Thin Film
Room 2022 - Session TF+EM-FrM

In-Situ/Ex-Situ & Real-Time Monitoring and Characterization

Moderator: C. Stoessel, Southwall Technologies

8:00am **TF+EM-FrM1 Parameter Uncertainties and Higher-Order Effects in the Analytic First-Order Solution for the Complex Refractive Index and Thickness of a Thin Film on a Substrate**, ***I.K. Kim***, *D.E. Aspnes,* North Carolina State University

We recently reported a solution in the thin-film limit of the general problem of determining the complex refractive index ñ = n+i@kappa@ and thickness d of an isotropic film on an isotropic substrate from the changes induced in polarimetric data by deposition or removal. Here, we consider uncertainties in n, @kappa@, and d in terms of uncertainties in the measured Fourier coefficients of the intensity. Taking advantage of the fact that the uncertainty @delta@(@DELTA@R/R) in the reflectance is much higher than the uncertainty @delta@(@DELTA@@rho@/@rho@) in the relative complex reflectance ratio, we obtain an analytic expression that gives the uncertainties of n, @kappa@, and d in both relative and absolute terms. The expression can be used to establish conditions where one or the other is determined with maximum accuracy. In contrast to expectations from ellipsometry, the relative uncertainties @delta@n/n and @delta@d/d can be significantly different. By adding noise to simulated data, we investigate the range of linearity and higher-order nonlinearities. Symmetric fluctuations of the Fourier coefficients about their average values can yield highly asymmetric fluctuations about the parameter values corresponding to the coefficient averages, particularly d. We describe a procedure for correcting the results for these asymmetries. Finally, we confirm all results with polarimetric data obtained by cyclically physisorbing and desorbing a monolayer of H@sub 2@O on oxidized GaAs.

8:20am **TF+EM-FrM2 Optical and Morphological Studies on SiO@sub 2@-like Films Deposited by Means of Ion Bombardment- Assisted Expanding Thermal Plasma CVD**, ***A. Milella***, *M. Creatore, M.A. Blauw, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

The role of ion bombardment in the growth of plasma-deposited thin films has been often investigated in literature as a route towards film matrix densification at low temperature, this latter being a requirement when thermally sensitive substrates, such as polymers, are studied. In the present paper we report our latest results on the densification of SiO@sub 2@-like films by applying an external rf bias to the substrate holder during film deposition by means of an Ar-fed expanding thermal plasma, in which hexamethyldisiloxane and oxygen are injected downstream. A comprehensive study of the optical properties of the deposited films, as determined by Spectroscopic Ellipsometry, with increasing dc bias voltage will be presented. In particular, it will be shown that ion bombardment can effectively improve film density when parameters such as the energy of the ions impinging the surface of the growing film and the ion-to-depositing radical flux ratio, are carefully controlled. Densification of film network by ion bombardment can be furthermore assessed by Fourier Transform IR spectroscopy, following changes in SiOSi asymmetric stretching absorption band with dc bias voltage. Film porosity increases with increasing deposition rate which results in a different absorption band shape. Surface morphology evolution of SiO@sub 2@-like films deposited under increasing dc bias voltage conditions as determined by Atomic Force Microscopy will be presented. In absence of ion bombardment, films display growth of spherical nodules distributed uniformly across the surface, with heights and lateral dimensions depending on the process parameters selected. Quantitative analysis shows that both RMS roughness and mean peak-to-valley distance decrease almost exponentially with increasing dc bias voltage. These results correlate with refractive index trends as determined from spectroscopic ellipsometry.

8:40am **TF+EM-FrM3 Real-Time X-ray Studies of Surface and Thin-Film Processes**, ***K. Ludwig***, *Y. Wang, A. Özcan, G. Ozaydin, C. Sanborn, A. Bhattacharyya, R. Chandrasekaran, T.D. Moustakas,* Boston University; *R. Headrick, H. Zhou,* University of Vermont **INVITED**

A new facility for the time-resolved x-ray study of surface and thin film processes is now in use at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory. To promote flexibility, the base spectrometer is designed so that modest-sized processing/vacuum chambers can be rolled onto it. This design allows multiple specialized chambers to be constructed, optimized for experimentation, and then moved onto the diffractometer for real-time x-ray studies. Here results from studies of wide-bandgap group III-nitride growth on sapphire by plasma assisted molecular beam epitaxy (PA-MBE) will be discussed. These experiments have examined migration-enhanced epitaxy, the early stage kinetics of sapphire surface nitridation, and Ga droplet formation with subsequent nitridation to form GaN nanodots. Studies examining the spontaneous nanopatterning and smoothening of surfaces by ion bombardment will also be presented. This research is partially supported by DOE DE-FG02-03ER46037 and by NSF DMR-0507351.

9:20am **TF+EM-FrM5 Novel Annealing Treatments Applied to Binary Alloy Thin Films**, ***J.R. Skuza***, *R.A. Lukaszew,* The University of Toledo; *E.M. Dufresne,* Argonne National Lab; *C. Cionca, R. Clarke,* University of Michigan, Ann Arbor; *A. Cebollada,* Instituto de Microelectronica de Madrid, Spain

Rapid thermal annealing (RTA) is widely used for electronic materials processing, from the activation of dopants to the healing of lattice defects caused by ion implantation. Here, we describe an innovative application of x-ray undulator radiation to simultaneously anneal and probe the structural evolution that occurs during annealing in real-time. X-ray Rapid Thermal Annealing (XRTA) is similar to laser annealing, but there is a unique advantage in that the x-ray energy can be tuned to the absorption edge of a particular element, thereby permitting efficient annealing of buried layers and nanostructures. In our studies at the MHATT/XOR (Sector 7) beam line at the Advanced Photon Source, we have used XRTA to enhance the degree of chemical order in epitaxial and equiatomic FePt thin films. We have chosen this particular binary alloy system because it exhibits an interesting fcc-fct phase transformation. This phase transformation allows for the real-time tracking of the degree of chemical ordering achieved due to the appearance of a forbidden reflection in fcc structures [(001) peak] and the doubling of the fundamental reflection [(002) peak]. These results will be compared to the ones obtained with traditional resistive annealing. We will demonstrate that undulator radiation offers unique possibilities for materials processing AND real-time structural probing. @FootnoteText@ This work was partially supported by the National Science Foundation (DMR Grant #0355171), the American Chemical Society (PRF Grant #41319-AC), and the Research Corporation Cottrell Scholar Award. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38.

9:40am **TF+EM-FrM6 In-Situ Studies of Stress Evolution during the Heteroepitaxial Growth of Group III-Nitrides**, ***J.M. Redwing***, *S. Raghavan, X. Weng, J.D. Acord, E.C. Dickey,* Penn State University **INVITED**

The group III-nitrides (GaN, AlN, InN and related alloys) are an important class of III-V semiconductors that form the basis for commercial high brightness blue/green light emitting diodes, laser diodes and high power microwave electronics for military and communication applications. Due to difficulties associated with the bulk crystal growth of GaN, group-III nitride thin films are grown heteroepitaxially on substrates such as sapphire, silicon carbide and silicon. These substrates have significantly different lattice constants and coefficients of thermal expansion than GaN, which can result in thin film stress, dislocation formation and film cracking. In addition to the epitaxial and thermal mismatch stresses, which are well known, growth-related stresses due to developing film morphology also play an important role, but are not as well understood for the GaN materials system. In this study, we have utilized in-situ wafer curvature measurements to study the magnitude and evolution of growth stress during the metalorganic chemical vapor deposition of group III-nitride thin films. Specific examples will be presented including the case of GaN growth on silicon and AlGaN growth on silicon carbide. By combining the in-situ measurements with post-growth atomic force microscopy and cross-sectional transmission electron microscopy, we correlate the growth stress to microstructural changes in the film arising from island coalescence and dislocation bending and demonstrate that dislocation density reduction in AlGaN films primarily occurs when the film is growing under a compressive stress. Methods to mitigate stress and reduce film cracking including the use of compositionally graded buffer layers will also be discussed.

10:20am **TF+EM-FrM8 In Situ ATR - FTIR Spectroscopy of Hf (IV) Tert Butoxide and Tetrakis Ethyl Methyl Amino Hf Adsorption on Si (100), Si (111) and Ge**, ***K. Li***, *S. Dubey, T.M. Klein,* The University of Alabama

Hafnium oxide ultra thin films on Si are being developed to replace thermally grown SiO2 gates in CMOS devices. In this work, a specially designed attenuated total reflectance - fourier transform infra-red

spectroscopy (ATR-FTIR) reaction cell has been developed to observe chemisorption of hafnium (IV) t-butoxide (HtB) and tetrakis ethyl methyl amino hafnium (TEMAH), onto a Si (100), Si (111) and Ge ATR crystals heated up to 250Â°C and under 1 torr of vacuum allowing the observation of initial reaction pathways in real time. Chemisorption spectra were compared to spectra of the liquid precursor and to spectra generated by density functional theory (DFT) calculations of liquid, monodentate and bidentate adsorbed precursors. Asymmetric stretching modes located at 1017 cm-1 and 1250cm-1 present in the chemisorbed spectra but not in the liquid spectra of HtB indicate that the adsorbed hafnium containing group is prevalent as a bidentate ligand on Si (111). Surface concentration of the chemisorbed species was dependant on the substrate temperature and precursor partial pressure allowing for determination of heats of adsorption of the t-butyl groups, which is 26.5 kJ/mol for HtB on Si (111).

10:40am **TF+EM-FrM9 In Situ Defect Spectroscopy: Probing Dangling Bonds during a-Si:H Film Growth by Subgap Absorption**, *I.M.P. Aarts, A.C.R. Pipino,* ***M.C.M. Van De Sanden,*** Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

Detecting ultralow defect concentrations in a-Si:H thin films is of great importance for improving the efficiency of a-Si:H-based solar cells. Likewise, from a more fundamental point of view, it is essential to obtain understanding of the role of surface defect states during the growth process. Yet, a paucity of experimental techniques capable of detecting these surface and or bulk defect states is readily available. Using the technique of evanescent-wave cavity ringdown spectroscopy, we have realized a unique and absolute absorption technique capable of detecting defect states such as dangling bonds with an unprecedented sensitivity that can be applied in situ and during film growth as we will demonstrate for hotwire chemical vapor deposited a-Si:H. We deposited a thin a-Si:H film (from 0 up to 800 nm thickness), onto a total-internal reflection surface of a ultralow-loss monolithic folded optical resonator. Subgap absorption spectra between wavelengths of 1170 and 1245 nm are obtained and show the typical broad absorption feature due to dangling bonds defect states present in the bulk and at the interfaces. The minimal detectable absorption of the technique is 3 10@super -8@ optical loss, which is equivalent to 3 10@super 8@ dangling bonds/cm@super 2@. Furthermore, from the real time experiments the defect distribution in the film could be established and showed that the highest defect concentration was present at the interface of the a-Si:H with the substrate while the surface defect density was approximately ten times smaller. Moreover, changes in surface dangling bond concentration (formation- and decay-curves) could be monitored in real-time under various growth conditions.

11:00am **TF+EM-FrM10 In Situ Monitoring of Hafnium Oxide Atomic Layer Deposition**, ***J.E. Maslar***, *W.S. Hurst, D.R. Burgess, W.A. Kimes, N.V. Nguyen,* NIST

In situ monitoring of atomic layer deposition processes has the potential to yield insights that will enable efficiencies in film growth, in the development of deposition recipes, and in the design and qualification of reactors. However, demonstrations of in situ monitoring of actual atomic layer deposition processes are limited. In this work, the species present in the gas phase during atomic layer deposition of hafnium oxide were investigated in an attempt to gain insight into the chemistry of this system and evaluate potential in situ gas phase optical monitors. Hafnium oxide was deposited on a silicon substrate using tetrakis(ethylmethylamino) hafnium and water as the hafnium and oxygen sources, respectively. In situ Raman and infrared absorption spectroscopy measurements were performed in a research-grade, horizontal-flow reactor under a range of deposition conditions. Density functional theory quantum calculations of vibrational frequencies of expected species were used to facilitate identification of observed spectral features. Gas phase measurements performed at the wafer surface were compared to measurements performed at the chamber exhaust to investigate the utility of exhaust-based optical measurements for deposition monitoring. Results of in situ gas-phase measurements were compared with results of ex situ hafnium oxide film characterization, vacuum ultraviolet spectroscopic ellipsometry and infrared absorption spectroscopy, in an effort to correlate observed gas phase species with deposited film properties.

11:20am **TF+EM-FrM11 In-situ and Real-Time Spectroscopic Ellipsometry on Organic Semiconductors during Growth**, *U. Heinemeyer,* Universit@um a@t T@um u@bingen, Germany*; S.M. Kowarik,* Oxford University, UK, Germany*; A. Gerlach,* ***F. Schreiber,*** Universit@um a@t T@um u@bingen, Germany*; G. Humphreys, R. Jacobs,* Oxford University, UK

We demonstrate the use of in-situ and real-time spectroscopic ellipsometry as a non-invasive technique for following the growth of organic semiconductor thin films of diindenoperylene and pentacene. It is possible to take spectra in the spectral range between 1.25eV and 5 eV sufficiently fast (~ 1 sec) to follow organic molecular beam deposition in detail. We show how this technique can be used to detect spectral changes occurring during growth of these complex materials. From the vibrational progression of the HOMO-LUMO transition we analyze the time/thickness evolution of the exciton-phonon (Huang-Rhys) parameter S. We discuss our results and their implications for organic device fabrication in the context of a recent real-time structural study which found structural and orientational transitions during growth.@footnote 1@ @FootnoteText@ @footnote 1@S. Kowarik et al., Phys. Rev. Lett. 96, 125504 (2006).

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