

Monday Afternoon, October 31, 2011

In Situ Spectroscopy and Microscopy Focus Topic
Room: 106 - Session IS+AS+SS-MoA

In Situ Characterization of Solids: Film Growth, Defects, and Interfaces

Moderator: M. Salmeron, Lawrence Berkeley National Laboratory

2:00pm **IS+AS+SS-MoA1 A New Approach to Defect Evolution Studies – Combined In Situ Experiments and Electron Tomography.** *I.M. Robertson, J. Kacher, G. Liu*, University of Illinois at Urbana-Champaign **INVITED**

Electron micrographs are two-dimensional images capturing specific instances in the evolution of the microstructure and composition as well as the electronic and magnetic state. As these yields no insight as to how the state evolved, *a posteriori* knowledge is used to determine the most likely pathway. This challenge can be addressed by conducting experiments *in situ* in the transmission electron microscope, which allows direct observation and in some cases quantification of the reactions and interactions responsible for the evolved structure. The information, however, remains two-dimensional and with increasing use of this technique it is becoming apparent that lack of three-dimensional knowledge is hindering interpretation. Information in the beam direction can be recovered by applying electron tomography, but this is a relatively new technique to defect studies and despite its potential it remains a static snapshot. In this talk, I will illustrate how time-resolved deformation studies have improved our understanding of the behavior of dislocations and how this information has informed the development of new models. I will also demonstrate how three-dimensional images yield a better understanding of complex dislocation interactions and configurations. Finally, I will address the challenges faced in combining these two techniques such that three-dimensional snapshots of the evolving microstructure can be acquired periodically.

2:40pm **IS+AS+SS-MoA3 Real-time Oxide Growth Characterization using Atomic Force Microscopy.** *G. Rijnders*, University of Twente, the Netherlands **INVITED**

Complex oxides have attracted great interest since they exhibit a rich spectrum of physical properties such as ferromagnetism, antiferromagnetism, colossal magnetoresistance, ferroelectricity, dielectricity, and superconductivity. Novel heteroepitaxial devices based on these complex oxides, like spin-polarized ferromagnetic tunnel junctions, superconducting devices and piezoelectric devices, have great potential and are currently under investigation in many groups.

The nature of the above-mentioned physical properties in complex oxides is determined by very small characteristic length scales, comparable to the unit cell lattice parameters of complex oxide. Because of these small characteristic length scales, growth control on an atomic level as well as understanding of the different mechanisms affecting the growth mode is essential for the fabrication of epitaxial heterostructures.

Two independent processes, i.e., nucleation and growth of islands, play an important role during vapor-phase epitaxial growth on an atomically flat surface. Here, nucleation causes the formation of surface steps and subsequent growth causes the lateral movement of these steps. Both processes are determined by kinetics, since they take place far from thermodynamic equilibrium. These kinetic processes affect the final surface morphology and are, therefore, extensively studied. I will demonstrate the applicability of high-pressure RHEED as well as Scanning Force Microscopy (SFM) to monitor to the growth of complex oxides during Pulsed Laser Deposition (PLD). Because of recent developments, SFM is nowadays also used to study dynamic processes, such as thin film growth and surface reaction mechanisms.

We have realized a system, in which SFM can be performed during Pulsed Laser Deposition (PLD). Deposition and force microscopy are performed in one vacuum chamber and via a fast transfer (in the order of seconds) the surface of a sample can be scanned. In our system we take advantage of the *pulsed* deposition process, because microscopy measurements can be carried out between the pulses. This provides real-time morphology information on the microscopic scale during growth. The transfer mechanism allows switching between microscopy and deposition with a re-position accuracy of ± 500 nm which gives new opportunities to study growth processes. Furthermore, it can provide information if RHEED is not possible, for example during amorphous and polycrystalline growth.

In this contribution, I will highlight recent advances in oxide thin film growth as well as the latest equipment developments.

3:40pm **IS+AS+SS-MoA6 An Auger Electron Analyzer System for In Situ MBE Growth Monitoring.** *W.L. Calley*, Georgia Institute of Technology, *P.G. Staib*, Staib Instruments, *J.E. Lowder, J.D. Greenlee, M.W. Moseley, W.E. Henderson, W.A. Doolittle*, Georgia Institute of Technology

Auger Electron Spectroscopy (AES) analysis is a surface sensitive technique for thin film analysis, able to detect nearly all elements [1]. Not only can AES help determine the species present at the surface, but AES can also yield information about the chemical bonding [1]. However, this analysis tool has historically been an *ex situ* technique with a few noted exceptions [2]. Herein we demonstrate the capabilities and usefulness of an Auger probe, the Staib *In situ* Auger Probe (SIAP) that has a sufficient working distance (tested up 82 mm) so as to not shadow beam fluxes allowing use during growth. The probe leverages an existing RHEED gun as an e-beam source for Auger electron excitation.

The configuration and operation of the SIAP has been described in detail [3]. The tool is installed on an MBE system configured for Terfenol growth, a miscible alloy of TbFe₂ and DyFe₂. Initial growths performed without Auger monitoring exhibited substantial oxidation even after Ar etched to remove surface contamination, figure 1. The SIAP was then employed to determine the sources of oxygen contamination.

Three sources of O were identified. The growth chamber had a high enough partial pressure of oxygen to oxidize the highly reactive rare earth elements. After 30 hours in the chamber, uncapped Tb showed a substantial increase in the ratio of O to Tb, figure 2. The Tb source material also delivered O and the rate of O delivery increased with cell temperature, figure 3. A final oxygen source was identified to be the Tb/SiO₂ interface as shown in the SIMS data in figure 4. Figure 5 shows the Si wafer with C and O present at the surface. After growth is initiated the C is not detected after 40 Å of deposition, however, the O can be detected until 200 Å are deposited, indicating intermixing with the SiO₂ interface.

Further tests were conducted starting with a layer of Dy and depositing part of a monolayer of Tb in 2% increments. Figure 6 shows a clear distinction between bare Dy and 2, 4, 6, 8, and 10% monolayer coverage of Tb on a Dy layer, demonstrating the SIAP's sensitivity is at least 2% of a monolayer for these heavy elements.

The SIAP is complementary to existing RHEED systems. While RHEED gives information about the crystal structure of the growing film, the SIAP provides chemical information. This is especially useful when working with films without line compositions. The SIAP coupled with a future closed loop control system may enhance growth of films with multiple oxidation states or other similar phase/chemical transitions. Finally this technique could give information about transitions between layers in multilayered films grown via MBE.

4:00pm **IS+AS+SS-MoA7 Quantum Size Effect Driven Structure Modifications of Bi-films on Ni(111).** *T.R.J. Bollmann, R. van Gastel, H. Zandvliet, B. Poelsema*, University of Twente, The Netherlands

We have investigated the initial growth of Bi/Ni(111) using Low Energy Electron Microscopy (LEEM) and Selected Area Low Energy Electron Diffraction (μ LEED). Bismuth represents an interesting material since 1) it has a tendency for allotropism, 2) it forms several ordered alloys with Ni and 3) with Bi being a neighbor of Pb in the periodic system, one may find evidence for quantum size effects in ultrathin Bi layers. Indeed we obtain ample evidence for Bi/Ni(111) as being a very rich system, even at a fixed substrate temperature of 474 K.

We find first that the deposition of Bi leads to the formation of a surface alloy with a $(\sqrt{3}\times\sqrt{3})\text{-R}30^\circ$ structure at a Bi-coverage of 1/3. Continued Bi deposition leads to the formation of an incommensurate wetting layer with a continuously decreasing lattice parameter, finally ending in a (7×7) structure. From the variation of the step position at the buried interface, nicely accessible with LEEM, we conclude that the dealloying of the $\sqrt{3}$ phase is incomplete and that the (7×7) wetting layer in fact involves two layers with a small, but finite Bi content in the second layer. Upon further Bi deposition elongated, 3-4 layers high nanowires emerge, with a $p(5\times 2)$ structure and a width of about 80 nm, oriented along $\langle 110 \rangle$ and $\langle 100 \rangle$ -azimuths. Further deposition of Bi leads to different (sometimes coexisting) structures: (3×3) -patches with a thickness of three atomic layers and patches with a matrix structure ($m_{11}=3, m_{12}=1, m_{21}=1, m_{22}=2$) and a thickness of five atomic layers. This accurate height assignment is uniquely enabled by the analysis of LEEM-IV data.

The results are fully consistent with quantum size effect driven thin film morphology: the different film structures and their thicknesses nicely fit with integer numbers of nodes in their specific Fermi wave function, even for the seven layers thick (7x7) structure obtained at a lower temperature of 422 K. Tensor LEED calculations of the interlayer spacing of the different structures concur with this assignment.

The influence of the structure and morphology on electronic properties of various materials is well known. The interaction between electronic and crystal structure should be reciprocal. The Bi/Ni(111) system provides a nice and we think first illustration: electronic properties, in particular quantum size effects, actually drive the structure of the thin bismuth films.

4:20pm **IS+AS+SS-MoA8 Growth and Structure of Sm on an Ultrathin Al₂O₃/Ni₃Al(111) Film: A Comprehensive Study**, J.F. Zhu, Q. Xu, S. Hu, X. Feng, D. Chen, University of Science and Technology of China

The growth and electronic structure of vapor-deposited Sm onto a well-ordered Al₂O₃/Ni₃Al(111) ultrathin film under ultrahigh vacuum (UHV) conditions at room-temperature has been studied comprehensively using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), scanning tunneling microscopy (STM) and low electron energy diffraction (LEED). Our results indicate that at room temperature Sm grows in a layer-by-layer fashion for the first two layers, followed by three-dimensional (3D) growth. The interaction of Sm with Al₂O₃ thin films is so strong that deposited Sm is immediately oxidized at beginning. Both the oxidation states of Sm²⁺ and Sm³⁺ are found at low coverages (<1 ML) with the situation that the concentration of Sm²⁺ dominates below 0.2 ML and subsequently that of Sm³⁺ dominates. With increasing Sm coverage, the metallic state of Sm gradually appears. Annealing the film of 0.2 ML Sm/Al₂O₃ at T < 500 K results in further oxidation of the Sm species where all the Sm²⁺ species converts to Sm³⁺. Further annealing at higher temperatures leads to loss of Sm from the surface via subsurface diffusion.

4:40pm **IS+AS+SS-MoA9 In Situ Study of the Reaction Mechanism Kinetics of Pt ALD from (¹⁰⁹Cp)PtMe₃ and O₂**, I.J.M. Erkens, A.J.M. Mackus, H.C.M. Knoops, F. Roozeboom, W.M.M. Kessels, Eindhoven University of Technology, Netherlands

Atomic layer deposition (ALD) of noble metals and noble metal oxides on high-aspect-ratio 3D nanostructures has a wide variety of potential applications in sensing and catalysis. Despite several studies,¹⁻³ much is still unknown about the reaction mechanism of Pt ALD using (¹⁰⁹Cp)PtMe₃ and O₂, which can be considered a model system for noble metal ALD processes. Questions remain regarding the surface species and reactions, and the temperature dependence of the growth per cycle (GPC). In this contribution we expand the understanding of the Pt ALD mechanism by combining quadrupole mass spectrometry (QMS) and spectroscopic ellipsometry (SE). Using these in-situ techniques to study the process as a function of temperature between 100 and 300°C, we have gained a unique perspective, which has led to several new insights. The time-resolved QMS data for CH₄ and CO₂ show that combustion and other ligand reactions at the surface occur in sequence, while competing for the available carbon atoms. Quantification of the data showed that approximately 80% of the C atoms are combusted during the O₂ pulse. By performing the QMS measurements in a temperature series, valuable information was obtained on the rate of combustion of the hydrocarbon ligands at the Pt surface during the O₂ pulse. Using a combination of QMS and SE data, we were able to formulate a mechanism explaining growth inhibition at low temperatures. This mechanism manifests itself through three temperature dependent growth regimes: no growth below 100°C; limited growth between 100 and 250°C; and full growth between 250 and 300°C. Using results from surface science literature a likely explanation for these regimes was given. This involves the cyclopentadienyl ligands at the Pt surface forming reactive intermediates or being thermally decomposed. The mechanism was corroborated by QMS and SE data on post-plasma treatment cycles, by which catalytic activity was temporarily restored. We were therefore able to link the temperature dependence of the GPC to combustion kinetics. A detailed description of our methods and results will be given in our contribution.

1. Aaltonen *et al.*, *Electrochem. Solid-State Lett.* **6**, C130 (2003).
2. Kessels *et al.*, *Appl. Phys. Lett.* **95**, 013114 (2009).
3. Setthapun *et al.*, *J. Phys. Chem. C* **114**, 9758 (2010).

5:00pm **IS+AS+SS-MoA10 In Situ Surface Analytical Characterization of Electronic Devices: Thin Film Solar Cells and Lithium Ion Batteries as Examples**, A. Thissen, SPECS Surface Nano Analysis GmbH, Germany

Electronic devices have revolutionized everyday life in industrial countries over the last decades. Especially devices for energy conversion and storage like thin film solar cells and lithium ion batteries are of importance for the future. Recently two main tasks for research and development are dominant: miniaturization for sophisticated applications targeting at the nanoscale, and designing low cost large scale devices. In both fields the device performance is strongly determined by materials quality, composition, combination and last but not least by processes at materials interfaces. Nanostructures, minimization of material consumption and the need to improve device efficiencies consequently leads to the widespread focussing on thin film preparation. For thin film devices surface and interface analysis like photoelectron spectroscopy and surface (spectro-)microscopies are an important tools for material and device characterization. Classical well defined model experiments already reveal important insights using highly integrated vacuum systems for analysis and preparation. But analysis of materials and devices under near ambient conditions and even in situ during operation is an inevitable future development to improve the significance of data for development and quality management. In this respect the application of techniques like Near Ambient Pressure XPS, XPS from liquids and solid liquid interfaces, hard x-ray PES (HAXPS), Near Ambient Pressure SPM on solar cell and lithium ion battery materials is the challenging tasks for manufacturing companies of surface analytical equipment.

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