of film thickness was diminished. Based on these findings, a relationship between electrical performance and the geometric design parameters of ink film thickness and trace width was proposed.

3:20pm **H1-2-MoA-6 Exploring Diffusion and Segregation Phenomena on the Nano Scale by *in Situ* Tem Heating Studies (Virtual Presentation)***, Yolita Eggeler (yolita.eggeler@kit.edu),* Laboratory for Electron Microscopy, KIT, Germany **INVITED**

At high temperatures, local diffusion and segregation phenomena affect thermo-mechanical properties of high-performance alloys. This is fascinating from a fundamental point of view but also important in view of the exploitable service lives of high temperature components. Therefore, these processes need to be investigated using *in situ* analytical electron microscopy. This can be achieved by combining multiple heating/cooling steps in the transmission electron microscope (TEM). MEMS based heating chips are used to expose micro machined specimen with specific microstructures to well defined temperature intervals, during which local diffusion/segregation phenomena take place. After cooling energy dispersive X-ray spectroscopy (EDXS) detectors allow to capture elemental distributions maps. Maps which are taken after different accumulated exposure times allow to study the kinetics of nano scale diffusion and segregation phenomena. As one key element of the *in situ* study, two elements of the microstructure (a γ' phase particle and the adjacent γ channel) are used as an intrinsic nano-diffusion-couple (NDC). A thermodynamic equilibrium is established at one temperature followed by annealing at a different temperature. The kinetics in which the new equilibrium is reached is studied using STEM-EDXS. The NDC approach is not only well suited to study interdiffusion across interfaces in two phase model systems, as will be demonstrated in the first part of the study, where experimental results shed new light on the predictions of thermodynamic/kinetic modelling procedures. It also allows to study segregation phenomena to linear and planar defects in compositionally complex alloys, the second key topic which will be investigated. It will be shown that chemical segregation to planar defects can be interpreted as a local phase transformation. Kinetic results on how segregation proceeds will be presented. Special emphasis will be placed on discussing the potential and the limitations of this type of *in situ* investigations and areas in need of further work.

4:00pm **H1-2-MoA-8 *In-situ* Spectroscopic Ellipsometry Based Real-Time Growth Monitoring of Metal-Oxide Atomic Layer Deposition Processes***, Ufuk Kilic (UFUKKILIC@UNL.EDU), S. G. Kilic, M. Hilfiker, A. Mock, D. Sekora,* University of Nebraska-Lincoln, USA*; G. Melendez,* Polytechnic University of Puerto Rico*; N. Ianno, C. Argyropoulos, E. Schubert, M. Schubert,* University of Nebraska-Lincoln, USA

Within the last decade, Atomic Layer Deposition (ALD) of conformal metal-oxide ultra-thin films has provoked an unprecedented interest due to the materials' potential roles in several applications including on-chip photonic devices, ultra-fast switching systems, and next generation transistors [1]. While downsizing of material dimensions for devices applications is an ongoing demand from industry, the ultra-precise control of growth processes during the fabrication of complex systems is a requirement for advanced manufacturing technologies. The integration of spectroscopic ellipsometry (SE), an optical, contactless, and non-invasive technique, into ALD processes has been demonstrated as a powerful and widely-used tool for in-*situ* thin film growth monitoring [2].

In this study, we successfully optimized the oxygen plasma enhanced ALD growth for three different metal-oxides: ZnO, WO_3, and TiO_2, by employing $Zn(CH_3)_2$, $(tBuN)_2(Me_2N)_2W$, and $Ti(OC_3H_7)_4$ organometallic precursors, respectively. To analyze the *in-situ* SE data which were measured within and across multiple cycles during plasma-enhanced ALD of metal-oxide thin films, *a dynamic dual box model is proposed.* The model consists of five layers (substrate, mixed native oxide and roughness interface layer, metal oxide thin film layer, surface ligand layer, ambient) with two of them acting as dynamic parameters (metal oxide thin film layer thickness and surface ligand layer void fraction) to unravel in-cycle kinetics of the metal-oxide ALD growth process. *In-situ* SE data analysis revealed a dynamic surface roughening process with fast kinetics followed by subsequent roughness reduction with slow reaction kinetics upon cyclic exposure to precursor materials and plasma enhanced chemical surface reactions. The proposed dynamic dual box model may be generally applicable to monitor and control metal oxide growth during atomic layer deposition and can be further implemented for precise feedback control and real-time optimization of deposition parameters.

References:

[1] George, S. M., Chem. Rev. 110.1 (2009): 111-131.

[2] Kilic, U., et al.,J. Appl. Phys.*:1805.04171*(2018).

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