Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific Salon 1 - Session H1-2-TuA
Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces II

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1:40pm **H1-2-TuA-1 Complex Study of Thermally Induced Order Reactions in Cu-Au Thin Films***, **Alla Sologubenko**, M Volpi, P Okle, R Spolenak,* ETH Zürich, Switzerland

The development of thermally and structurally stable Cu- and Au- based thin films or nano-modulated materials for modern electronic and catalytic applications is the main goal of our work. In our study we follow an effect of thermal treatment on microstructure evolution in Cu-X at.% Au thin films sputter-deposited on rigid and viscoelastic substrates. Complex characterization of thermally induced changes of the material microstructure was carried out by a combination of techniques, transmission electron microscopy (TEM), including time-resolved in-situ heating TEM, and reflectance anisotropy spectroscopy (RAS). While TEM is a well-established technique for phase analyses of nano-dimensional objects, RAS is hardly known as a tool for the microstructure and phase analyses [1]. The validation of RAS as a technique for phase finger-printing is an alternative goal of our work. Most simple specimen preparation requirements, a non-destructive nature of the optical set-up, high sensitivity to the microstructure state of the material are very attractive features of RAS. The comparison of the TEM and RAS data sets acquired from the same material confirms the unprecedented phase sensitivity of the optical technique and justifies its employment as a prompt, high quality and throughout, routine material characterization method.

Thermally induced phase reactions in Cu-Au bulk alloys are well studied. However, there is little information reported on phase evolution and microstructure stability against thermal annealing in continuous Cu-Au thin films or dewetted nano-modulated structures. A balance between kinetic rates of phase reactions, grain growth and dewetting is affected by an increase of the interface and strain energy contributions to the Gibbs free energy of the thin film system, which in turn can have an effect on the temperature-composition phase fields and the grain morphology.

Our studies confirmed that phase configurations in Cu-Au thin films of 80 and 200 nm thicknesses, accord with the 350°C section of the Cu-Au binary phase diagram [2]. Both, TEM and RAS revealed the stable solid-solution state of Cu-15 at.% Au films in annealed films. The formation of intermetallic phases in Cu-25 at.% Au and Cu-50 at.% Au films upon 350°C annealing was also detected by both, TEM and RAS, but only RAS could reveal the two-phase state of the annealed Cu-25 at.% Au and Cu-50 at.% Au films. The in-situ heating TEM studies show that the 350°C annealing results in nearly concurrent ordering and grain growth in the films with Au content higher than 15 at.%. The time-resolved in-situ heating TEM studies are performed to estimate kinetic rates of both processes.

2:00pm **H1-2-TuA-2 Kinetics Dependence of Microstructure and Stress Evolutions in Polycrystalline Cu Films: Real-time Diagnostics and Atomistic Modelling***, **Clarisse Furgeaud***[1]*, C Mastail, A Michel, L Simonot,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; E Chason,* Brown University, USA*; G Abadias,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France

Thin films are currently used in order to decrease the size and improve performances of integrated components in electronic devices. Sputter-deposition is commonly used for growth of metallization layers. It's well established that microstructure, morphology and residual intrinsic stress are strongly correlated to deposition parameters. By combining *in situ* and real-time diagnostics tools a better understanding of the development of film microstructure and intrinsic stress could be achieved for high-mobility metals [1] highlighting the key role of the early stages of growth in the design of thin films morphology.

However, the interplay between deposition parameters and growth kinetics is unexplored, such as the interdependence between growth rate, pressure, flux interruption/resumption on stress build-up and post-growth-relaxation kinetics. In this study, we propose a methodology based on three different *in situ* and real-time diagnostics tools: Multiple-beam optical stress sensor (MOSS), electrical resistance and surface differential reflectance spectroscopy (SDRS) implemented during sputter-deposition of a model system Cu thin film. Such methodology allows us to obtain relevant and quantitave information on growth and relaxation kinetics. This study was complemented by a systematic *ex situ* characterization by AFM, XRD, and TEM to relate film morphology and microstructure to deposition parameters used.

Besides this experimental approach, we have addressed the atomistic mechanisms responsible for these kinetic effects by computational modelling. We have developed a versatile kinetic Monte Carlo (kMC) code based on a 3D rigid lattice to mimic as much closely as possible the real sputter-deposition conditions. The originality of this code lies on its ability to capture the energetic deposition conditions intrinsic to the sputtering deposition process. Indeed, energetic species constituting the incoming flux are able to drastically alter (sub-)surface processes, such as adatom diffusion and defect creation, and subsequent morphology, microstructure and stress. Finally, the capability of the code to predict stress caused by the diffusion of adatoms in and out of the grain boundaries will be further examined with the final objective to provide a multiscale, predictive computational tool to study the growth and stress kinetics.

[1] G. Abadias *et al*., Volmer-Weber growth stages of polycrystalline metal films probed by in situ and real time optical diagnostics, APL, 107, 183105 (2015)

2:20pm **H1-2-TuA-3 Understanding the Crystallization of Amorphous Films with Embedded Seed Crystals using High-resolution STEM Composition and Structural Mapping***, **Paul Rasmussen**, J Rajagopalan, R Berlia,* Arizona State University, USA

It has been shown recently [1] that by systematically embedding nanometer sized seed crystals into amorphous thin films, their thermally induced crystallization process and final microstructure (mean grain size, grain aspect ratio, and spatial distribution) can be explicitly controlled. Here, we describe the characterization of the seed crystals and their relation to the final grain size, size dispersion and texture of the crystallized films through a combination of spatially resolved, composition and structural mapping in a scanning transmission electron microscope (STEM). We examined two different films (NiTi and TiAl) with a variety of seed crystals (Ti, Cu, Cr) in this work. First, we used energy dispersive X-ray spectroscopy (STEM-EDXS) to obtain the chemical composition with nanometer scale spatial resolution and identified seed crystals (regions with sharply elevated seed element content) in the films. To complement this information, we used automated crystal orientation mapping (ACOM) via precession electron diffraction to identify amorphous (film matrix) and crystalline regions (seed crystals) as well as the orientation of the seed crystals. The combination of STEM-EDXS and ACOM analysis allowed us to map the size dispersion, areal density and spatial distribution of seed crystals and correlate them with the final microstructure of the crystallized film.

1. R. Sarkar and J. Rajagopalan, "Synthesis of thin films with highly tailored microstructures," *Materials Research Letters* 6, 398-405, 2018

2:40pm **H1-2-TuA-4 *In-situ* Investigation of the Oxidation Behavior of Metastable CVD $Ti_{1-x}Al_xN$ Using Combined Synchrotron XRD and DSC***, **Christian Saringer**, M Tkadletz,* Montanuniversität Leoben, Austria*; A Stark,* Helmholtz Zentrum Geesthacht, Germany*; C Czettl,* Ceratizit Austria GmbH, Austria*; N Schalk,* Montanuniversität Leoben, Austria

Although hard protective $Ti_{1-x}Al_xN$ coatings deposited by physical vapor deposition methods are well investigated today, their microstructure and properties when synthesized by chemical vapor deposition (CVD) still offer new and scientifically challenging questions. This is mainly owing to the extraordinary structure of CVD $Ti_{1-x}Al_xN$ coatings, typically consisting of Al-enriched Al(Ti)N and Al-depleted Ti(Al)N epitaxial nanolamellae. Within this work, the oxidation behavior of such a nanolamellar coating has been examined using a combination of *in-situ* analytical methods. The coating investigated was composed of approximately 66 wt.-% Al(Ti)N and 32 wt.-% Ti(Al)N face centered cubic phase fractions as well as small amounts of wurtzitic AlN (< 2 wt.-%) deposited on a TiN baselayer. Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) on a powdered sample were simultaneously performed at the P07 beamline at the synchrotron PETRA III in Hamburg during a continuous annealing cycle from 100 to 1400 °C in ambient atmosphere. Together with the DSC signal a sequential Rietveld refinement of the XRD data allowed to precisely determine the onset temperatures of phase transformations and oxidation reactions along with

[1] **Student Award Nominee**

the quantitative phase composition at any given temperature. The results showed that while the TiN baselayer already started to oxidize to rutile at temperatures below 550 °C, the Al-containing phases still retained their chemical stability. For the Ti(Al)N and Al(Ti)N phases the onset of oxidation could be observed at approximately 700 and 850 °C, respectively, evidencing the positive influence of Al on the oxidation resistance of $Ti_{1-x}Al_xN$ based coatings. At 1000 °C, oxidation of the coating to rutile and alumina was completed, however, upon further annealing above 1250 °C rutile and alumina were found to form the ternary oxide Al_2TiO_5. The sophisticated combination of *in-situ* DSC and XRD at a synchrotron with subsequent Rietveld analysis is a novel approach for the investigation of the thermal stability of metastable coating systems and the results presented demonstrate the potential power of this method. Additionally, annealing in ambient air of the same CVD $Ti_{1-x}Al_xN$ coating on single crystalline alumina substrates with subsequent microstructural analysis allowed to validate the results provided by the *in-situ* investigation of the powdered sample with the behavior of the solid coating.

3:00pm **H1-2-TuA-5 In-situ X-ray Characterization of Liquid-solid Transition Phase in Small Volume**, ***Mohamed Kbibou***, *L Barrallier,* Mechanics, Surfaces and Materials Processing Laboratory, France*; M El Mansori,* Arts et Métiers ParisTech d'Aix en Provence, Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France*; L Heraud,* Mechanics, Surfaces and Materials Processing Laboratory, France

This research paper presents a novel in-situ X-ray characterization of microstructure and evolution of residual stress during solidification process in small volume, which involves the occurrence of various mechanisms operating concurrently. This is illustrated by the solidification of binary eutectic alloy Bi58%wt-Sn42%wt using in-situ X-ray diffraction cell of laboratory instrument to understand the fundamental physical mechanisms that control the liquid-solid transition phase. The diffraction cell is outfitted with a heater under inert atmosphere, temperature control system, thermal isolation and transparent window making X-ray scattering analysis possible at higher temperature. The experimentally obtained temperature dependence of crystal mesh parameters, phase's percent and residual stress is discussed. A Radial Distribution Function Analysis (RDFA) is given at the melting phase of the alloy to describe the short-range order (SRO) and atomic distribution. Also discussed is the evolution of phase transformations and residual stresses on the surface of alloys from room temperature to melting point. The possibilities of this in-situ X-ray characterization method to master interplay between microstructure, solidification process variables and functional properties of compounds are highlighted.

4:00pm **H1-2-TuA-8 Novel Quantitative Thin Film Thickness and Chemical State Analysis X-ray Techniques**, ***Wenbing Yun***, *B Stripe, S Shesadri, S Lewis, X Yang, R Qiao, S Lau,* Sigray, Inc., USA

X-ray based techniques have long been used for thin film characterization, and commonly known approaches include total fluorescence x-ray spectrometry (TXRF) and grazing incidence x-ray scattering systems. However, these laboratory-based approaches have poor spatial resolution due to the limited brightness of the x-ray sources used. On the other hand, techniques based on synchrotron facilities (large particle accelerators that provide intense beams of x-rays) such as micro x-ray fluorescence and micro x-ray absorption spectroscopy (microXRF and microXAS) can provide powerful, spatially resolved information, including: thickness variation, chemistry (e.g. oxidation state and bond lengths), and compositional variation. Such information can be achieved by rastering a focused, high brilliance x-ray beam at microns-scale resolution across the thin film.

Until now, such capabilities at high, microns-scale resolution have been exclusively available at synchrotron facilities, which have limited accessibility and a competitive application process. Sigray, through patented breakthroughs in x-ray source and x-ray optic technologies, has developed two major systems for spatially resolved thin film studies: the AttoMap microXRF system and the QuantumLeap x-ray absorption spectroscopy system.

Here we present the two breakthrough systems and their recent applications, which both provide non-destructive capabilities and the ability to spatially resolve thin films *in situ*, for instance under high temperature and mechanical strain. The microXRF system has spatial resolution down to microns and sub-Angstrom sensitivities, which has enabled it to map thickness variations of coatings and on the order of angstroms with high repeatability and accuracy. The x-ray absorption spectroscopy (XAS) system provides important chemical information for a given element of interest, such as oxidation state and reactivity, bond lengths, atomic geometry, and nearest neighbor information (such as atomic type).

We will present recent trace-level results of thin films with ~1% repeatability, such as Ar, Hf, Ni and Ti measurements and standard-less ratios for fast and non-destructive characterization. Moreover, we will also present some recent findings on chemical state analysis using the XAS system for applications including battery electrodes and catalyst layers.

4:20pm **H1-2-TuA-9 Effect of Heat Treatment on Microstructure of Erbia Film on Steel Substrate with Yittria Buffer Layer Fabricated by MOCVD**, ***Kenji Matsuda***, *M Tanaka, S Lee,* University of Toyama, Japan*; Y Hishinuma,* NIFS, Japan*; K Nishimura, T Tsuchiya,* University of Toyama, Japan

Erbia and yittria are the promising materials to realize an advanced breeding blanket system because of good electrical resistivity and effective hydrogen permeation suppression. Erbia thin film fabricated via MOCVD process with the yittria buffer layer was formed on steel (SUS316) substrate before and after thermal cycles to investigate the effect of thermal cycling, and their microstructure was confirmed by electron microscopes (SEM, TEM and STEM) and atomic force microscope (AFM) in the present work.

The surface morphology of samples after thermal cycling has small granular structure than samples before thermal cycling and without yittria buffer layer. According to cross sectional observation by TEM and STEM, erbia and yittria have different columnar structure, while yittria buffer layer did not avoid diffusion of elements from SUS316 substrate to erbia layer. The thermal cycling test had not been affected to the growth direction of erbia and yittria layers, which is mostly cube-cube relationship

5:00pm **H1-2-TuA-11 Study of Volmer-Weber Thin Film Growth Mechanisms by Coupling *in situ* Resistivity, Optical and Mechanical Measurements**, ***Quentin Herault***, *S Grachev, I Gozhyk, H Montigaud,* Saint-Gobain Recherche/CNRS, France*; R Lazzari,* Institut des Nano Sciences de Paris - Sorbonne Université, France

Völmer-Weber growth mode is characteristic of some materials, such as Ag and Au. Before obtaining a uniform film, this growth mode involves complex steps of growth: island nucleation, island growth, percolation and coalescence. It is still a challenge to study these steps with *ex situ* techniques, especially when thin films are not stable after deposition and oxidation. Indeed, low melting points materials -Ag for example- are very mobile due to their low diffusion energy. *In situ* measurements become important to obtain representative information about growth phenomenon happening during deposition process.

To do so, we decided to develop a homemade *in situ* resistivity measurement setup into our DC magnetron sputtering chamber. Coupled to an existing *in situ* mechanical stress measurement setup, this system provided information about coalescence start (mechanical compressive pick), percolation threshold (resistivity fall) and uniform film (mechanical tensile pick). In parallel, our measurements were compared to optical measurement, providing complementary information about coalescence start.

With this setup and playing on deposition technique (continuous and sequentially interrupted), we measured a more or less delayed percolation threshold. We also measured a change in grain size distribution. In addition, using different deposition conditions (power and pressure) and sublayers, we tuned growth in order to finally propose growth mechanisms during Ag thin film deposition, function of deposition rate and diffusion.

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