Thin Films
Room Makai - Session TF-MoM
Advances/Innovation in Synthesis & Characterization

Moderator: Franz Himpsel, University of Wisconsin Madison, USA

8:00am **TF-MoM1 ToF-SIMS Depth Profiling of Full Organic/inorganic Hybrid Devices with Low-Energy Cesium Ions***, **Céline Noël**,* University of Namur, Belgium*; L. El Fissi, L.A. Francis,* Université Catholique de Louvain*; L. Houssiau,* University of Namur, Belgium

In the last few years, growing attention has been brought to devices based on hybrid (organic/inorganic) multilayered materials as they allow for highly versatile properties, such as tunable optical and electronic features, malleability, transparency and cost-efficiency that could find applications in a large variety of devices such as OPVs, OLEDs, sensors, microfluidics, fuel cells, etc. . Forthcoming technological advances will require detailed knowledge of layers and interfaces composition and morphology in order to optimize device efficiency, stability, processing conditions.

ToF-SIMS is a well-suited technique to obtain key information such as the in-depth molecular composition of each layer and diffusion at the interfaces. However, for hybrid materials, depth profiling remains challenging as ion sources which are efficient on organic materials are generally not efficient on inorganic ones. Numerous dynamic-SIMS studies of interfacial migration between organic/inorganic layers have been reported, but no molecular signal could be monitored. Recently, low-energy (500 eV) Cs^+ ions were shown to possibly offer a reliable solution for depth-profiling hybrid systems [1]. Using this novel approach, the present work presents molecular depth-profiling on complex OLEDs interfaced materials showing that each layer, until the substrate, could be successfully identified by its specific molecular signal within a reasonable sputtering time.

In parallel, oxide/polymer hybrid materials were investigated with future applications in microfluidics, BioMEMS and lab-on-chip devices. Samples consisted of TiO_2 or Al_2O_3 coating on three different polymers, namely cyclic olefin copolymer (COC), polyimide (PI) and SU-8 (a negative photoresist). Again, all samples were easily depth profiled by low-energy Cs+, with characteristic molecular fragments monitored on each polymer even after the oxide layer is sputtered. This again proves that low-energy Cs^+ is an efficient solution to depth profile hybrid materials. We also compared metal diffusion in different oxides coating and polymers. Issues like homogeneity, contamination or non-stochiometry near the interface could be addressed by ToF-SIMS analyses; matrix effects and ion beam induced modifications were discussed based on complementary XPS measurements.

With the development of new technologies, an increasing number of applications are expected to require in-depth molecular information of organic/inorganic materials. The present work shows how ToF-SIMS can answer this demand, opening the way for the characterization of such novel applied materials.

[1] C. Noël and L. Houssiau, J Am Soc Mass Spectrom, 2016. 27(5): p. 908-16.

8:20am **TF-MoM2 Amplitude Contrast High Resolution Electron Microscopy of A-site Associated Oxygen Octahedral Rotations in Artificial Perovskite Superlattices***, **Dean Miller**, J.G. Wen,* Argonne National Laboratory, USA*; X. Wu,* Temple University, USA

Artificially structured perovskite superlattices offer rich opportunities for novel ferroelectricity. We have developed a new high-resolution TEM imaging technique that allows the direct observation of A-site associated oxygen octahedral rotations in perovskite oxide superlattices that reveals the underlying mechanisms of enhance ferroelectricity in complex heterostructures. By combining the amplitude-contrast high-resolution electron microscopy and DFT calculations, we show that a highly polar $CaTiO_3$ phase with a $BiFeO_3$-like structure can be stabilized in $(CaTiO_3)_n/(BaTiO_3)_n$ superlatice. Amplitude contrast imaging (ACI) relies on both spherical and chromatic aberration correction for TEM imaging. Under ACI conditions, atomic resolution channeling contrast can be realized, allowing one to obtain directly interpretable high-resolution electron microscopic images with discrimination between light and heavy atomic columns. Using this imaging approach, we were able to image the atomic structure in a $BaTiO_3/CaTiO_3$ superlattice with high spatial accuracy and discrimination between Ba and Ca columns, providing direct visualization of the Ca and Ba associated oxygen octahedral rotations. Combined with the first-principles calculations, we found that a highly polar metastable "interface phase" of CaTiO3 with a structure of BiFeO3 is stabilized by the mechanical and electrical boundary conditions of the BaTiO3/CaTiO3 superlattice. Under this new mechanism, a large number of perovskites with the CaTiO3 type structure will become good candidates for novel highly-polar multiferroic materials.

8:40am **TF-MoM3 Controlled Growth of Transition-Metal Nitride Alloy Films via Hybrid HIPIMS/Magnetron Co-Sputtering using Synchronized Metal-Ion Irradiation***, **Grzegorz Greczynski**, J. Lu, O. Tengstrand,* Linköping University, Sweden*; I. Petrov, J.E. Greene,* Linköping University, Sweden, University of Illinois at Urbana-Champaign*; W. Kölker, S. Bolz, C. Schiffers, O. Lemmer,* CemeCon AG, Germany*; L. Hultman,* Linköping University, Sweden **INVITED**

Growth of thin films by physical vapor deposition (PVD) typically requires elevated substrate temperatures and/or ion irradiation to ensure high adatom mobilities necessary for film densification. However, obtaining densification via high incident gas-ion energies extracts a steep price in the form of residual ion-induced compressive stress resulting from both recoil implantation of surface atoms and trapping of rare-gas ions in the lattice. Our solution for these issues employs high-power pulsed magnetron sputtering (HIPIMS) owing to the high ionization degree of sputter-ejected metal atoms, and the time separation of metal- and gas-ion fluxes incident at the substrate. The former implies that ion fluxes originating from elemental targets operated in HIPIMS are distinctly different from those obtained during dc magnetron sputtering (DCMS). The latter feature allows us to suppress the role of gas-ion irradiation, by synchronizing the pulsed substrate bias with the metal-rich-plasma portion of the HIPIMS pulse.[1]

We carry out experiments in a hybrid configuration with one target powered by HIPIMS and the other operated in DCMS mode (HIPIMS/DCMS).[2,3] This allows us to probe the roles of intense metal-ion fluxes from HIPIMS-powered targets on film growth kinetics, microstructure, and physical properties over a wide range of transition metal nitride M_1M_2N alloy compositions. Model materials systems include TiAlN, TiSiN, TiTaN, and TiAlTaN. In a series of extensive experiments, we established that the essential factors determining film growth pathways include (i) the average metal-ion momentum transfer per deposited atom , (ii) metal-ion charge state, and (iii) mass of metal ion assisting the growth.[4]

Based on the above results, a new PVD approach is proposed which relies on the hybrid concept to grow dense, hard, and stress-free thin films with no external heating.[5] TiTaN and TiAlTaN film densification is achieved by pulsed synchronized bombardment with Ta^+/Ta^{2+} metal ions which are film constituents; this, in turn, minimizes film stress. The preliminary results are very promising. For example, with as little as 8 mol% of TaN, fully-dense TiTaN alloys with high hardness and low residual stress can be obtained at temperatures $T_s < 150$ °C (due to plasma heating). This novel approach expands the PVD process envelope to allow the use of temperature-sensitive substrates, including plastics.

[1] G. Greczynski, J. Lu, J. Jensen, I. Petrov, J.E. Greene, S. Bolz, W. Kölker, Ch. Schiffers, O. Lemmer and L. Hultman, *JVSTA* 30 (2012) 061504-1

[2] G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, and L. Hultman, *Surf. Coat. Technol.* 206 (2012) 4202.

[3] G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, and L. Hultman, *Vacuum* 86 (2012) 1036

[4] G. Greczynski, J. Lu, J. Jensen, I. Petrov, J.E. Greene, S. Bolz, W. Kölker, Ch. Schiffers, O. Lemmer and L. Hultman, *Thin Solid Films,* 556 (2014) 87

[5] G. Greczynski, J. Lu, I. Petrov, J.E. Greene, S. Bolz, W. Kölker, Ch. Schiffers, O. Lemmer and L. Hultman, *JVSTA* 32 (2014) 041515

9:20am **TF-MoM5 Evaluation of Perturbation Induced by Ionic Clusters Bombardmen: XPS and Electrochemical Coupled Approach***, **Arnaud Etcheberry**,* Paris Saclay University, France

Evaluation of perturbation induced by ionic clusters bombardmen: XPS and Electrochemical coupled approach.

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The XPS profiling is a key technique to provide quantitative compositional profiles of ultra thin and thin films. XPS profiling needs ion guns etching which can induce perturbations of the XPS probed films. It is particularly

true when fragile films are submitted to the etching procedure as for example organic films, oxide etc. Rational evaluation of the exact nature of the perturbation is an very important question which needs accurate approach to compare different etching procedure and to propose calibrated etching strategy. In this paper we treat the evaluation of perturbation induced by ionic argon cluster gun which is a very interesting method to provide very different conditions to perform XPS profiling as soon as possible close to the actual compositional profile. To perform that we use as supporting material InP a well known semiconductor for which problem of preferential etching is well documented. We chose to combine on same samples (n,p & undoped) XPS, UPS and electrochemical characterizations to evaluate the impact of a ionic or ionic cluster bombardment on the responses of the surface. We show that modifying the size of the cluster, the energy, the angle we induced very important modulation of the perturbations. The interesting feature of our proposal is that XPS modification: position of Peak Energy, valence band, fwhm, atomic ratio are related to the electric ones: capacitive response, I-V toward electrochemical processes, anodic dissolution. This coupling approach gives rise to a set of experimental data which are used as calibration information to provide adapted perturbation by an ion cluster bombardment. Moreover electrochemical diode has the advantage to be easily broken so it is compatible with XPS, Electrochemistry sequences which allows very fast experimental cycles. For example perturbation induced by ionic bombardment can be eliminated by dissolution of the semiconductor induced by chemical etching or by anodic oxidation. Both provide quantitative evaluation of the depth of the perturbed zone before a complete recovering of the initial XPS or electrochemical responses. We propose in this paper to detail several facets of this interfacial chemistry study

9:40am **TF-MoM6 TOF-SIMS Parallel Imaging MS/MS - Making Data Interpretation Easier***, **John Newman**, S.R. Bryan, G.L. Fisher, P.E. Larson, J.S. Hammond,* Physical Electronics, USA*; R.M.A. Heeren,* Maastricht University*; S. Iida, H. Chang, T. Miyayama,* Ulvac-PHI

Over the last quarter century Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) has been successfully used to characterize the molecular composition of the outermost layers of solid surfaces. However, even with mass resolutions greater than 15,000 *m/Δm* and mass accuracies better than 10 ppm, making definitive chemical assignments of higher mass peaks above ~200 *m/z* has continued to be a challenge. This problem has become even more pronounced with the advent of cluster beams (e.g. Au_3, Bi_3, C_{60} and Ar gas cluster) which provide substantially improved yields for higher mass fragment ions. To overcome this shortcoming, Physical Electronics has developed a revolutionary TOF-SIMS tandem mass spec method specifically designed to unambiguously identify the composition of higher mass secondary ions [1]. The method allows for MS/MS spectra (MS^2) of select secondary ions of interest (precursor ions) to be acquired in parallel with conventional TOF-SIMS spectra (MS^1); both being simultaneously generated from the same analytical volume. The precursor ion, defined by a 1 Da selection window, is deflected from the MS^1 secondary ion stream into an argon filled high energy (1.5 keV) collision-induced-dissociation (CID) cell. In the CID cell, the precursor ions collide with argon atoms which results in partial fragmentation of the precursor ions. The precursor and its fragment ions are then accelerated into a linear TOF analyzer and recorded by a pulse-counting detector. In both the MS^1 and MS^2 data, a full mass spectrum is collected for each image pixel, with spatial resolutions in the tenths of a micrometer. As the MS^2 spectra are predominantly generated from single molecular ions, they are much cleaner and simpler than conventional MS^1 spectra which usually contain secondary ions from multiple chemical species. The MS/MS fragmentation spectrum (MS^2) is used to identify the composition of the precursor ion by either identification of the fragmented ions and/or comparison to spectra contained in on-line databases. Applications of this new method will be shown for a variety of materials including polymers, pharmaceuticals, tissue cross sections, and other organics.

References

[1] P.E. Larson, J.S. Hammond, R.M.A. Heeren and G.L. Fisher, Method and Apparatus to Provide Parallel Acquisition of MS/MS Data, U.S. Patent 20150090874, April 2015

10:20am **TF-MoM8 Atomic Layer Deposition of Thin VO_2 Films to Enable Smart, Functional Coatings***, **Virginia Wheeler**, B.P. Downey, M. Currie, M. Tadjer, A. Kozen,* US Naval Research Laboratory, USA*; R. Bell, M. Thompson,* Cornell University, USA*; D.J. Meyer, F.J. Kub, C. Eddy Jr.,* US Naval Research Laboratory, USA

VO_2 is a phase change material that exhibits significant changes in thermal emittance, optical transmittance and reflectance, and intrinsic electrical properties due to a metal-insulator phase transition (MIT) at a critical temperature (T_c). Electrical and optical properties across the MIT are strongly reliant on microstructural characteristics which are dependent on deposition technique. While several different methods have been explored to deposit VO_2 films, atomic layer deposition (ALD) provides a way to obtain large area film uniformity, abrupt interfaces and angstrom-scale control of thickness conformally across planar and high surface area nanostructures. Thus, this method could be used to integrate VO_2 films into complex electronic and optical devices for additional functionality. Moreover, as-deposited films are amorphous which can be subsequently annealed to tailor the crystallinity and thus the MIT properties. Here, we will show the properties of amorphous and crystalline ALD VO_2 films and discuss their integration with other materials to achieve functional optical and electrical coatings.

Amorphous ALD VO_2 films were deposited at 150°C using TEMAV and ozone precursors. XPS revealed that beneath ~1nm of atmospheric contamination, there was no residual carbon impurities and only a single VO_2 peak was evident. Electrical measurements showed an exponential change in resistance of ten orders of magnitude from 77-500K, though no characteristic sharp transition was detected. This resulted in an average activation energy of -0.20eV and temperature coefficient of resistance of 2.39% at 310K.

To realize sharp MIT transitions, ALD VO_2 films were crystallized with an optimized ex-situ anneal at 650°C in $1.5x10^{-5}$ Torr of oxygen for 1-4hrs depending on film thickness. Electrical measurements showed that the R_{off}/R_{on} ratio increased from 3.4 to 7083 as VO_2 thickness increased from 12 to 92nm. The T_c also increased with increasing thickness, while all films exhibited relatively low hysteresis (<8°C). Temperature dependent near-IR measurements also show an increase in the change in reflectivity (up to 80%) and decrease in transmission (up to 60%) with film thickness.

ALD is a preferred method to deposit on soft materials due to its low deposition temperature. However, for VO_2 films, this benefit is negated by the higher anneal temperatures required for crystallization. To overcome this problem, laser annealing was investigated as an alternative crystallization approach. Initial results show that by varying the laser power one can tailor the local temperature within the VO_2 film to attain the required crystallinity without affecting the underlying substrate.

11:00am **TF-MoM10 PACSURF 2016 PLENARY LECTURE: Detecting the Invisible with Electron Beams: The Hidden Secrets of Nanocrystals, Interfaces and Surfaces at Atomic Resolution***, **Christian Kisielowski**,* Lawrence Berkeley National Laboratory **INVITED**

As heterogeneous materials scale below 10 nm, a suitable combination of single digit nanocrystals with their rich variety of tunable surfaces and interfaces allows tailoring unprecedented materials with novel structure-function relationships. The design of new catalysts [1] or investigations of polymers at atomic resolution [2] may serve as examples. This contribution describes research that aims at exploiting the emerging ability to analyze and understand such materials by directly determining their atom arrangement in three-dimensions using aberration-corrected transmission electron microscopy [3]. Attempts to unravel the atomic structure of such nanoscale composites in this manner must explicitly address their pronounced sensitivity to the probing radiation that can unintentionally alter their pristine structure, often beyond recognition. We address this challenge by applying low dose-rate in-line holography [4], which allows operating electron microscopes with dose rates as low as 5-10 e/Å2s that help maintaining structural integrity at atomic resolution to an unexplored end. The approach mimics best practices in biological research but achieves atomic resolution with single atom sensitivity by the acquisition of large image series. In essence, the method captures series of entirely noise dominated single images that are reconstructed to obtain electron exit wave functions of the radiation sensitive matter with unprecedented contrast and resolution. We observe a variety of previously unknown atom configurations in surface proximity of CoOx nanocrystals and coatings that are hidden behind unusually broadened diffraction patterns but become visible in real space images because the phase problem is solved. The observed structures are drastically altered by an exposure of the material

to water vapor or other gases, which is investigated at atomic resolution in environmental electron microscopy. It is shown for Rh/W catalysts that electron beam-induced atom dynamics can be entirely suppressed even for atom clusters made from less than 10 atoms. Resultantly, chemical compositions can be determined by contrast measurements alone and functional processes can be triggered and tracked in real time at atomic resolution.

[1] J. A. Haber et al., Multiphase Nanostructure of a Quinary Metal Oxide Electrocatalyst Reveals a New Direction for OER Electrocatalyst Design, Advanced Energy Materials 5 (2015) 1402307

[2] D. Lolla et al., Polyvinylidene fluoride molecules in nanofibers, imaged at atomic scale by aberration corrected electron microscopy, Nanoscale 8 (2016) 120 - 128

[3] F.R. Chen et al., In-line three-dimensional holography of nanocrystalline objects at atomic resolution,Nature Commun. 7:10603 doi: 10.1038/ncomms10603 (2016)

[4] C. Kisielowski, Observing atoms at work by controlling beam-sample interactions, Advanced Materials27 (2015) 5838-5844

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