

Monday Morning, October 29, 2012

Spectroscopic Ellipsometry Focus Topic

Room: 19 - Session EL+TF+AS+EM+SS+PS+EN+NM-MoM

Spectroscopic Ellipsometry for Photovoltaics and Semiconductor Manufacturing

Moderator: M. Creatore, Eindhoven University of Technology, the Netherlands, H. Wormeester, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

8:20am **EL+TF+AS+EM+SS+PS+EN+NM-MoM1 Multichannel Spectroscopic Ellipsometry: Applications in I-III-V₂ Thin Film Photovoltaics**, *R.W. Collins, D. Attygalle, P. Aryal, P. Pradhan, N.J. Podraza*, University of Toledo, *V. Ranjan, S. Marsillac*, Old Dominion University **INVITED**

Multichannel spectroscopic ellipsometry (SE) has been applied successfully as an in situ, real time tool for optimizing, monitoring, and controlling multi-stage deposition processes in various thin film photovoltaics (PV) technologies. A particularly challenging process optimization problem involves the thermal co-evaporation of individual elements of Cu, In, Ga, and Se in a three-stage process, which has proven to produce high quality Cu(In_{1-x}Ga_x)Se₂ (CIGS) materials and high performance PV devices. This three-stage process provides a high level of flexibility in determining the phase, composition, and microstructure of the film, but also generates greater challenges in run-to-run reproducibility of the optimized process. Information extracted from real time SE measurements includes the evolution of the bulk layer and one or more surface layer thicknesses, as well as layer dielectric functions. The layer dielectric functions can be analyzed further to extract the phase and alloy compositions and the defect density or grain size, which can assist in understanding the fabrication process, in optimizing solar cells, and ultimately in monitoring and controlling the optimized process for improved reproducibility. In this study, the focus is on analysis of ellipsometric (ψ , Δ) spectra acquired by real time SE in order to characterize (i) the structural and compositional evolution in (In,Ga)₂Se₃ film growth from In, Ga, and Se fluxes in the first stage, (ii) the transition from Cu-poor to Cu-rich CIGS at the end of the second stage, which occurs under Cu and Se fluxes, and (iii) the transition from Cu-rich to the desired Cu-poor CIGS, which defines the end of the third and final stage, and occurs under a second application of In, Ga, and Se fluxes. After the transition from Cu-poor to Cu-rich material in the second stage, a Cu_{2-x}Se phase near the surface of the bulk layer is tracked. In the Cu-rich to Cu-poor transition, this Cu_{2-x}Se phase has fully reacted with In, Ga, and Se to form CIGS. Studies using a standard Mo substrate and 2 μ m thick CIGS for solar cells have also revealed features in the (ψ , Δ) spectra characteristic of the anticipated changes in the near surface phase composition as established by detailed modeling on thinner and smoother films. Although careful analysis of real time SE is expected to provide quantitative information on the surface properties and their evolution in this case of solar cells, control of the deposition has been successful simply by monitoring real time changes in the ellipsometric (ψ , Δ) spectra.

9:00am **EL+TF+AS+EM+SS+PS+EN+NM-MoM3 Contribution of Plasma Generated Nanoparticles to the Growth of Microcrystalline Silicon Deposited from SiF₄/H₂/Argon Gas Mixtures**, *J.-C. Dornstetter, S. Kasouit, J.-F. Besnier*, Total S.a, France, *P. Roca i Cabarrocas*, LPICM-CNRS, Ecole Polytechnique, France

Despite the low fabrication cost of thin film silicon solar modules, this type of technology remains non competitive in main stream markets because of the high BOS costs, due to the low energy conversion efficiency of this type of modules (~10%). We have recently shown that microcrystalline silicon films deposited using SiF₄/H₂/Argon RF capacitive plasmas have excellent structural and transport properties, compared to films deposited using conventional SiH₄/H₂ mixtures, allowing for a very good carrier collection, even for thick cells, and Voc values of 0.55 V, without device optimization, thus opening up the path for the realization of high performance solar cells. However, little is known so far about the growth mechanism of this type of materials and the reason for such interesting properties. Studies of silicon thin films deposition from SiF₄/H₂ mixes, under conditions different from ours, suggested that the growth is due to the deposition of SiF₂ radicals, followed by the abstraction of fluorine by hydrogen. Previous work within our group has also shown that deposition occurs only when particles are present in the plasma, and that growth starts from crystallites without any amorphous phase. We present here a systematic study of the growth of

microcrystalline films, together with the composition of nanoparticles attracted by thermophoresis to cold traps located both on the walls of the plasma chamber and in the fore line as a function of deposition conditions. The composition of the deposit on the traps is found to be amorphous at low power/ low hydrogen conditions and becomes crystalline when either of them increases. This correlates well with an increase in atomic hydrogen concentration in the plasma, as estimated by actinometry. The crystalline fraction of the deposited film was measured using in-situ ellipsometry and was found to correlate with the composition of the deposit on the cold traps. Deposition rate is drastically reduced when a water cooled trap is installed on the walls of the plasma chamber, and switches off at high H₂ flow rates. Under these conditions, TEM and AFM images, show that at the initial stages of the growth the film is constituted of sparse, hexagonal crystalline particles, having sizes on the order of few tens of nanometers. We interpret the data above as a result of plasma-generated nanocrystals being a significant contribution to the deposited film. This may explain the excellent electronic properties of the films, as the particles are formed in the bulk of the plasma region, free from energetic ions bombardment. We will correlate the structural properties and the film growth mechanisms to the properties of solar cells.

9:20am **EL+TF+AS+EM+SS+PS+EN+NM-MoM4 Multichannel Spectroscopic Ellipsometry for CdTe Photovoltaics: from Materials and Interfaces to Full-Scale Modules**, *P. Koirala, J. Chen, X. Tan, N.J. Podraza*, The University of Toledo, *S. Marsillac*, Old Dominion University, *R.W. Collins*, The University of Toledo

Real time spectroscopic ellipsometry (RTSE) has been implemented in studies of the evolution of the semiconductor structural and optical properties during sputter deposition of thin film polycrystalline CdS/CdTe solar cells on transparent conducting oxide (TCO) coated glass substrates. Analysis of the real time optical spectra collected during CdS/CdTe deposition requires an optical property database as a function of measurement temperature for all substrate components. These include not only soda lime glass, but also an SiO₂ layer and three different SnO₂ layers. We report optical functions parameterized versus temperature for the glass substrate and its overlayers starting from room temperature and ending at elevated temperature above which the semiconductor layers are deposited. In fact, such a database has additional applications for on-line, through-the-glass monitoring applications of coated glass at elevated temperature. In the RTSE studies, knowledge of the temperature dependent optical functions of the substrate components enables an accurate substrate temperature determination before the onset of deposition and is critical for accurate extraction of the semiconductor layer optical properties. We implement RTSE to study the filling process of the surface roughness modulations on the top-most SnO₂ substrate layer and modification of the optical properties of this layer. This modification is further studied post-deposition by infrared spectroscopic ellipsometry. In addition to providing information on interface formation to the substrate during film growth, RTSE also provides information on the bulk layer CdS growth, its surface roughness evolution, as well as overlying CdTe interface formation and bulk layer growth. Information from RTSE at a single point during solar cell stack deposition assists in the development of a model that can be used for mapping the completed cell stack properties, which can then be correlated with device performance. Independent non-uniformities in the layers over the full area of the cell stack enable optimization of cell performance combinatorially.

9:40am **EL+TF+AS+EM+SS+PS+EN+NM-MoM5 Determination of Electronic Band Gaps from Optical Spectra**, *R.A. Synowicki*, J.A. Woollam Co., Inc.

The band gap of a material E_g is defined theoretically as the lowest energy for electronic transition from the valence to conduction bands in a solid. For an ideal material free of defects this is the photon energy or wavelength where the optical properties change from transparent to absorbing. However, real materials contain defects which cause absorption to begin below the band gap (i.e. the Urbach Tail) making determination of the true band gap position difficult. For example, in a solar cell the measured absorption edge represents the onset of transitions first due to defects, then from band to band. Empirical methods used to determine the band gap in real materials with defects include the Tauc plot and the Mott-Davis plot. More theoretical mathematical dispersion models such as the Tauc-Lorentz, Cody-Lorentz, and Herzinger-Johs models have been developed which include an adjustable band gap parameter. The various plots and dispersion model methods will be discussed and applied to different materials measured optically via spectroscopic ellipsometry, intensity transmission, reflection, absorption, or a combination of these methods.

10:00am **EL+TF+AS+EM+SS+PS+EN+NM-MoM6 Optical Modeling of Plasma-Deposited ZnO: Extended Drude and its Physical Interpretation**, *H.C.M. Knoop, M.V. Ponomarev, J.W. Weber, N. Leick, B.W.H. van de Loo, Y.G. Melese, W.M.M. Kessels, M. Creatore*, Eindhoven University of Technology, the Netherlands

High-quality transparent conductive oxides such as ZnO are important due to their electrical and optical properties. To improve these properties the responsible physical processes have to be understood. Traditionally, charge-carrier-scattering processes are investigated by combining morphology data and Hall measurements. This contribution discusses the extensive optical modeling of plasma-deposited ZnO and how its interpretation directly provides insight into the relevant charge-carrier-scattering processes at different length scales. The interpretation is generalized to the concept of frequency-dependent resistivity, which is used to explain the applicability of different Drude models.

Thin films (50-1000 nm) of Al-doped and undoped ZnO were deposited using an expanding thermal plasma MOCVD process.¹ Conditions of high pressure and high diethyl zinc flow allowed for dense films with low electrical resistivities (e.g., $4 \times 10^{-4} \Omega \text{ cm}$ at 300 nm). The films were analyzed with variable-angle spectroscopic ellipsometry (SE) (0.75 – 5.0 eV), FTIR reflection spectroscopy (0.04 – 0.86 eV), Four-point-probe (FPP), and Hall measurements.

The SE and FTIR data were combined and fitted with classical and extended Drude² models. The high intensity of the Drude in the FTIR range resulted in a high sensitivity with which the carrier concentration and mobility could even be determined for thin (~40 nm) undoped ZnO films. An extended Drude model was needed to correctly model the SE energy range, which was explained by the dominance of ionized impurity scattering and a reduction of this scattering for higher photon energies. The grain-boundary-scattering mobility could be determined by the difference between optical and Hall mobilities.³ When combined with FPP results, the effective mobility can be determined from these optical techniques without the use of Hall measurements. The optical response above the band gap was modeled by a PSEMI or Tauc-Lorentz oscillator model, where a broadening and shift of the transition was seen for increasing carrier concentration.⁴

These insights and a generalized view of electron scattering in ZnO at different length scales will be presented.

1. Ponomarev et al., *J. Appl. Phys.* **Submitted** (2012)
2. Ehrmann and Reineke-Koch, *Thin Solid Films* **519**, 1475 (2010)
3. Steinhäuser et al., *Appl. Phys. Lett.* **90**, 142107 (2007)
4. Fujiwara and Kondo, *Phys. Rev. B* **71**, 075109 (2005)

10:40am **EL+TF+AS+EM+SS+PS+EN+NM-MoM8 The Ellipsometric Response of Single-Crystal Silicon to Doping**, *H.G. Tompkins*, Consultant

The current wisdom is that for ellipsometry in the UV-vis-NIR spectral range, doping of single-crystal silicon can be ignored. We study the ellipsometric response of silicon doped with arsenic at various levels. We also studied the response after implant (before activation) and after the activation (anneal). We find that for samples implanted with 1E18 atoms/cm³, the single-crystal silicon was not amorphized. Implants of 2E19 atoms/cm³ and higher left an amorphous layer on the surface of the wafer the thickness of which was about the depth of the implant. Activation of the sample implanted with 2E19 atoms/cm³ returned the sample to single-crystal silicon and the ellipsometric response in the UV-vis-near_IR is essentially that of undoped silicon. However, the response in the mid-IR is that the extinction coefficient is no longer zero. For samples implanted with 2.5E20 atoms/cm³ and greater, annealing did not return the UV-vis-near_IR ellipsometric response to that of single-crystal silicon. Although this amount of other material (arsenic) is still less than about one tenth of one percent, our conjecture is that the microstructure simply could not be returned to that of a single crystal. As with the lower doped sample, the mid-IR spectral region showed significant increase in the extinction coefficient.

11:00am **EL+TF+AS+EM+SS+PS+EN+NM-MoM9 The Effect of Stress on the Optical Properties Semiconductor Films**, *A.C. Diebold, G.R. Muthinti, M. Medikonda, T.N. Adam*, College of Nanoscale Science and Engineering, University at Albany, *A. Reznicek, B. Doris*, IBM Research at Albany Nanotech

Here we review the impact of stress on the complex dielectric function of semiconductor films measured using spectroscopic ellipsometry. Two relevant examples of stressed semiconductor layers are pseudomorphic epitaxial layers fabricated during semiconductor manufacturing and strained silicon on insulator (sSOI) wafers. Stress is known to shift the energies of direct gap critical point transitions in semiconductors. The biaxial stress in pseudomorphic films grown on silicon wafers can be as high as that used during opto-elastic studies of bulk semiconductors. The amount of stress in

un-relaxed, pseudomorphic films of Si_{1-x}Ge_x on Si (100) reaches 1 GPa for alloys with 20% Ge and is more than 3 GPa for films with > 50% Ge. The bi-axial stress in sSOI is typically ~1 GPa. An elastic theory approach for the effect of strain on the k*p determined band structure and optical transition energy is well known. Both low shear stress and high shear stress approximations can apply to the shift in transition energy depending on the magnitude of the spin orbit splitting energy vs the magnitude of the shear stress. Until recently it was difficult to obtain sets of samples that test both approximations. Here we discuss results from our recent study of pseudomorphic films of Si_{1-x}Ge_x on Si (100) from x= 0.05 to 0.75 which covers both low and high shear regimes. We also present our recent study of the dielectric function of thinned sSOI which illustrates the impact of stress on the optical transitions for the Si layer on sSOI. All of these samples are examples of new materials being used in semiconductor research. The results of this study are directly transferred into cleanroom spectroscopic ellipsometry systems used for process control during manufacturing.

11:20am **EL+TF+AS+EM+SS+PS+EN+NM-MoM10 Numerical Ellipsometry: Spectroscopic n-k Plane Analysis of Thin Films Growing on Unknown Layered Substrates**, *F.K. Urban, D. Barton*, Florida International University

Spectroscopic ellipsometry measurements on thin films commonly make use of prior knowledge of the structure and optical properties of the underlying substrate. However, imprecision in substrate statistics propagates into the solution for the film of interest. Thus it is more accurate to have a method for solving for film properties which simultaneously obtains whatever is needed about the substrate. And it makes solutions possible whether or not book data or previous substrate solutions are available. In this work we apply Complex Analysis in the n-k plane to achieve solutions employing the well-know reflection equations. The method is carried out at each measured wavelength and does not necessitate an *a-priori* assumption of optical property dependencies on wavelength. The mean square error has been improved by many orders of magnitude, a selected limit of 10⁻¹⁴ as opposed to 1 to 30 or so for least squares. Thus the full accuracy of the ellipsometer is now available for more accurate measurements of film thickness and optical properties. The method requires six measurements during growth. The first is used to determine the relationship between Rp and Rs at the film-substrate interface. The following four are used to uniquely determine the values of Rp, Rs, and film n, k, and d. The final measurement confirms the unique solution. Suitability of the model is tested by comparing measurements at two of more wavelengths for self consistency. Results for n and k of the growing film are examined across the measurement spectrum in comparison with parameterizations in common use.

Monday Afternoon, October 29, 2012

Spectroscopic Ellipsometry Focus Topic

Room: 19 - Session EL+TF+BI+AS+EM+SS-MoA

Spectroscopic Ellipsometry: From Organic and Biological Systems to Inorganic Thin Films

Moderator: M.S. Wagner, The Procter & Gamble Company

2:00pm **EL+TF+BI+AS+EM+SS-MoA1 Biochemical Optical Sensors Based on Highly-Ordered Slanted Columnar Thin Films**, *D. Schmidt, K.B. Rodenhausen*, University of Nebraska-Lincoln, *J. VanDerslice, T.E. Tiwald, J.A. Woollam Co., Inc., E. Schubert, M. Schubert*, University of Nebraska-Lincoln

Highly-ordered three-dimensional nanostructure thin films offer substantially increased surface area for attachment of organic layers, and in addition, new detection principles due to the physical properties of the nanostructures. For example, upon material attachment the optical birefringence of the nanostructures changes due to screening of polarization charges. Because of these advantages, highly-ordered three-dimensional nanostructure thin films lend themselves as suitable candidates for studying of organic attachments as well as for low-cost humidity sensing, for example.

We utilize glancing angle electron-beam deposition for fabrication of highly spatially coherent metal slanted columnar thin films. Subsequently, the nanostructures may be further functionalized with thin conformal coatings by means of atomic layer deposition. The ellipsometry model analysis and resulting anisotropic optical properties of hybrid metal slanted columnar thin films determined by generalized spectroscopic ellipsometry in the visible and near-infrared spectral region will be discussed. We will be reviewing research in this area and report in particular on in-situ monitoring of organic attachments using ellipsometry combined with quartz crystal microbalance with dissipation. Exemplarily, we discuss studies of fibronectin protein adsorption, octanethiol chemisorption (self-assembled monolayer growth) on platinum coated titanium slanted columnar thin films as well as relative humidity sensing.

2:20pm **EL+TF+BI+AS+EM+SS-MoA2 Studies of Optical Properties of Hybrid J-aggregates and Nanocrystal Quantum Dots Layers for Photonic Applications**, *K. Roodenko, H.M. Nguyen, L. Caillard, A. Radja, O. Seitz, Yu.N. Gartstein, A.V. Malko, Y.J. Chabal*, The University of Texas at Dallas

The integration of organic materials and inorganic nanocrystal quantum dots (NQDs) on the nanoscale offers the possibility of developing new photonic devices that utilize the concept of resonant energy transfer between an organic material and NQDs. Electromagnetic coupling that takes place between excitons—bound electron-hole pairs—at the interfaces of the hybrid composite can be utilized for light-emitting, photovoltaic and sensor applications.

As the key ingredients for the nanocomposite material system reported in this work are the J-aggregates (JA, dye self-assembled molecules) that have exceptional optical absorption due to their strong oscillator strength. NQDs on the other hand combine a variety of important properties, such as high quantum yields, excellent photo- and chemical stability, and size dependent, tunable absorption and emission. Excitation energy transfer in NQDs / J-aggregate hybrids is characterized by their strong excitonic transitions at room temperature with spectrally well-defined absorption and emission.

In order to understand the energy transfer mechanisms in such complex systems, optical properties of JA and NQDs/JA hybrid systems were characterized by means of spectroscopic ellipsometry and polarized IR spectroscopy.

Spectroscopic ellipsometry in 0.6-5 eV spectral range was employed to study optical properties of J-aggregates drop-casted on silicon surfaces. Thin JA films were found to exhibit strong optical anisotropy due to the specific molecular orientation of thin layers on Si substrates. Variation of optical properties due to the deposition of nanocrystal quantum dots (NQDs) was systematically studied for applications in new photonic devices that utilize excitonic energy transfer from NQDs to JA layer. Ellipsometric results were cross-referenced with atomic force microscopy (AFM) data to derive a quantitative understanding of the distribution of NQDs upon deposition on JA layer. Integration of hybrid colloidal NQD/JA structures could be potentially attractive for a range of optoelectronic applications.

2:40pm **EL+TF+BI+AS+EM+SS-MoA3 Love and Death, the Story of Most Proteins and Most Surfaces as Told by Spectroscopic Ellipsometry**, *T. Benavidez, K. Chumbuni-Torres, J.L. Felhofer, C.D. Garcia*, The University of Texas at San Antonio **INVITED**

Biosensors are analytical platforms that integrate a biological recognition element with a signal transducer. Because they have the potential to provide rapid, real-time, and accurate results, biosensors have become powerful tools in clinical and biochemical settings. Our group is particularly interested in the development of electrochemical biosensors based on enzymes adsorbed to nanomaterials. When integrated to microfluidic devices, these sensors offer sensitivity, portability, low cost, and the possibility of analyzing turbid samples. Adsorption was selected to immobilize the biorecognition element because it is one of the simplest and most benign methods, avoiding cross-linking reactions or additional components (such as entrapping polymers). Most importantly, as adsorption is a required (and sometimes limiting) step for any immobilization mechanism, the identification of key variables influencing this process can be applied to a variety of strategies. Although several techniques have been used to study the adsorption of proteins to nanomaterials,¹ only a few of them provide information about the kinetics of the process in real time. This is a critical aspect, as most of the post-adsorption conformational changes occur within a few minutes after the interaction.² Among those, reflectometry was used by our group to perform the first kinetic study related to the interaction of proteins with carbon nanotubes.³ These kinetic studies have been recently extended to the interaction of enzymes (D-amino acid oxidase,⁴ catalase,⁵ and glucose oxidase⁶) by variable angle spectroscopic ellipsometry, which enabled a more thorough analysis of the interaction process with a much more versatile experimental design.^{7,8} The use of VASE demonstrated that a number of variables, (being the amount of enzyme only one of them) can influence the biological activity of proteins adsorbed to the substrate. Furthermore, our results indicate that the activity of enzymes adsorbed to nanomaterials can be directly related to the kinetics of the adsorption process (dG/dt).⁵

Please see supplemental document for figures and footnotes.

3:40pm **EL+TF+BI+AS+EM+SS-MoA6 Detailed Photoresist and Photoresist Processing Studies using Spectroscopic Ellipsometry**, *C. Henderson*, Georgia Institute of Technology **INVITED**

Spectroscopic ellipsometry has become an invaluable tool for the study of a wide variety of thin film systems. In particular, it has become extremely valuable in the development and study of advanced photoresists and of lithographic processes used in the production of integrated circuits and other related semiconductor devices. In our work, we have used spectroscopic ellipsometry to study a variety of problems related to photoresists including swelling phenomena, exposure induced refractive index changes, and ultra-fast dissolution phenomena. We have combined spectroscopic ellipsometry with quartz crystal microbalance techniques to simultaneously study thin film optical properties, thickness, film mass, and film modulus. Such techniques have been particularly useful in understanding the dissolution properties of polymeric photoresists developed for 193 nm lithography. This talk will review some of the applications for spectroscopic ellipsometry in this field and in particular will highlight some of the results of our work made possible using spectroscopic ellipsometry.

4:20pm **EL+TF+BI+AS+EM+SS-MoA8 Ellipsometric Characterization of a Thin Titaniumoxide Nanosheets Layer**, *H. Wormeester, G. Maidecchi, S. Kumar, A. Kumar, A. ten Elshof, H.J.W. Zandvliet*, MESA+ Institute for Nanotechnology, University of Twente, The Netherlands

The photochemical properties of titaniumoxide make this a widely studied material. Of special interest is a thin nanostructured layer of such a material. A variety of a nanostructured material is the single sheet titaniumoxide that can be obtained by delaminating a layered titanate, with stoichiometry $Ti_{1-x}O_{2+4x}$ ($x=0.0875$). The slight titanium deficiency leads to a negatively charged nanosheet that can be used as a building block in a layer by layer assembled composite film [1]. In this work we used Langmuir Blodgett to deposit successive thin layers of nanosheets. The electronic properties of these layers were investigated with ellipsometry and Scanning Tunneling Microscopy (STM). The optical spectra show the well known absorption peak at 4.6 eV for titaniumoxide nanosheets. The optical spectra can be well modeled with a Cody-Lorentz dielectric function profile providing a bandgap of ... eV, a value also found from STM IV spectroscopy. The Cody-Lorentz profile also indicates a slight below band gap light absorption by the nanosheet material.

4:40pm **EL+TF+BI+AS+EM+SS-MoA9 Preparation of Abrupt LaAlO₃ Surfaces Monitored by Spectroscopic Ellipsometry**, C.M. Nelson, M. Spies, L.S. Abdallah, S. Zollner, Y. Xu, H. Luo, New Mexico State University

LaAlO₃ is a polar perovskite oxide, used as a single-crystal substrate in oxide epitaxy. It has created much interest for novel electronic applications, because a two-dimensional electron gas is formed at LaAlO₃/SrTiO₃ heterostructures. The purpose of our work is twofold: First, we are interested in an accurate determination of the complex refractive index of LaAlO₃ at room temperature. Second, we studied the impact of various cleaning methods on the abruptness of the LaAlO₃ surface.

We obtained a commercial single-side polished LaAlO₃ substrate with 2-inch diameter and a (100) pseudo-cubic surface orientation. The surface was polished with an rms roughness below 0.8 nm. We determined the ellipsometric angles ψ and Δ for LaAlO₃ at 300 K from 0.7 to 6.5 eV. For a bulk insulator with a clean smooth surface, the phase change Δ should be zero or π below the band gap. In practice, this never happens, because surfaces are covered with overlayers (adsorbed organic or water vapors). Surface roughness has a similar effect on the ellipsometric spectra as a surface overlayer. Even for an abrupt bulk/air interface, there is a thin (~0.5 nm) transition region where the electron wave functions leak from the crystal into the ambient. For the as-received sample, the data were described with a Tauc-Lorentz model for LaAlO₃, plus 2.1 nm of surface layer thickness (described as an effective medium with 50% density of the bulk). After ultrasonic cleaning in acetone, the overlayer thickness decreased to 1.8 nm. Next, we mounted the wafer in a UHV cryostat, pumped down to below 10⁻⁸ Torr, and acquired an ellipsometric spectrum at 70°. The surface layer thickness was reduced to 1.2 nm, presumably because a part of the adsorbed surface layer (especially water) desorbed under vacuum.

So far, everything worked as expected, but here it gets interesting: We heated the sample to 700 K for about an hour to desorb the remaining surface overlayer. After cooling down to 300 K, we measured the ellipsometric angles again at 70° angle of incidence from 0.7 to 6.5 eV. The ellipsometric angle Δ at 2 eV was reduced to below 0.2°, consistent with a surface layer thickness of less than 1 Å, much less than the surface roughness specified by the supplier (8 Å).

In conclusion, a macroscopically smooth and clean LaAlO₃ surface was prepared by ultrasonic cleaning of the wafer in acetone, followed by heating in UHV to 700 K. The resulting surface layer thickness was below 1 Å, as measured by spectroscopic ellipsometry. We will report Tauc Lorentz parameters. We will also describe the temperature dependence of the LaAlO₃ dielectric function from 77 to 700 K. This work was supported by NSF (DMR-11104934).

5:00pm **EL+TF+BI+AS+EM+SS-MoA10 Determination of the Refractive Index of a Gold-Oxide Thin Film Using X-Ray Photoelectron Spectroscopy and Spectroscopic Ellipsometry**, K. Cook, G.S. Ferguson, Lehigh University

A two-step procedure will be presented for measuring the complex refractive index of an electrochemically produced oxide film on a gold surface. In the first step, the composition and the thickness of the oxide film were determined using angle-resolved X-ray photoelectron spectroscopy. The experimental composition defined the system, thereby avoiding assumptions about the film stoichiometry that would otherwise be required. The value of thickness derived from these measurements was then used to calculate n and k from ellipsometric data collected across the visible spectrum (350 - 800 nm).

Tuesday Afternoon Poster Sessions

Spectroscopic Ellipsometry Focus Topic

Room: Central Hall - Session EL+TF+AS+EM+SS-TuP

Spectroscopic Ellipsometry Poster Session

EL+TF+AS+EM+SS-TuP1 Ellipsometric Characterization of Iron Pyrite (FeS₂) and Samarium Sesquisulfide (Sm₂S₃) Thin Films. A. Sarkar, N.J. Ianno, University of Nebraska-Lincoln, J.R. Brewer, Rare Earth Solar

Iron pyrite (FeS₂) and samarium sesquisulfide (Sm₂S₃) are transition metal chalcogenides characterized as absorbing semiconductors with bandgaps of 0.95 eV and 1.8 eV respectively. Synthesis of both *n*-type and *p*-type samples have been reported in the form of single crystals and thin films for both materials. As a result of these properties they have received considerable interest as photovoltaic absorber materials. We present the characterization of FeS₂ and Sm₂S₃ thin films using spectroscopic ellipsometry. FeS₂ thin films were synthesized by sulfurizing DC magnetron sputtered iron films and reactive ion sputtered iron (III) oxide films in H₂S / Ar atmosphere. Sm₂S₃ thin films were synthesized by reactive ion sputtering of Sm in an H₂S / Ar atmosphere. This analysis gives the optical properties of chalcogenide films from near-UV (300 nm) to the mid-IR (20 μm). This can then be correlated to the structural and electronic properties as well. The analysis is corroborated with results obtained from Raman spectroscopy, scanning electron microscopy, profilometry, X-ray diffraction (XRD), and Van der Pauw measurements. The ellipsometric results can be used to access different processing methods for synthesizing FeS₂ and Sm₂S₃, to determine the presence of different phases and intermediate products. This work will lay the foundation for employing *in situ* ellipsometry as a process monitor and quality control tool during manufacture of earth abundant chalcogenide thin films.

EL+TF+AS+EM+SS-TuP2 Temperature Dependence of the Dielectric Function of Germanium by Spectroscopic Ellipsometry. A.A. Medina, L.S. Abdallah, S. Zollner, New Mexico State University

Germanium has important applications in photovoltaics as a substrate for III/V triple-junction solar cells, especially in space vehicles and for terrestrial concentrator-based applications. Unfortunately, the optical properties of germanium (complex refractive index and absorption coefficient) and their temperature dependence (important to consider the effects of the space environment or the radiation-induced heating in concentrators) are not as well known as for silicon, which limits the accuracy of modeling for solar cells and Ge-based optical interconnects. In this work, we report precision measurements of the complex refractive index of germanium from 0.5 to 6.6 eV at room temperature using variable-angle spectroscopic ellipsometry. To improve accuracy, especially at photon energies below 2 eV, we used a Berek waveplate compensator. By cleaning a commercial Ge wafer in isopropanol followed by deionized water, we were able to reduce the native oxide thickness to 1.3 nm. Heating the wafer in UHV at 700 K did not reduce the oxide thickness further. (The oxide thickness can be determined with precision measurements of Δ below the band gap on a single-side polished wafer.) From the ellipsometric angles of the Ge wafer measured at three angles of incidence (65, 70, and 75°), we calculated the dielectric function from 0.5 to 6.6 eV, by correcting for the effects of a native oxide.

Mounting our wafer in a compact UHV cryostat allowed temperature-dependent measurements from 80 to 700 K at 70° angle of incidence. Using similar methods as described above, we determined the dielectric function at different temperatures. We also determined the critical-point parameters (amplitude, energy, phase angle, and broadening) of the E_0 , E_1 , $E_1+\Delta_1$, E_0' , and E_2 critical points as a function of temperature. To separate the non-resonant contributions from the critical-point line shapes, we calculated the second derivative of the dielectric function with respect to photon energy and fitted the result to analytical line shapes with two-dimensional critical points. In general, our results are in good agreement with those of Viña *et al.* However, our results cover a wider spectral range and are more accurate because of the use of a compensator. Work is in progress to form thermal oxides on Ge wafers by annealing in oxygen, which will allow a multi-wafer analysis for Ge similar to work on Si by Herzinger *et al.*

This work was supported by NSF (HRD-0803171 and DMR-11104934) and the New Mexico Louis Stokes Alliance for Minority Participation.

Reference: L. Viña, S. Logothetidis, M. Cardona Phys. Rev. B **30**, 1979 (1984).

Authors Index

Bold page numbers indicate the presenter

— A —

Abdallah, L.S.: EL+TF+AS+EM+SS-TuP2, **5**;
EL+TF+BI+AS+EM+SS-MoA9, **4**
Adam, T.N.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM9, **2**
Aryal, P.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM1, **1**
Attygalle, D.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM1, **1**

— B —

Barton, D.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM10, **2**
Benavidez, T.: EL+TF+BI+AS+EM+SS-MoA3, **3**
Besnier, J.-F.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM3, **1**
Brewer, J.R.: EL+TF+AS+EM+SS-TuP1, **5**

— C —

Caillard, L.: EL+TF+BI+AS+EM+SS-MoA2, **3**
Chabal, Y.J.: EL+TF+BI+AS+EM+SS-MoA2, **3**
Chen, J.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM4, **1**
Chumbuni-Torres, K.: EL+TF+BI+AS+EM+SS-
MoA3, **3**
Collins, R.W.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM1, **1**; EL+TF+AS+EM+SS+PS+EN+NM-
MoM4, **1**
Cook, K.: EL+TF+BI+AS+EM+SS-MoA10, **4**
Creatore, M.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM6, **2**

— D —

Diebold, A.C.:
EL+TF+AS+EM+SS+PS+EN+NM-MoM9, **2**
Doris, B.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM9, **2**
Dornstetter, J.-C.:
EL+TF+AS+EM+SS+PS+EN+NM-MoM3, **1**

— F —

Felhofer, J.L.: EL+TF+BI+AS+EM+SS-MoA3, **3**
Ferguson, G.S.: EL+TF+BI+AS+EM+SS-MoA10,
4

— G —

Garcia, C.D.: EL+TF+BI+AS+EM+SS-MoA3, **3**
Gartstein, Yu.N.: EL+TF+BI+AS+EM+SS-MoA2,
3

— H —

Henderson, C.: EL+TF+BI+AS+EM+SS-MoA6, **3**

— I —

Ianno, N.J.: EL+TF+AS+EM+SS-TuP1, **5**

— K —

Kasouit, S.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM3, **1**
Kessels, W.M.M.:
EL+TF+AS+EM+SS+PS+EN+NM-MoM6, **2**
Knoops, H.C.M.:
EL+TF+AS+EM+SS+PS+EN+NM-MoM6, **2**
Koirala, P.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM4, **1**
Kumar, A.: EL+TF+BI+AS+EM+SS-MoA8, **3**
Kumar, S.: EL+TF+BI+AS+EM+SS-MoA8, **3**

— L —

Leick, N.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM6, **2**
Luo, H.: EL+TF+BI+AS+EM+SS-MoA9, **4**

— M —

Maidecchi, G.: EL+TF+BI+AS+EM+SS-MoA8, **3**
Malko, A.V.: EL+TF+BI+AS+EM+SS-MoA2, **3**
Marsillac, S.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM1, **1**; EL+TF+AS+EM+SS+PS+EN+NM-
MoM4, **1**
Medikonda, M.:
EL+TF+AS+EM+SS+PS+EN+NM-MoM9, **2**
Medina, A.A.: EL+TF+AS+EM+SS-TuP2, **5**
Melese, Y.G.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM6, **2**
Muthinti, G.R.:
EL+TF+AS+EM+SS+PS+EN+NM-MoM9, **2**

— N —

Nelson, C.M.: EL+TF+BI+AS+EM+SS-MoA9, **4**
Nguyen, H.M.: EL+TF+BI+AS+EM+SS-MoA2, **3**

— P —

Podraza, N.J.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM1, **1**; EL+TF+AS+EM+SS+PS+EN+NM-
MoM4, **1**
Ponomarev, M.V.:
EL+TF+AS+EM+SS+PS+EN+NM-MoM6, **2**
Pradhan, P.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM1, **1**

— R —

Radja, A.: EL+TF+BI+AS+EM+SS-MoA2, **3**

Ranjan, V.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM1, **1**
Reznicek, A.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM9, **2**
Roca i Cabarrocas, P.:
EL+TF+AS+EM+SS+PS+EN+NM-MoM3, **1**
Rodenhausen, K.B.: EL+TF+BI+AS+EM+SS-
MoA1, **3**
Roodenko, K.: EL+TF+BI+AS+EM+SS-MoA2, **3**

— S —

Sarkar, A.: EL+TF+AS+EM+SS-TuP1, **5**
Schmidt, D.: EL+TF+BI+AS+EM+SS-MoA1, **3**
Schubert, E.: EL+TF+BI+AS+EM+SS-MoA1, **3**
Schubert, M.: EL+TF+BI+AS+EM+SS-MoA1, **3**
Seitz, O.: EL+TF+BI+AS+EM+SS-MoA2, **3**
Spies, M.: EL+TF+BI+AS+EM+SS-MoA9, **4**
Synowicki, R.A.:
EL+TF+AS+EM+SS+PS+EN+NM-MoM5, **1**

— T —

Tan, X.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM4, **1**
ten Elshof, A.: EL+TF+BI+AS+EM+SS-MoA8, **3**
Tiwald, T.E.: EL+TF+BI+AS+EM+SS-MoA1, **3**
Tompkins, H.G.:
EL+TF+AS+EM+SS+PS+EN+NM-MoM8, **2**

— U —

Urban, F.K.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM10, **2**

— V —

van de Loo, B.W.H.:
EL+TF+AS+EM+SS+PS+EN+NM-MoM6, **2**
VanDerslice, J.: EL+TF+BI+AS+EM+SS-MoA1,
3

— W —

Weber, J.W.: EL+TF+AS+EM+SS+PS+EN+NM-
MoM6, **2**
Wormeester, H.: EL+TF+BI+AS+EM+SS-MoA8,
3

— X —

Xu, Y.: EL+TF+BI+AS+EM+SS-MoA9, **4**

— Z —

Zandvliet, H.J.W.: EL+TF+BI+AS+EM+SS-
MoA8, **3**
Zollner, S.: EL+TF+AS+EM+SS-TuP2, **5**;
EL+TF+BI+AS+EM+SS-MoA9, **4**