

## Spectroscopic Ellipsometry Focus Topic

Room: 304 - Session EL+AS+EM+EN+SS-ThM

### Spectroscopic Ellipsometry for Photovoltaics and Instrument Development

**Moderator:** Mariadriana Creatore, Eindhoven University of Technology, Netherlands, Tino Hofmann, University of Nebraska-Lincoln

8:00am **EL+AS+EM+EN+SS-ThM1 Spectroscopic Ellipsometry Characterization in the Photovoltaic Device Configuration, Nikolas Podraza, University of Toledo** **INVITED**

Thin film large area photovoltaics (PV) are a maturing field, yet challenges remain in manufacturing and fundamental research. Even the simplest thin film PV devices consist of multiple layers of doped or undoped semiconductors, transparent conducting front contacts, and metal back contacts. Characteristics of each layer, along with the interfaces between layers, all have an impact upon device performance. Within each layer, the material may evolve with thickness or exhibit spatial non-uniformity. Furthermore, studies of each thin film material can be difficult, as fundamental property measurements on special substrates may not accurately represent the characteristics of the material in the final device configuration. Spectroscopic ellipsometry (SE) data, collected over the infrared to ultraviolet, is sensitive to layer thicknesses, interface formation, and surface roughness as well as the optical response of each component in the form of the complex dielectric function spectra ( $\epsilon = \epsilon_1 + i\epsilon_2$ ) for samples deposited on arbitrary reflective substrates. Variations in  $\epsilon$  for a given layer can be linked to order (amorphous vs. crystalline, grain size, crystal phase), composition, and characteristics of opto-electronic response (band gap, dc electrical properties). In situ real time SE (RTSE) is now often applied to study the growth evolution of component materials within device configurations for hydrogenated silicon (Si:H), cadmium telluride (CdTe), and copper indium gallium diselenide (CIGS) PV. This utilization of RTSE provides a means of monitoring layer characteristics as materials are being processed in the device structure and generates appropriate structural models for analysis of similar samples when only ex situ SE measurements are available. Appropriate structural models derived from RTSE have been applied to analyze ellipsometric spectra collected over 6 inch x 6 inch rigid substrates and assess the spatial uniformity in characteristics of each layer in the sample. These maps of optically derived material properties can be compared to electrical device performance (efficiency, open circuit voltage, short circuit current, fill factor) and used to guide PV optimization principles. The optical ( $\epsilon$ ) and structural (layer thickness) information gained from SE is input into quantum efficiency simulations for comparison with experimental PV device measurements. These comparisons are used to assess both opto-electronic performance of devices and validity of models used in SE data analysis as well as further guide device development by identifying sources of optical and electrical losses.

8:40am **EL+AS+EM+EN+SS-ThM3 Application of Pseudo-Bulk Approach in Ellipsometric Studies of Polycrystalline Photovoltaic Thin Films, Sukgeun Choi, National Renewable Energy Laboratory, J. Li, University of Toledo, I. Repins, National Renewable Energy Laboratory**

Fundamental band gap is one of the key properties of semiconducting materials, which directly influences the functionality and performance of many photonic and photovoltaic (PV) devices. Photoluminescence (PL) and optical absorption spectroscopies are widely used to determine the band-gap energy  $E_g$ . For polycrystalline thin-film PV materials, however, it is often challenging to unambiguously interpret PL data owing to the presence of multiple peaks associated with various types of defect structures. To estimate  $E_g$  from optical absorption spectrum, on the other hand, a straight segment of the absorption coefficient curve needs to be chosen. But this selecting procedure is somewhat arbitrary, which leads to an inaccurate  $E_g$  value.

Spectroscopic ellipsometry (SE) accurately determines material's optical function spectra over a wide spectral range. For semiconductor thin-film structures, a multilayer analysis is generally used to extract the optical information from SE data. Although mainly surface overlayer artifacts need to be corrected for SE data well-above the band gap in the analysis, several contributions should be considered for those near (and below) the band gap, such as the optical characteristic of substrate, presence of interfacial layers, and finite thickness of film in addition to the artifacts from surface overlayers. As a result, the obtained optical function spectrum and  $E_g$  value become somewhat model dependent with an increased uncertainty.

To reduce complications in mathematical modeling of SE data and improve the accuracy of resulting near-band-gap optical function spectrum, we introduce the *pseudo-bulk* approach, where SE measurements are performed on thin films grown on macroscopically roughened substrate surface. The essence of this approach is in suppressing the reflection of probing light from the film/substrate interface and below. Thus, no thickness fringes appear in the SE data, despite the thin-film nature of sample, and the band-gap onset can be clearly observed with a post-growth chemo-mechanical polishing of the film surface. We apply the *pseudo-bulk* approach to study near-band-gap optical properties of  $\text{Cu}_2\text{ZnSnSe}_4$  and related PV absorber materials. We present a non-monotonic temperature-dependence of  $E_g$  for  $\text{Cu}_2\text{ZnSnSe}_4$  and the clear band-gap onset of  $\text{Cu}_2\text{SnSe}_3$  at around 0.45 eV for the first time. SE results are explained by the results from the electronic structure calculations. The applicability and limit of this approach are also discussed.

9:00am **EL+AS+EM+EN+SS-ThM4 Real-Time and Through-the-Glass Mapping Spectroscopic Ellipsometry for Analysis and Optimization of CdS:O Window Layers of CdTe Superstrate Solar Cells, Xinxuan Tan, R.W. Collins, P. Koirala, J. Li, N.J. Podraza, University of Toledo**

In-situ real-time spectroscopic ellipsometry (RT-SE) has been applied for the analysis of CdS:O films sputter deposited on c-Si substrates from a CdS target using different flow ratios of  $\text{O}_2/(\text{Ar}+\text{O}_2)$  from 0 to 0.05. RT-SE studies of the CdS:O layers from the film side provide the complex dielectric function spectra of each the layers over a spectral range of 0.75 to 6.5 eV and its dependence on oxygen content in the material as deduced by energy dispersive X-ray spectroscopy (EDS). Ex-situ infrared ellipsometry of these samples enables extension of the dielectric function data to  $\sim 0.04$  eV and provides information on free carrier conduction and chemical bonding in the material. In similar RT-SE studies, data acquired during the growth of CdS:O/CdTe layers on transparent conducting oxide (TCO) coated glass superstrates have been analyzed to determine the structural evolution of the layers in the configuration used for CdTe solar cells, with the CdS:O serving as an n-type window layer for the p-type CdTe absorber. The results of this analysis assist in the development of a realistic optical model for the multilayer structure of the solar cell. Using this optical model ex-situ through-the-glass spectroscopic ellipsometry (TG-SE) has been implemented toward the analysis of glass/(TCO-stack)/CdS:O/CdTe solar cells in the superstrate configuration.

For the solar cells, CdS:O layers with different oxygen contents were deposited on 15 cm x 15 cm TCO coated glass superstrates. A 16 x 16 array of dot cells each with an area of 0.125 cm<sup>2</sup> was fabricated on the superstrate in order to optimize efficiency improvements through combinatorial methods. Because the as-deposited superstrate/film-structure undergoes additional processing steps during device fabrication, three sets of TG-SE mapping data were acquired on (i) as-deposited, (ii) CdCl<sub>2</sub>-treated (an activation step), and (iii) back-contact coated device structures. With an optical database that has been established for both as-deposited and CdCl<sub>2</sub> treated CdS:O, CdTe, and back contact materials, each of the TG-SE mapping data sets were analyzed based on an optical model deduced from RT-SE studies of the CdS:O and CdS:O/CdTe depositions. Thickness and compositional non-uniformity observed over the area by mapped by TG-SE enables correlations between solar cell performance and basic property parameters of the component layers including layer thicknesses and compositions. The resulting correlations provide a pathway to expedite solar cell optimization.

9:20am **EL+AS+EM+EN+SS-ThM5 Combined Optical Emission Spectroscopy and Spectroscopic Ellipsometry Collected During Thin Film Deposition, Anna Barnes, M.M. Junda, N.J. Podraza, University of Toledo**

Plasma processes are commonly used to deposit thin film layers for a variety of optical, electronic, and coating applications. Two common processes widely used in the fabrication of thin films are physical vapor deposition (sputtering) and plasma enhanced chemical vapor deposition (PECVD). Non-contacting optical probes, such as spectroscopic ellipsometry (SE) and optical emission spectroscopy (OES), are particularly attractive techniques to study these deposition processes in situ during film growth. Connecting studies involving SE and OES offers the ability to observe and interpret the growth of thin films from plasma over time using variant parameters, though in different ways. Real time SE (RTSE) provides a means of monitoring the deposited material itself, while OES can be used to track variations in the plasma employed for the deposition. Tracking the time dependence of both film and plasma properties is desirable as variations in material properties resulting from changes in plasma conditions may impact the final device performance. In this particular

study, we look at the growth evolution of semiconductor, transparent conducting oxide (TCO), and metal contact layers commonly used in thin film photovoltaic devices. Case studies involve undoped, n-type, and p-type hydrogenated amorphous silicon prepared by PECVD, as well as zinc oxide, indium tin oxide, and silver prepared by magnetron sputtering on either smooth test substrates (glass, crystal silicon wafers) or in the full device configuration. Variations in thin film structure (bulk layer thickness, surface roughness) and optical properties in the form of the complex dielectric function spectra ( $\epsilon = \epsilon_1 + i\epsilon_2$ ) are obtained as a function of time by RTSE. Results from RTSE ( $\epsilon$ , structure) are interpreted to determine order (grain size, amorphous vs. nanocrystalline), electronic transitions (band gap, free carrier absorption characteristics), and morphology evolution as appropriate for the given material layer. OES indicates the presence and relative strength of plasma emission peaks, which correspond to the species present in the plasma and their relative concentrations. Analysis of RTSE and OES data collected simultaneously is sought to identify links present between these plasma and film characteristics.

9:40am **EL+AS+EM+EN+SS-ThM6 Optical Insights into Graphene Functionalized by Atoms, Biomolecules and Metal Nanoparticles**, *Maria Losurdo, M. Giangregorio, G.V. Bianco, P. Capezzuto, G. Bruno*, CNR-IMIP, Italy

New opportunities for energy production and storage, catalysis, biosensing, drug delivering and plasmonics are offered by graphene-based materials. In order to make all those applications viable technologies, it is mandatory to functionalize graphene for modulating reproducibly its properties and for better understanding the surface and interfacial electronic phenomena in graphene hybrids.

To this aim, this contribution discusses the optical properties measured by spectroscopic ellipsometry in the 0.6-6.5 eV of graphene functionalized by:

- (1) the covalent attachment of hydrogen, nitrogen, oxygen, and fluorine atoms, which strongly affect the optical properties of graphene through a partial sp<sup>2</sup>-to-sp<sup>3</sup> conversion of carbon.
- (2) the non-covalent interaction with organic molecules such as porphyrins that interact with graphene through p-systems.
- (3) a variety of metals nanoparticles, like Au, Ag, Ga, to create a versatile graphene-based platform for plasmonics in frequency range from the terahertz to the visible.
- (4) plasmonic nanoparticles and subsequent proteins to create an electro-optical sensing graphene platform.

The graphene is grown by chemical vapor deposition (CVD) and transferred to glass substrates with coverage higher than 98%. This assures large area graphene samples that can easily accommodate the ellipsometric probing light spot avoiding uncontrolled effects due to undefined substrate/graphene boundaries. With the availability of high quality samples, effect of thickness and anisotropy, which have been debated for a while, are clarified.

Data on the real time monitoring of graphene optical properties by spectroscopic ellipsometry that allows for an unprecedented control over the degree of functionalization will also be presented.

The perspective of this work is twofold. From the fundamental point of view, in the investigated spectral range, the band structure of graphene has saddle van Hove-like singularities at the M points of the Brillouin zone, with possible excitonic effects. Focusing on the analysis of these singularities, many-body effects for all the graphene-derivates mentioned above are described.

From the technological point of view, it will be shown how the optical measurements can serve to clarify and explain the occurrence and stability of the doping of graphene by the various heteroatoms and molecules, the electron transfer between graphene and metals and molecules, and finally the sensitivity of the graphene-platform in sensing gases and biomolecules.

Spectroscopic ellipsometry data of functionalized graphene are corroborated by Raman spectroscopy, microscopies and electrical characterizations.

11:00am **EL+AS+EM+EN+SS-ThM10 Enhanced Sensitivity to Surface-Normal Dielectric Function of Uniaxial-Anisotropic Materials via Attenuated Total Reflection Ellipsometry**, *Thomas Tiwald, J.A. Woollam Co., Inc., J. VanDerslice, Z. Xiao, J.S. Huang*, University of Nebraska Lincoln

It is often difficult to determine the surface-normal dielectric functions of anisotropic materials, because of lack of sensitivity to optical properties out of the surface plane[1][2]. The primary cause is the large angle of refraction that occurs as the light enters from low index medium like air. In these circumstances, the penetrating light beam bends strongly towards surface normal, resulting in electric fields that are oriented primarily in the surface plane. This is a particular problem for absorbing films, since most of the light collected by the detector is reflected from the ambient/film interface. We use a total internal reflection method to enhance ellipsometric

sensitivity to optical properties of uniaxial absorbing materials in the out-of-plane direction. This non-destructive technique is illustrated using a P3HT poly(3-hexylthiophene) film on fused silica, and the results are compared to the standard air/film/substrate method.

[1] D.E. Aspnes. *J. Opt. Soc. Am.*, **70**, 10, 1275 (1980).

[2] G. E. Jellison Jr. and J. S. Baba, *J. Opt. Soc. Am. A23*, 2 468 (2006).

11:20am **EL+AS+EM+EN+SS-ThM11 Infrared to Ultraviolet Optical Properties of Gadolinium Gallium Garnet (Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>) and Bismuth Germanate (Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub>) Single Crystals**, *Kiran Ghimire, H. Haneef, N.J. Podraza*, University of Toledo

The optical properties of commercially available oxide single crystals gadolinium gallium garnet (Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>) and bismuth germanate (Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub>) have been studied over a maximum spectral range of 0.034 to 6.5 eV by multiple spectroscopic ellipsometry and transmittance measurements, via a multichannel ellipsometer from the near infrared to ultraviolet, a Fourier transform infrared (FTIR) ellipsometer, and a spectrophotometer. Spectroscopic measurements from each instrument and over the respective spectral ranges have been analyzed differently yet yield optical properties over the full measured range. Near infrared to ultraviolet ellipsometric spectra are analyzed using a divided spectral range procedure whereby information below and above the band gap are fit to models with separate physically realistic parameterizations of the complex dielectric function spectra ( $\epsilon = \epsilon_1 + i\epsilon_2$ ) that share the same structural parameters—surface roughness thickness in these cases. The surface roughness thicknesses are then fixed and direct numerical inversion is used to determine  $\epsilon$  over the continuous spectral range. Analysis of transmittance and FTIR ellipsometric spectra also relies upon fixing surface roughness from near infrared to ultraviolet spectroscopic ellipsometry analysis and either direct numerical inversion or parametric models to determine  $\epsilon$ . In the vicinity of the band gap, the absorption coefficient ( $\alpha$ ) obtained from  $\epsilon$  is then combined with low values of  $\epsilon$  obtained from transmittance below the absorption edge, where ellipsometry lacks sensitivity. The combined  $\alpha$  from transmission and ellipsometry is used to determine the band gap of the materials. Unlike Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>, the band gap of the Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> is sufficiently within the measured spectral range so critical point analysis has been performed on Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> by extending the measured spectral range up to 6.5 eV, where the material was found to have additional critical points. FTIR ellipsometric spectra are analyzed with a parametric model combining Gaussian and Lorentzian broadened resonance features to represent modes attributed to chemical bonding and lattice vibrations. The results of these analysis procedures yield  $\epsilon$  from the infrared to ultraviolet, from which information on the band gap, electronic transitions, and vibrational modes are obtained.

11:40am **EL+AS+EM+EN+SS-ThM12 Cu surface reactions in hydrochloric solution probed on the atomic scale by polarization optical methods and STM**, *Christoph Cobet, Gh. Barati, V. Solokha, K. Hingerl*, Johannes Kepler University, Austria

Electrochemical reactions on metal electrodes have been in the focus of many scientific studies and Cu is probably the most investigated example. Mainly, the interest on Cu is motivated by questions concerning e.g. the corrosion behavior or the optimization of electro-polishing procedures. Classical electrochemical approaches contain usually a description of the occurring reaction products and concentrations. However, it is evident that a fundamental understanding also requires knowledge about the microscopic occurrence of the metal-electrolyte interface. Desirable is a fundamental knowledge as it is obtained already for surfaces in UHV. But unfortunately, most of the classical surface sensitive techniques cannot be applied in liquid environments. Thus it is not surprising that many fundamental issues in electrochemical reactions are still unsolved.

In our work we combine reflection anisotropy spectroscopy, spectroscopic ellipsometry, and a homemade electrochemical scanning tunneling microscope to study Cu single crystals in hydrochloric solutions. With these methods we enabled monitoring of the local appearance as well as the dynamics of interface transformations/reactions on the atomic scale. In particular it was possible to explain for the (110) surface in more detail the correlation of Faraday-current and structural transformation. Here, the Cl adsorption minimizes the surface energy by a formation of monoatomic steps parallel to the [001] direction which finally ends in a faceting of the surface. It turns out that characteristic redox peaks in cyclic voltammograms correlate with the stabilization of certain arrangements of these steps. The structures are formed first by Cu dissolution and at higher anodic potentials by rearrangement of Cu atoms in the surface. It is remarkable that the latter process compares nicely with oxide/chloride induced surface transformations which are observed in UHV. The comparison with the UHV results in turn is used to achieve a more comprehensive model for the processes in electrochemical environment.

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