Applied Surface Science
Room: C2 - Session AS+EM+MS+TF-MoM

Spectroscopic Ellipsometry I
Moderator: M.S. Wagner, Proctor and Gamble

8:20am **AS+EM+MS+TF-MoM1 Optical Properties of Bulk GaSe and InSe Single Crystals**, ***S.G. Choi,*** National Renewable Energy Laboratory, *C. Martinez-Tomas, V. Munoz Sanjose,* Universitat de Valencia, Spain, *D.H. Levi*, National Renewable Energy Laboratory

III-VI compounds generally crystallize in layered-structures characterized by strong covalent interactions *within* the layers but weak Van der Waals binding *between* the layers. This unique structural characteristic has made III-VI compounds attractive for their potential applications in nonlinear optics. Among these compounds, in particular, InSe has been considered as a promising candidate for thin film photovoltaic (PV) material owing to its energy bandgap, optical and transport properties. Recently, high-quality epitaxial InSe thin films have been grown on GaSe substrates, and PV device structures containing *n*-InSe and *p*-GaSe have been successfully fabricated [1].

In order to design and optimize a high-performance PV device structure, knowledge of optical properties of constituent materials over a wide spectral range is required. However, large discrepancies were found in the properties of GaSe and InSe available in the literature, which have been measured mostly by reflectance methods with the Kramers-Kronig transformation employed to obtain the dielectric functions. Here, we present ellipsometrically determined pseudodielectric function $\langle\varepsilon\rangle=\langle\varepsilon_1\rangle+i\langle\varepsilon_2\rangle$ spectra from 0.73 to 6.45 eV of bulk GaSe (ε-phase) and InSe (γ-phase) single-crystals grown by a vertical Bridgman method. The surfaces with minimum overlayers were obtained by peeling off the top few layers from the sample surface and ellipsometric measurements were immediately followed under flowing N_2 environment, which yields good approximations to the intrinsic dielectric responses. The measured spectra exhibited a number of interband-transition critical-point structures, and their energy values were obtained precisely from numerically calculated second-energy-derivatives of $\langle\varepsilon\rangle$ assuming the parabolic-band critical-point model.

Data obtained in this work can be used to model PV device structures utilizing GaSe and InSe, and the critical-point energies determined will be useful for theoreticians to perform fine band structure calculations of III-VI compounds.

The work done at Universitat de València was supported in part by the Spanish Project MAT2007-06841. This abstract is subject to U.S. government rights.

[1] J.F. Sánchez-Royo, J. Appl. Phys. 90, 2818 (2001).

8:40am **AS+EM+MS+TF-MoM2 Ellipsometric Porosimetry for the Microstructure Characterization of Plasma-Deposited SiO_2-Like Films**, ***M. Creatore***, *N.M. Terlinden, G. Aresta, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

SiO_2 layers have been deposited from Ar/O_2/hexamethyldisiloxane mixtures in a remote expanding thermal plasma setup enabling a good control of both the ion flux (by changing the deposition chemistry and the arc plasma parameters) as well as the ion energy. This latter is achieved by an additional rf substrate biasing or a tailored ion biasing technique, i.e. a low frequency pulse-shaped bias. The role of the ion energy and ion-to-growth flux ratio on the film microstructure and densification at low substrate temperature (100ºC) has been investigated by means of ellipsometric porosimetry. This technique monitors the refractive index change due to the adsorption (and desorption) of ethanol vapors in the volume of macro-meso-micro pores in the SiO_2 layer. From the analysis of the adsorption isotherm and the presence of hysteresis during the desorption step as a function of the equilibrium partial pressure, the open porosity in the layer can be determined. It is found that both biasing techniques lead to densification of the deposited layer, which experiences a transition from micro-/ mesoporosity to microporosity and eventually non-porosity, as function of the increasing ion energy. Although both biasing techniques lead to a comparable critical ion energy value per deposited SiO_2 unit (about 100 eV), the ion-to-growth flux ratio and ion energy are not found to be interchangeable parameters. In fact, in the case of the rf bias, the meso- and large micropores are first affected leading to a quantitative decrease of porosity, i.e. from 11% to 3% at an ion energy less than 20 eV. A further increase in ion energy eventually reduces the presence of smaller micropores leading to non porous films at energy of 45 eV. When the pulse-shaped biasing technique is adopted, the micro- and mesopores are simultaneously affected over the whole range of available ion energy, leading to a non porous layer only at very high energy values, i.e. 240 eV. This difference is attributed to the increasing ion-to-growth flux ratio accompanying the rf biasing, as a consequence of the rf plasma generation in front of the substrate.

9:00am **AS+EM+MS+TF-MoM3 Industrial Applications of Spectroscopic Ellipsometry**, ***J.A. Woollam,*** J.A. Woollam Company, Inc., *J.N. Hilfiker, P. He*, J.A. Woollam Company Inc. **INVITED**

Spectroscopic Ellipsometry (SE) has been used for decades for basic research on surfaces and thin films. Hundreds of articles, review papers, and books describe SE use in physics, chemistry and surface and materials engineering. Far less is available describing industrial applications because companies gain competitive advantage using SE and are not motivated to publish.

Without revealing anyone's proprietary information, this talk reviews examples of SE use in industry. This involves both production quality control (QC), and product development. Best known is SE for QC in integrated circuit manufacturing. Others include integrated circuit critical dimension (CD) metrology, read-write heads, display technologies, optoelectronics, photovoltaics (crystalline and thin film), optical coatings, web-coaters, wear surfaces, and protective coatings. Industrial SE applications include ex-situ, in-situ, and in-line metrology.

9:40am **AS+EM+MS+TF-MoM5 Spectroscopic Ellipsometry Studies of Sputtered Vanadium Oxide Thin Films**, ***N.J. Podraza,*** *B.D. Gauntt, M.A. Motyka, E.C. Dickey, M.W. Horn*, The Pennsylvania State University

Vanadium oxide (VO_x) thin films have been used for the last twenty years as the imaging material in uncooled infrared imaging devices. The important material properties for this application are a high thermal coefficient of resistance (TCR), controllable resistivity (ρ), low electrical noise and process compatibility with standard IC fabrication. However, vanadium can adopt many different oxidation states, yielding a number of stable metal oxides, which can lead to difficulties in reliable and consistent device fabrication. In this work, VO_x thin films were fabricated via pulsed-DC magnetron sputtering in an argon and oxygen atmosphere under variable total pressure and oxygen-to-argon ratio deposition conditions in order to investigate the variability in desired material properties. In situ real time spectroscopic ellipsometry (RTSE) has been applied to stuffy films prepared under variable deposition conditions in order to evaluate the microstructural evolution of VO_x during film growth and changes occurring to the surface and bulk material upon initial exposure to atmosphere. These films were characterized ex situ using a number of complementary techniques including, Rutherford backscattering spectroscopy (RBS) in order to obtain the oxygen content, x; transmission electron microscopy (TEM) to determine film crystallinity; glancing incidence X-ray diffraction (GIXRD) was used to ensure localized measurements from the TEM were representative of the entire film; and I-V curve measurements as a function of temperature were used to determine the film resistivity and TCR. By varying deposition conditions, the film resistivity was varied over seven orders of magnitude from ~10^{-3} to 10^4 Ω-cm and the TCR spanned from -0.1 to -3.5 %/K. The growth evolution, complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$), and structure are correlated to these electrical properties. Films produced at low oxygen-to-argon ratios exhibit nanocrystalline V, V_2O, and VO phase material dependent on the specific deposition conditions, while films produced at higher oxygen-to argon ratios are amorphous. In both the nanocrystalline and amorphous phases, features in e obtained from spectroscopic ellipsometry have been shown to correlate with the oxygen content and resistivity and RTSE studies have been used to monitor changes occurring at the film / ambient interface after the vanadium oxide is exposed to air. This array of techniques were used to establish the roles deposition parameters play in the final structure and composition of each film, as well as to determine the resulting effects of these characteristics on the electronic transport and optical properties.

10:00am **AS+EM+MS+TF-MoM6 Real Time Spectroscopic Ellipsometry Studies of Si:H and Ge:H Thin Films for Microbolometer Applications**, ***D. Saint John***, *E.C. Dickey, N.J. Podraza*, The Pennsylvania State University

Thin film hydrogenated silicon (Si:H) and germanium (Ge:H) have been of wide interest as thin film semiconducting materials, and are now of growing interest for use in infrared sensing uncooled microbolometers, although the impact of the growth evolution and structure on device performance is only beginning to be determined. Ideal properties for incorporation of these layers in microbolometers include: a high temperature coefficient of resistance (TCR); controllable resistivity (ρ); low 1/f noise within frequencies of interest; and process compatibility with standard IC fabrication. In this work, n- and p-type doped Si:H and undoped Ge:H thin films have been prepared by plasma enhanced chemical vapor deposition (PECVD) with resulting resistivities ranging from 1.5 to 2500 Ω cm and TCR ranging from –0.8 to –4.0 %/K and studied using real time spectroscopic ellipsometry (RTSE). These films, monitored in situ during growth by RTSE, have been shown to exhibit changes in microstructure as a function of deposition conditions. For example, films prepared at low hydrogen dilution may remain amorphous throughout growth (a-Si:H), while films prepared at higher dilution may initially grow as amorphous until a bulk layer thickness where microcrystallites nucleate and eventually coalesce into a single-phase microcrystalline layer (μc-Si:H). A combination of in-situ RTSE, transmission electron microscopy (TEM), and electrical measurements (ρ, TCR, 1/f noise) have been used to study the effects of deposition conditions on the resulting microstructure during film growth and the dependence of the electrical properties on this microstructure. Studies of p-type a-Si:H have shown that both TCR and ρ increase with hydrogen dilution for fixed doping gas-to-silane ratio, which suggests that optimizing the TCR for a film of a given resistivity may potentially be obtained by varying both the hydrogen and doping gas dilutions. n-type a-Si:H and mc-Si:H films were evaluated in order to quantify changes in TCR and r resulting from microstructural differences (a-Si:H: ρ= 250 Ω cm, TCR = –3.8 %/K; μc-Si:H: ρ = 1.5 Ω cm, TCR = –0.8 %/K). Growth evolution studies of undoped Ge:H films prepared under variable hydrogen dilution conditions show transitions from amorphous to microcrystalline material at higher hydrogen dilution and relatively high TCR values ranging from –2.2 to –3.6 %/K as dilution is increased within the amorphous growth regime.

10:40am **AS+EM+MS+TF-MoM8 Non-destructive Determination of Spatial Distributions of Free-Charge-Carriers in Low Doped Semiconductors using THz Ellipsometry**, ***T. Hofmann***, University of Nebraska-Lincoln, *C.M. Herzinger*, J. A. Woollam Co. Inc., *M. Schubert*, University of Nebraska - Lincoln

The non-contact and non-destructive optical determination of spatial distributions of free-charge-carriers in low doped semiconductor homo- and heterojunctions addresses fundamental physical properties of device related structures. However, the optical characterization of low density free-charge-carriers, particularly for hole densities with their intrinsically lower mobility parameters than electron densities is very challenging. For low carrier densities the plasma frequencies are located at within the terahertz (THz) spectral region and measurements of plasma frequency properties in a at THz frequencies have been used for the determination of free-charge-carrier properties in single crystals (e.g. [1,2]). The characterization of free-charge-carrier properties in low-doped homo- and heterostructures remains a challenge.

Here we report on the non-invasive optical measurement of hole diffusion profile in a p-p$^+$ Silicon homojunction by spectroscopic ellipsometry in the terahertz (0.2 to 1.5 THz) and mid-infrared (9 to 50 THz) spectral regions. In the terahertz region a surface guided wave resonance with transverse-electrical polarization is observed at the boundary of the p-p$^+$ homojunction, and which is found to be extremely sensitive to the low-doped *p*-type carrier concentration as well as to the hole diffusion profile within the p-p$^+$ homojunction. Effective mass approximations allow determination of homojunction hole concentrations as p=2.9x10^{15} cm^{-3}, p^+=5.6x10^{18} cm^{-3}, and diffusion time constant D_t = 7.7x10^{-3} μm^2, in agreement with previous electrical investigations.

[1] D. Grischkowsky, Soren Keiding, Martin van Exter, and Ch. Fattinger, J. Opt. Soc. Am. B **7**, 2006 (1990).

[2] M. Herrmann, M. Tani, K. Sakai, and R. Fukasawa, J. Appl. Phys. **91**, 1247 (2002).

11:00am **AS+EM+MS+TF-MoM9 Ellipsometric Depth Profiling of Polymer-Blend Films for Organic Electronics and Photovoltaics**, ***L.J. Richter***, *D.S. Germack, D.M. DeLongchamp, D.A. Fischer, V.M. Prabhu, D.J. Gundlach,* National Institute of Standards and Technology, *J.E. Anthony,* University of Kentucky, *N. Shin, D. Yoon*, Seoul National University, Korea

Interest has emerged in the development of devices based on organic materials and low energy, low cost, roll-to-roll fabrication techniques. Two specific target applications have received particular attention: organic transistors to enable macroelectronics (large area displays, RFID tags, etc.) and organic photovoltaics. Common to both applications is the development of optimal inks: for macroelectronics, small crystallizable molecules in an inert polymer binder, for photovoltaics, fullerene based acceptors blended in an active polymer donor. Critical to a proper understanding of the device performance is an understanding of the vertical profile of the fabricated film. For thin film transistors, segregation of the small molecule semiconductor to the interfaces is essential. For PV, segregation of the fullerene can be both advantageous (if at the cathode) and deleterious (if at the anode). Spectroscopic ellipsometry studies of the vertical profile are daunting, as the systems are in general anisotropic with individual component spectra that are strongly dependent on the local order. We present SE studies of both TFTs and OPV devices using a multiple sample approach to remove correlations in the resultant models. The optical depth profiles are compared to both NEXAFS studies of the interface composition and neutron reflectivity studies of similar processed films. We find good agreement between the SE and less model dependent techniques. The studies illuminate general principles of the influence of interfacial free energy on the resultant segregation of the species.

11:20am **AS+EM+MS+TF-MoM10 Thickness Variations Determined by Spectroscopic Ellipsometry in Organometallic Chemical Vapor Deposition: Connection to Growth Processes**, ***X. Liu***, *D.E. Aspnes*, North Carolina State University

Lateral thickness variations are commonly observed for films deposited by organometallic chemical vapor deposition (OMCVD). The variations are typically systematic near boundaries between growth and adjacent surfaces, for example masks. We use spectroscopic ellipsometry to study thickness variations for the heteroepitaxy of GaP by OMCVD on (001) GaAs, thermally generated SiO_2, (001) Si, and nanoscopically roughened Si surfaces using trimethylgallium (TMG) and phosphine (PH_3) sources, showing that the variations provide information about details of OMCVD growth that would be difficult to obtain in any other way. Our reference surface is the polycrystalline GaP inadvertently deposited on the Mo susceptor that surrounds the 2 in. wafers. We find that the thicknesses of the deposited GaP films increase or decrease accurately exponentially toward the edge. Using an analytic Green-function approach based on the one-dimensional diffusion equation, we show that for our growth conditions (4 Torr chamber pressure), the exponential thickness variations are due to differences in chemical reactivities of the various surfaces, especially on the different catalytic effects that they exert on PH_3 decomposition. The results show directly that different parts of the surface, including the susceptor, are in constant contact with each other through lateral gas-phase diffusion. The data are explained by assuming that growth occurs via a precursor that is formed by heterogeneous catalysis, largely desorbs, and involves both Ga and P, for example the H-P=Ga-CH_3 dimer adduct. To distinguish this process from selective area growth (SAG), which takes place with a similar configuration, we also solve the SAG problem analytically, in this case using a conformal map. For SAG the thickness near mask edges is found to vary as $r^{-1/2}$, where r is the lateral distance away from the edge. The distinctive differences in these thickness dependences indicate that SAG growth occurs via a different mechanism.

11:40am **AS+EM+MS+TF-MoM11 Optical Anisotropy Induced by Oblique Incidence Ion Bombardment of Ag(001)**, ***H. Wormeester***, *F. Everts, B. Poelsema*, University of Twente, The Netherlands

Oblique incidence ion sputtering has become a widely used method for the creation of highly regular patterns of lines and dots. On a Ag(001) surface oblique incidence sputtering creates a ripple pattern that exhibits plasmonic features. The photon energy of this plasmonic feature depends on the ripple periodicity. The development of these anisotropic features was measured in-situ with the optical technique Reflection Anisotropy Spectroscopy (RAS).

The ion induced nanopatterning was done with 2 keV Ar ions with a flux of a few mA/cm2 in a temperature range of 300 - 420K. With RAS, a periodicity of ripples above 200 nm is measured by a shift in photon energy of the plasmon resonance. Features with a smaller periodicity show a plasmon resonance around 3.65 eV. For very grazing incidence sputtering, 80o polar angle of incidence, only a resonance feature around 3.65 eV is observed. High resolution LEED measurements after sputtering confirm the formation of 1D nanoripples.

For a polar angle of incidence of the ion beam of 70o a shift in the maximum of the plasmon resonance feature is observed. These spectra can be well described within the Rayleigh-Rice description for scattering from a slightly rough surface. The formation of nanoripples, i.e. a roughening of the surface perpendicular to the direction of the ion beam in one direction suffices to describe the measured optical data. The evolution of the rms, wavelength and wavelength distribution of the ion induced nanoripples is obtained from the in-situ measurements. For a polar angle of the ion beam of 61o we find that also the roughening in the direction along the nanorippels has to be taken into account to describe the optical spectra.

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