Thin Films
Room 329 - Session TF-ThA
In-Situ / Ex-Situ & Real-Time Monitoring

Moderator: R.A. Lukaszew, University of Toledo

2:00pm **TF-ThA1 Thin-film Cavity Ringdown Spectroscopy (tf-CRDS) for Ultra-sensitive and Direct Detection of Defect-related Absorptions in a-Si:H Thin Films***, **I.M.P. Aarts**[1], B. Hoex, A.H.M. Smets, R. Engeln,* Eindhoven University of Technology, The Netherlands*; M. Nesládek,* Limburgs Universitair Centrum, Belgium*; W.M.M. Kessels, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

We have explored the applicability of cavity ringdown spectroscopy with respect to the measurement of small, defect-related absorptions in thin films. First of all, the validity of the method has been confirmed by rigorous studies on the issues that arise when placing an optical transparent substrate inside the high-finesse optical cavity: it has been found that the stability of the cavity, the build-up time of the electromagnetic field inside the cavity as well as the changes in output signal are not significantly affected by the substrate. Furthermore, the losses caused by surface scattering induced by the sample's surface roughness have been estimated employing surface morphology data obtained from atomic force microscopy. It is shown that surface scattering will eventually limit the absorption sensitivity of the technique, which is as good as 10@super -7@ per pass. Subsequently, as a proof-of-principle, measurements have been performed on several samples of hydrogenated amorphous silicon (a-Si:H) thin films in a broad spectral range (0.7 - 1.7 eV) using an optical parametric oscillator laser. The absorption values of the a-Si:H films of various thickness (5 - 1000 nm) have been corrected for interference effects that have been modeled in a straightforward but complete manner. The optical absorption spectra obtained revealed good agreement with conventional transmission-reflection and photothermal deflection spectroscopy (PDS) measurements and the spatial distribution as well as the bulk and surface defect densities in the a-Si:H thin film have been determined. From the results, it can be concluded that tf-CRDS is an ultra-sensitive absorption technique that does not require any calibration. The technique is therefore very promising for a broad range of thin film research fields and currently experiments are carried out to detect ultra-low doping levels of rare earth metals in silicon and to apply the technique real time during film growth of a-Si:H.

2:20pm **TF-ThA2 Quasi-Real Time in-situ FT-IR Spectroscopy of Doped and Undoped SiO@sub 2@ Deposition from TEOS / Ozone Chemistry***, J.E. Crowell,* ***L.D. Flores,*** University of California, San Diego

Application of quasi- real time in-situ infrared spectroscopy to the chemical boundary layer (CBL) region formed during atmospheric pressure chemical vapor deposition is investigated for silicate glass deposition from TEOS / Ozone, and upon addition of phosphorus and boron dopants. The CBL-FT-IR methodology provides direct chemical measurement of the deposition intermediates formed upon dopant addition allowing for measurement of both film forming precursors and film formation processes. Similarly, CBL difference spectroscopy (CBL-DS) provides a sensitive measurement of the time needed for attainment of steady state reactor conditions after introduction or switching of reagents. Partial least squares Beer's law quantitative methods applied to the isolated form of ethoxysilanol (3737 cm@sup -1@) show that its concentration is reduced by a factor of 2 during growth of PSG under steady state conditions. We have developed a PLS methodology to quantitate reactive chemical mixtures of TEOS and ozone and found the chemical kinetics to be independent of added phosphite (i.e. [k@sub TEOS@/k@sub OZONE@]@sub PSG@ ~ [k@sub TEOS@/k@sub OZONE@]@sub USG@). Considering the ca. 2.8-fold enhancement in deposition rate observed upon phosphorus addition along with the measured reduction in gas phase isolated silanol groups illustrates that gas phase ethoxysilanol species are the main film deposition intermediates in equilibrium with SiO@sub 2@ film growth. This result shows that real time CBL-DS is a powerful methodology to determine the chemical mechanisms of film growth as well as the associated chemical kinetics of gas phase processes responsible for their growth. Spectroscopic differences and comparisons for PSG, BSG, and BPSG film growth and the associated intermediates will additionally be made.

2:40pm **TF-ThA3 Numerical Analysis of the Three-phase Problem in Optical Diagnostics***, **K.F. Flock**, D.E. Aspnes,* North Carolina State University

One of the major unsolved problems in optical diagnostics is the practical simultaneous determination of n, k, and t, i.e., the real and imaginary parts of the complex refractive index and the thickness, respectively, of a depositing film, ideally at the monolayer or near-monolayer level. This capability is particularly important for purely sample-driven feedback control of deposition processes such as OMCVD. For very thin layers analysis can be done in principle within the three-phase (substrate/overlayer/ambient) model, since the underlying substrate, no matter how complicated, can be represented approximately as a pseudodielectric function and the material deposited between measurements can be considered uniform in composition. Current optical diagnostic tools, such as our PDA-based polarimeter, return three pieces of information, i.e., the p- or s-polarized reflectance and the phase and amplitude of their ratio, and hence are well suited for this approach. Wavelength-by-wavelength analysis of electrochemical modulated-reflectance data, a related application, has been done previously in the three-phase model with marginal results. Here, we use a simple analytic approach to investigate correlations among n, k, and t to gain better insight into the nature of these solutions. We find that the correlation among the three parameters would be exact if the power reflectance were an analytic function. This explains the high sensitivity to experimental uncertainty, which in wavelength-by-wavelength applications would require accuracies of the order of 1 part in 10@super 6@ for consistent results. We present a method that circumvents this difficulty by taking advantage of spectral dependences. Applications discussed include the determination of n, k, and t for sub-nm-scale layers of Ga and AlAs on GaAs.

3:00pm **TF-ThA4 Mapping Epitaxial Interfaces with Ultrabright X-rays***, **R. Clarke**,* University of Michigan, Ann Arbor **INVITED**

A new direct structure determination technique, Coherent Bragg Rod Analysis (COBRA), has been developed@footnote 1@ that reveals the atomic structure of epitaxial thin films and interfaces with sub-Angstrom resolution. The measurements take advantage of the high brilliance of x-ray synchrotron radiation from undulator beam lines at the Advanced Photon Source, Argonne National Laboratory. In this presentation we will describe the capability of COBRA to reveal subtle details of the interface structure that cannot be accessed by existing structural methods. The method will be illustrated by several examples drawn from our recent work on epitaxial oxide films, including perovskite ferroelectric heterostructures. This work is carried out in collaboration with Y. Yacoby (Hebrew University, Jerusalem), R. Pindak (NSLS), and E. Stern (University of Washington) and is funded by the U.S. Department of Energy, Basic Energy Sciences, and by FOCUS, a National Science Foundation Frontiers of Physics Center. @FootnoteText@ @footnote 1@ 1. Direct determination of epitaxial interface structure: Gd2O3 passivation of GaAs, Y. Yacoby, E.Stern, J. Cross, D. Brewe, R. Pindak, D. Walko, E. Dufresne and R. Clarke, Nature Materials 1, 99-101 (2002).

3:40pm **TF-ThA6 Real Time X-ray Monitoring of Ta Film Thickness, Phase, and Texture Evolution during Sputter Deposition***, **D. Windover**,* Rensselaer Polytechnic Institute*; S.L. Lee,* ARDEC, Benet Laboratories*; T.-M. Lu,* Rensselaer Polytechnic Institute

This work focuses on X-ray reflectivity and diffraction techniques for real time monitoring of thin film deposition inside a sputtering system. An X-ray transparent, beryllium, cylindrical chamber was constructed to allow for diffraction and reflection from the multiple geometries necessary for X-ray characterization methods. A magnetron sputter head with varying target-sample distances was used as the deposition source. In this study, tantalum was deposited on silicon substrates. Fast X-ray diffraction and texture information was collected using a position sensitive area detector. Fast X-ray reflectometry was collected using an energy dispersive silicon detector. Examples of thickness, phase, and texture monitoring are presented. We conclude with a discussion on the advantages and potential limitations of the characterization approaches and their applicability to real time monitoring in deposition systems.

4:00pm **TF-ThA7 Epitaxial Growth of Nanostructured Metal/Metal Oxide Thin Films by Ultrahigh Vacuum In-situ TEM***, **M. Yeadon**,* IMRE, Singapore*; J. Yu,* National University of Singapore, Singapore*; W. Tian, H.P. Sun, X.Q. Pan,* University of Michigan*; C.B. Boothroyd,* IMRE, Singapore*; R.A. Lukaszew,* University of Toledo*; R. Clarke,* University of Michigan, Ann Arbor **INVITED**

The structure and properties of metal: metal oxide systems are of substantial importance in applications ranging from magnetic storage and

[1] **TFD Student Award Winner**

spintronic devices to supported catalysts. In some metal/oxide systems it is possible to achieve epitaxial growth and the properties of the films may strongly depend on the interfacial structure as well as their growth mode. Using a modified ultrahigh vacuum transmission electron microscope (the MERLION system), we have investigated the nucleation and growth of Ni thin films on electron transparent metal oxide substrates. The system is equipped with solid source electron beam evaporators together with gas injection capability, all within the polepiece of the electron microscope which has a base pressure of 1.5x10@super -10@Torr. The talk will focus on the early stages of nucleation and growth. Real-time video recordings of the observed microstructural evolution will be presented. Some results from related in-situ experiments involving the growth of other thin films and nanostructured materials will also be presented.

4:40pm **TF-ThA9 Growth of Epitaxial Two-dimensional Layers of Indium on Si(100) by Femtosecond Pulsed Laser Deposition***, **M.A. Hafez**, M.S. Hegazy, H.E. Elsayed-Ali,* Old Dominion University

The growth of high quality epitaxial metal films on Si is of interest to device technology. Pulsed laser deposition (PLD) produces energetic species, which result in the increase of the sticking coefficients and adatom surface mobility enhancing epitaxial growth. Compared to longer laser pulses, femtosecond (fs) laser pulses significantly alter the processes associated with ablation. Epitaxial growth of thin films by fsPLD has been previously reported. Heteroepitaxial growth of indium on Si(100)-(2x1) substrates is performed under ultrahigh vacuum (base pressure low 10@super -9@ Torr) with a Ti:sapphire laser (130 fs) at wavelength of 800 nm. Reflection high-energy electron diffraction (RHEED) is used during the deposition to study the growth dynamics and the surface structure of the grown films. Morphology of the indium films is examined by ex-situ atomic force microscopy (AFM). At a substrate temperature of ~145 °C, indium was initially found to grow two-dimensionally, and then three-dimensional islands were formed. Epitaxial indium thin films are found to grow at a deposition temperature of ~400 °C, which have a 3x4 structure as observed from the RHEED pattern. The RHEED analyses and intensity oscillations show that indium films grow with two-dimensional layers and the AFM reveals two-dimensional nucleation islands. Growth modes and nucleation of indium films at different deposition conditions are discussed.

5:00pm **TF-ThA10 Real-time Observation of Initial Stages of Copper Film Growth on Silicon Oxide using Reflection High-energy Electron Diffraction***, **J.T. Drotar**,* Rensselaer Polytechnic Institute

We have studied, in real time, the evolution of a thin (less than 200 Å) copper film deposited onto an oxidized silicon surface using reflection high-energy electron diffraction (RHEED). We show that quantitative measurements of island size and shape as functions of time are possible and the results are presented. While the film texture is initially random, texture competition leads to an absence of the low energy (111) and (200) oriented grains for later times. It is also found that the film surface is composed of facets that increase in size with time. This behavior is explained in terms of facet coalescence.

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