

Thin Film

Room: 307 - Session TF+AS-FrM

Thin Film Characterization

Moderator: Mark Davidson, University of Florida

8:20am **TF+AS-FrM1 Stability of Platinum Silicide Thin Films above 1000°C**, *Robert Fryer, R.W. Meulenberg, G.P. Bernhardt, R.J. Lad*, University of Maine

Stable, electrically conductive thin films are needed as components for sensors and actuators operating in harsh environments at temperatures above 1000°C, such as those found in turbine engines, power plants, and high temperature materials manufacturing. The Pt-Si thin film system has been extensively studied in the microelectronics industry but the focus has been on film characteristics below 800°C. In this work, Pt-Si films were grown at varying compositions and deposition temperatures on sapphire and fused silica substrates by electron-beam evaporation of Pt and Si sources in ultra-high vacuum ($<10^{-9}$ Torr); the chemical and thermal stability of the Pt-Si films, both in air and in vacuum, at temperatures between 1000–1200°C were studied. X-ray diffraction (XRD) of as-deposited films indicates the formation of a polycrystalline tetragonal-Pt₂Si phase for Pt-rich film compositions, an orthorhombic-PtSi phase near the Pt₅₀Si₅₀ composition, and an amorphous film for Si-rich film compositions. The electrical conductivities of these films, measured by a 4-point probe, are in the range of 1×10^6 to 5×10^4 S/m, with the conductivity decreasing at higher Si content. Annealing in vacuum at 1000°C causes grain growth and a marked increase in film conductivities. During annealing in air at 1000°C, film oxidation occurs leading to the formation of Pt-oxide phases coinciding with the Pt-Si phases, but only a ~3-fold decrease in film conductivities. After four hours at 1200°C in air, the Pt-Si films become insulating due to morphological roughening and formation of highly faceted Pt (111) and (200) nanocrystallites coexisting in a SiO₂ matrix. Scanning electron microscopy (SEM) revealed that the use of a 50 nm capping layer of amorphous Al₂O₃, grown by atomic layer deposition (ALD) on top of the Pt-Si films, helps retard oxidation thereby preserving film conductivities in the 10^6 – 10^4 S/m range and leading to greater film stability as a function of annealing time at 1000°C in air.

8:40am **TF+AS-FrM2 Bulge Testing for Mechanical Characterization of sp²/sp³ Carbon Thin Films**, *Joseph Rowley, R.C. Davis, R.R. Vanfleet, N. Boyer*, Brigham Young University, *S. Liddiard, M. Harker*, Moxtek, Inc, *L. Pei*, Brigham Young University

Bulge testing is a technique employed to measure material properties of thin films. Pressurized gas is applied to one side of a film and its subsequent deformation measured. In many cases, thin films are fragile and therefore difficult to handle. Bulge testing has the advantage of requiring much less handling than other methods, resulting in fewer samples lost to error or accident. Carbon membranes have a wide range of characteristics, depending on their bonding and nano-structure. They can have very desirable properties such as: being chemically inert, high wear resistance and low friction, and high hardness and/or strength. In this work, reactively sputtered sp² carbon, diamondlike carbon from a pulsed laser deposition process, and a carbon nanotube reinforced polymer were characterized. PEELS and Raman Spectroscopy were used to determine sp³/sp² ratios and density, CHN testing was used to determine hydrogen content, measuring the resonant frequency was a measure to check stiffness, and bulge testing was used to obtain the Young's Modulus and tensile strength.

9:00am **TF+AS-FrM3 Time Dependent Dielectric Breakdown Measurements of Porous Organosilicate Glass using Mercury and Solid Metal Probes**, *Dongfei Pei*, University of Wisconsin-Madison, *M.T. Nichols*, Applied Materials, *S.W. King, J.M. Clarke*, Intel Corporation, *Y. Nishi*, Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Time-dependent dielectric breakdown (TDDB) is a major concern for low-k organosilicate (SiCOH) dielectrics. To examine the effect of plasma exposure on TDDB degradation, both the time-to-failure (TTF) and charge-to-failure (CTF) measurements [1] were made on porous SiCOH before and after exposure to Ar plasma. Significant discrepancies between mercury and solid-metal probes are observed. With XPS measurement data, a significant amount of mercury was found to have drifted into the porous SiCOH film. This implies that the electrical measurement of porous low-k material under mercury probe may be inaccurate due to this mercury drift effect.

This work was supported by the Semiconductor Research Corporation under Contract 2012-KJ-2359 and by the National Science Foundation under Grant CBET-1066231.

[1] M. T. Nichols, H. Sinha, C. A. Wiltbank, G. A. Antonelli, Y. Nishi, and J. L. Shohet, *Appl. Phys. Lett* **100**, 112905 (2012)

9:20am **TF+AS-FrM4 The Equivalent Width as a Figure of Merit for XPS Narrow Scans**, *Matthew Linford, B. Singh*, Brigham Young University, *J. Terry*, Illinois Institute of Technology

X-ray Photoelectron Spectroscopy (XPS) is a widely used surface analytical tool that provides information about the near surface regions of materials. In particular, chemical state information is often obtained from peak fitting XPS narrow scans. And while indispensable for XPS data analysis, peak fitting can be a fairly subjective exercise. Herein we introduce the use of the equivalent width (EW) as an additional and less subjective figure of merit for XPS narrow scans. The EW_{XPS} is simply defined as the area of a narrow scan divided by the height of the maximum of its peak envelope. To limit any ambiguity in EW_{XPS} for a series of spectra, we may also list the peak position of the maximum of the envelope (PE_{max}). We provide and discuss four examples that demonstrate the use of these parameters including (i) four C 1s narrow scans of ozone-treated carbon nanotubes (EW_{XPS} ~ 2.11 – 2.16 eV for a Shirley background, and up to 2.88 eV for no background, PE_{max} ~ 284.4 – 284.5 eV), (ii) a series of silicon wafers with different oxide thicknesses (EW_{XPS} ~ 1.5 – 2.8 eV, PE_{max} ~ 99 – 103 eV), (iii) hydrogen-terminated silicon before and after derivatization with pentyl groups, and after annealing of the pentyl-modified material (EW_{XPS} ~ 0.7 – 1.0 eV, PE_{max} ~ 25.9 – 26.1 eV), and (iv) five C 1s narrow scans of nanodiamond samples, where three of the spectra showed charging (EW_{XPS} ~ 2.6 – 4.9 eV, PE_{max} ~ 272.7 – 293.9 eV). In this final example, EW_{XPS} was plotted against PE_{max} to identify the region corresponding to the materials that showed the least charging. EW_{XPS} and PE_{max} appear to correlate with the expected chemistries of all the systems studied. We calculate EW_{XPS} using a Shirley baseline and with no baseline at all. In setting the baseline limits for EW_{XPS}, we consider the derivative of C 1s narrow scans. We also show the application of EW_{XPS} to single, fitted components within a narrow scan. Other width functions are also discussed.

9:40am **TF+AS-FrM5 Characterization of Epitaxial Oxides for Electronics, Magnetics, and Photoactivity**, *Tiffany Kaspar*, Pacific Northwest National Laboratory
INVITED

Transition metal oxides offer an incredibly rich variety of properties which can be harnessed for countless applications. Unfortunately, this variety can be a curse as well as a blessing: the myriad oxidation states, crystal structures, and defects which may occur in the bulk and/or on the surface of any given oxide system makes it challenging to draw meaningful structure-property relationships without employing a full suite of materials characterization techniques. To keep the system as simple and well-defined as possible, and to explore materials and compositions not easily attainable by equilibrium techniques, epitaxial deposition of oxide thin films is widely utilized. However, even in these “simple” systems, thorough characterization of the crystallinity and structural defects, oxidation state, stoichiometry and dopants is critical. Unwelcome surprises are often found in nominally “good” material when one takes the time to investigate. Our laboratory has explored the electronic, magnetic, and photoactive properties of binary and complex oxides as epitaxial thin films, and several examples illustrating the importance of thorough thin film characterization will be presented. In our work on Cr-doped anatase TiO₂, a candidate dilute magnetic semiconductor (DMS), room temperature ferromagnetism was observed that appeared to depend sensitively on “preparation conditions.” We applied several characterization techniques, particularly x-ray diffraction (XRD) and transmission electron microscopy (TEM), and were able to correlate the presence of structural defects with room temperature ferromagnetic ordering. One of the most widely investigated materials as a potential DMS has been Co-doped ZnO, but the presence of intrinsic ferromagnetism in this system has been widely debated in the literature. We investigated very high quality epitaxial thin films with several x-ray absorption-based characterization techniques (XANES, EXAFS, XLD) to disprove the presence of intrinsic ferromagnetism in nominally defect-free material. In more recent work, we have explored the visible-light photoactivity of hematite Fe₂O₃ doped with Cr or V. XRD, x-ray photoelectron spectroscopy (XPS), scanning TEM (STEM), and XANES/EXAFS have been applied, as well as less widely utilized techniques such as non-Rutherford resonant elastic scattering (RES) to quantitatively measure oxygen stoichiometry non-destructively, and lab-based x-ray photoelectron diffraction (XPD) to elucidate unique surface oxidation features observed by XPS. The structural properties of doped hematite could then be correlated with the bandgap and spectroscopic photoconductivity measurements.

10:40am **TF+AS-FrM8 Low Energy Ion Scattering Data Analysis for Ultra Thin Films using TRBS**, *Thomas Grehl, P. Brüner*, ION-TOF GmbH, Germany, *B. Detlefs, E. Nolot, H. Grampeix*, CEA-LETI, France, *E. Steinbauer, P. Bauer*, Johannes Kepler University, Austria, *H.H. Brongersma*, ION-TOF GmbH, Germany

Low Energy Ion Scattering (LEIS) is well known for its extreme surface sensitivity, allowing elemental characterization and quantification of the outermost atomic layer. This makes it a valuable tool for thin film analysis, e.g. to gain insights to the early stages of film growth or determine film closure. Also contamination analysis can be performed, again making use of the high surface sensitivity to assess the surface composition as the basis for subsequent deposition steps.

In addition, distinct information about sub-surface layers is obtained in a non-destructive way, giving information about the depth distribution of elements up to 10 nm. Although the mechanism for this in-depth signal is well understood, a model for the quantification of the data needs to be established.

One way of modeling the data is demonstrated using TRBS [1], a specialized version of TRIM [2] which was optimized for simulating ion scattering. Combining the TRBS data for backscattering of primary ions and an empirical model for the energy dependent reionization probability gives promising results. By fitting the simulation to the measured data conclusions about film composition, thickness and interface quality can be drawn.

This approach will be demonstrated using different thin film examples. One of the sample sets consisting of $\text{HfO}_2/\text{Al}_2\text{O}_3$ stacks also characterized by AR-XPS, XRR and GIXRF will be discussed in detail. We will show the possibility to determine film thickness variations in the Å range. These measurements can be performed in a few minutes without destroying the sample by sputtering. At the same time, the composition of the outer atomic layer is detected, making the approach well suited for routine analysis of films during or after deposition.

[1] A particularly fast TRIM version for ion backscattering and high energy implantation, Biersack, J.P.; Steinbauer, E.; Bauer, P.; Nucl. Instr. and Meth. in Phys. Res., B61, 1991, 77-82

[2] The Stopping and Range of Ions in Solids; Pergamon, New York, 1985

11:00am **TF+AS-FrM9 Polarization-dependent X-ray Absorption Fine Structure Analysis of TES Pentacene Thin Films**, *Beatrix Pollakowski*, Physikalisch-Technische Bundesanstalt (PTB), Germany, *J. Wade, J.S. Kim*, Imperial College London, UK, *F.A. Castro*, National Physical Laboratory (NPL), UK, *J. Lubeck, R. Unterumberger*, Physikalisch-Technische Bundesanstalt (PTB), Germany, *A. Zoladek-Lemanczyk*, National Physical Laboratory, UK, *B. Beckhoff*, Physikalisch-Technische Bundesanstalt (PTB), Germany

Research in organic electronics shall open up alleys for many of its promising applications, including promising applications, including: light emitting diodes, photovoltaics, transistors, biosensors and photonic devices. Despite the diversity of device functionalities, all these applications are based on thin films of organic materials and in each case their performance is critically dependent upon the precise arrangement and packing structure of the organic molecules in thin films. Our research focuses on this fundamental issue, seeking to better understand the relationships between device performance and thin film morphology of organic semiconductors on the molecular scale [1,2].

A set of 6,13-Bis((triethylsilyl)ethynyl)pentacene (TES-PEN) samples has been prepared on a silicon substrate by using a well controlled printing technique.[2] Different substrate shift speeds were used to modify the layer thickness and the crystallinity.

All X-ray based measurements were carried out at the plane grating monochromator PGM beamline for undulator radiation in the laboratory of the Physikalisch-Technische Bundesanstalt PTB at BESSY II, providing tunable radiation of both high photon flux and high spectral purity in the soft x-ray range [3]. Different kinds of X-ray spectrometry (XRS) analyses were employed to determine the chemical binding state, elemental distribution depending on the depth, and lateral mass deposition.

To analyze the chemical binding state of the molecules, the method Near-Edge X-ray

Absorption Fine Structure spectroscopy (NEXAFS) in fluorescence mode has been employed. Varying the angle of incidence in the fluorescence mode the information depth can be tuned to a pre-selectable depth of interest. In addition, the mean penetration depth at large angles of incidence is high enough to analyze even thicker layers of up to a few hundreds of nanometers as is often the case for complex organic materials. For an analysis of the molecular orientation, the angle between the electric field vector and predominant direction of the molecules has to be varied.

Initial measurement sequences exhibit the potential of this X-ray spectrometry method to significantly contribute to the quantitative analysis of organic materials in thin films. In particular, polarization dependent NEXAFS offers a clear discrimination capability for the orientation of the molecules.

[1] S. Wood, J.S. Kim, D.T. James, W.C. Tsoi, C.E. Murphy, and J. S. Kim, J. Chem. Phys. 139, 2013, 064901

[2] D.T. James, J. M. Frost, J. Wade, J. Nelson, J. S. Kim, ACS Nano 7(9), 2013, 7983.

[3] J. Lubeck, B. Beckhoff, R. Fliegau, I. Holfelder, P. Hönicke, M. Müller, B. Pollakowski, F. Reinhardt, J.

11:20am **TF+AS-FrM10 Surface Induced Phases in Organic Thin Films: Methods of Crystal Structure Solutions**, *Roland Resel, C. Röthel, A. Pichler*, Graz University of Technology, Austria, *I. Salzmann*, Humboldt University, Germany, *R.G. DellaValle, O. Rosconi*, University Bologna, Italy, *T. Dingeman*, Delft University of Technology, Netherlands, *C. Simbrunner*, University Linz, Austria

A large number of organic molecules exhibit polymorphism and a well-known phenomenon are specific crystallographic phases which are present exclusively in thin films. Such crystallographic phases are often denoted as surface induced phases, since the presence of a surface during the crystallisation is of primary importance for their formation. In general, such thin-film polymorphs do not exist as macroscopic free standing single crystals, so that existing methods of crystal structure solution e.g. from single crystal diffraction or powder diffraction does not work. A number of surface induced crystal structures of conjugated molecules are solved during the last years, examples are in relevant molecules for organic electronic applications like pentacene or sexithiophene.

Two different methods of structure solution from a thin films will be introduced. Both methods are based on grazing incidence x-ray diffraction. In a first step the crystallographic unit cells and the lattice constants are determined by indexing the diffraction pattern. The evaluation of the molecular packing is based on either rigid body refinement or molecular dynamics simulations. While rigid body refinement is based on test structures and a comparison of the calculated diffraction intensities with the experimental intensities, molecular dynamics work on energy minimisation of the molecular packing. It is found that the approach works best for fully rigid molecules like pentacene or parylene. Good results are also obtained for semi-rigid molecules like ternaphthalene or molecules with flexible side-chains like dioctyl-terthiophene. In both cases the crystallographic unit cell is filled by two molecules. However an increasing number of molecules per unit cell (e.g. four) makes the solution of the surface induced phases difficult. Similarities and differences in the molecular packing between known crystal structures (from single crystal solutions) and surface induced phases will be discussed.

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