

Thursday Afternoon, November 3, 2011

Spectroscopic Ellipsometry Focus Topic

Room: 209 - Session EL+AS+EM+MS+PS+TF-ThA

Spectroscopic Ellipsometry for Photovoltaics, Metals and Oxide Thin Films

Moderator: M. Creatore, Eindhoven University of Technology, the Netherlands

2:00pm EL+AS+EM+MS+PS+TF-ThA1 Applications of Ellipsometry in Photovoltaics, D. Levi, National Renewable Energy Laboratory INVITED

With the growing possibility of anthropomorphic-induced climate change there has come increasing concern over energy-related emissions of carbon dioxide into the atmosphere. The search for low or no-carbon energy sources has intensified. This has led to a twenty first century gold rush into photovoltaics research and technology startups. Although the PV industry has maintained its exponential growth rate through the global economic downturn, electricity from photovoltaics is still a long ways from economic competitiveness with fossil fuel-based electricity sources. The U.S. Department of Energy recently announced the Sunshot program, with the expressed goal of \$1/Watt installed cost for utility scale PV plants by 2017. This aggressive goal will require radical advances in new and existing PV technologies.

This presentation will begin with an overview of the major PV technologies and the state of the rapidly evolving global photovoltaics industry. Photovoltaics is a natural arena for application of spectroscopic ellipsometry. Nearly all PV devices are made of multiple thin films of semiconductors and transparent conducting oxides. New materials are constantly being introduced. Film thickness, optical properties, interfaces, electronic properties, and film growth dynamics are all critical aspects of these devices and lend themselves to investigation through the use of spectroscopic ellipsometry. I will present several case studies of how we have applied spectroscopic ellipsometry in our research in photovoltaics at the National Renewable Energy Laboratory.

2:40pm EL+AS+EM+MS+PS+TF-ThA3 Comparison between Ex Situ and Real Time Spectroscopic Ellipsometry Measurements of Structurally Graded Si:H Thin Films, N.J. Podraza, University of Toledo

Analysis of spectroscopic ellipsometry measurements of graded thin films remains challenging, although analysis procedures and software have improved over the past several decades. Practical use of these processes remains somewhat time consuming and is often not fully utilized by the casual user. In this work, ex situ ellipsometric spectra collected for static samples and real time spectroscopic ellipsometry (RTSE) measurements collected during film growth will be compared to illustrate differences in results arising from the measurement procedures and analysis. As an application, consider hydrogenated silicon (Si:H) thin films used for solar cells. Devices typically incorporate either amorphous silicon (a-Si:H) or "nanocrystalline" silicon (nc-Si:H) absorber layers, although the best "nanocrystalline" absorber layers actually consist of mixed-phase amorphous+nanocrystalline (a+nc) material. Si:H thin films may initially (i) nucleate as amorphous and remain amorphous throughout growth; (ii) immediately nucleate as nanocrystallites; or (iii) initially evolve in the amorphous regime but nucleate crystallites which subsequently grow preferentially over the surrounding amorphous material until nanocrystallite coalescence. Analysis of ellipsometric spectra collected for (i) or (ii) simply involve using a substrate / bulk film / surface roughness model and complex dielectric function spectra ($\epsilon = \epsilon_1 + i\epsilon_2$) for the bulk material. For (iii), RTSE is ideally used to monitor the growth of Si:H that evolves through the amorphous, nanocrystalline, and mixed-phase regimes and a virtual interface analysis (VIA) procedure is used to extract ϵ for the amorphous and nanocrystalline components, the bulk and surface roughness thicknesses versus time, and the nanocrystalline fraction depth profile in the (a+nc) growth regime. For (a+nc)-Si:H films only measured with a single static ex situ measurement at the end of the deposition, obtaining ϵ and structural parameters of the film become less precise. Specifically, sensitivity to the variation in the nanocrystallite fraction with thickness may be lost and inaccurate ϵ for the component materials may be obtained. This work seeks to compare the structural and optical properties of (a+nc)-Si:H obtained by RTSE and VIA with those from analysis of static ex situ spectra with models using different structures, parameterizations in ϵ , and spectral range restrictions. These comparisons will be used to identify appropriate structural and dielectric function models to more accurately analyze

structurally graded thin films under different material and measurement circumstances.

3:00pm EL+AS+EM+MS+PS+TF-ThA4 Real-Time Spectroscopic Ellipsometry of Cu(In,Ga)Se₂ Thin Film Deposition: Copper Transition in 3-Stage Co-Evaporation Process, D. Attygalle, University of Toledo, V. Ranjan, Old Dominion University, P. Aryal, University of Toledo, S. Marsillac, Old Dominion University, R.W. Collins, University of Toledo

With record efficiencies above 20%, Cu(In,Ga)Se₂ (CIGS) based solar cells have shown the greatest potential for success among the thin film photovoltaics technologies. Thermal co-evaporation of individual elements has proven to produce extremely high quality CIGS materials, provides a high level of flexibility, but also generates greater challenges in process optimization. The limitations of existing process monitoring capabilities, hence the challenge of correcting process fluctuations in real time, has led the industrial community toward more controllable CIGS deposition processes. Real time spectroscopic ellipsometry (RTSE) can be used successfully in the monitoring of complicated processes -- including CIGS film preparation by co-evaporation using precursor films of (In_xGa_{1-x})₂Se₃. Information extracted from RTSE includes the evolution of bulk layer and surface roughness layer thicknesses, the composition and phase, as well as the layer dielectric functions, all of which can assist in understanding the fabrication process and in optimizing solar cells. In this study, the focus is on the transitions of Cu-poor to Cu-rich CIGS and vice versa by observing the changes in (ψ , Δ) spectra obtained by RTSE. The commonly used monitoring method, which involves observing the changes in emissivity of the film, largely depends on the apparatus design, the substrate, and the bulk layer thickness. When a CIGS film is prepared by exposing a precursor film of (In_xGa_{1-x})₂Se₃ to Cu and Se fluxes, thereby becoming Cu-rich, a semi-liquid Cu_{2-x}Se phase is believed to form on top of a bulk layer consisting of mixed phases of Cu(In,Ga)Se₂ and Cu_{2-x}Se [1]. A multilayer optical model, with appropriate effective medium approximation layers to represent this scenario, has shown good agreement with the observed (ψ , Δ) spectra. Since RTSE is highly sensitive to monolayer-level changes in the top-most layer, RTSE gives superior sensitivity in Cu-rich to Cu-poor end point detection, which occurs when the top Cu_{2-x}Se phase drops below detectable limits. Furthermore this method is less affected by the substrate and bulk layer thickness. Although careful analysis of RTSE can give a wealth of information about CIGS material properties and their evolution, this type of end point detection can be successful simply by monitoring the real time changes in the (ψ , Δ) spectra.

[1] J. AbuShama, R. Noufi, Y. Yan, K. Jones, B. Keyes, P. Dippo, M. Romero, M. Al-Jassim, J. Alleman, and D.L. Williamson, "Cu(In,Ga)Se₂ Thin-film evolution during growth from (In,Ga)Se₃ precursors", *Mat. Res. Soc. Symp. Proc.* paper H7.2.1, (2001).

3:40pm EL+AS+EM+MS+PS+TF-ThA6 Bulk Heterojunction Solar Cell Characterization by Phase Modulated Spectroscopic Ellipsometry, K. Uppreddi, L. Yan, HORIBA Scientific

The blend morphology, phase separation as well as crystallinity of organic photovoltaic solar cell are important properties to increase the efficiency. The performance of such cells is strongly influenced by blend composition and thermal annealing conditions. In this work we demonstrate the use of ellipsometry as a powerful and sensitive metrology means of monitoring organic solar cell based on the blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM). Ellipsometric measurements were performed on P3HT/c-Si, PCBM/c-Si and P3HT:PCBM/c-Si at an angle of incidence of 70 degree, across the spectral range 190 – 2100 nm (0.6-6.5 eV). Two different analysis protocols were used to model the P3HT:PCBM blend structure. In the first protocol effective medium theory was used to represent the optical constant of layer, where as in the second one the blend was treated as one single homogenous material. The approach renders investigation of final morphology and composition.

4:00pm EL+AS+EM+MS+PS+TF-ThA7 In Situ Spectroscopic Ellipsometry during Atomic Layer Deposition of Pt, Pd and Ru, N. Leick, J.W. Weber, M.J. Weber, A.J.M. Mackus, H.C.M. Knoops, W.M.M. Kessels, Eindhoven University of Technology, Netherlands

The precise thickness control of atomic layer deposition (ALD) and its conformal growth make ALD the method of choice for nanometer thin film deposition. Platinum-group metals such as Pt, Pd and Ru have many applications in the areas of nanoelectronics and catalysis and recently there has been considerable interest to deposit films of these materials by ALD. Spectroscopic ellipsometry (SE) is a powerful, noninvasive optical technique that can be used *in situ* during ALD to precisely monitor the thickness of the films. SE also provides information on the optical and

electrical properties of the films which is very relevant for their applications. Choi et al. [1] previously investigated the dielectric functions of Pt-group metal films with a thickness of ~400 nm as prepared by physical vapor deposition. For the aforementioned applications, however, the films are required to be much thinner, which leads to differences in film morphology as well as to dielectric functions that can be different from those of bulk films. In the spectroscopic ellipsometry work to be presented in this contribution we have therefore focused on films with thicknesses from 5 nm to 35 nm. *In situ* data was obtained during ALD in the photon energy range of 0.7 – 6.5 eV. Using a Kramers-Kronig consistent B-spline model to account for the thickness-dependent dielectric functions, we were able to obtain accurate ALD growth-per-cycle values for Ru, Pt and Pd ($1.00 \pm 0.06 \text{ \AA}$, $0.47 \pm 0.04 \text{ \AA}$, $0.14 \pm 0.02 \text{ \AA}$). Furthermore, the contributions from free-carriers (Drude term) and interband absorptions (Lorentz-oscillator contributions) were investigated by combining the SE data with FT-IR reflectance data such that the photon energy range of 0.04 eV – 6.5 eV was covered. In this range, it was possible to represent each film with a unique Drude-Lorentz model although some ambiguities about the Lorentz oscillator contributions remained in the case of Ru. It will be shown that the extracted thicknesses and electrical resistivities from this model are in line with data obtained from X-ray reflectometry and four-point probe measurements (for example Ru: $\rho_{SE} \sim 23 \mu\Omega\cdot\text{cm}$ and $\rho_{FPP} \sim 16 \mu\Omega\cdot\text{cm}$). Furthermore, in the case of Ru also the influence of the film roughness will be addressed.

[1] Choi et al., Phys. Rev. B **74**, 205117 (2006)

4:20pm **EL+AS+EM+MS+PS+TF-ThA8 Manipulating the Optical Properties of Metals: Sculptured Thin Films Coated by Atomic Layer Deposition**, D. Schmidt, N. Ianno, E. Schubert, M. Schubert, University of Nebraska - Lincoln

The fabrication of three-dimensional metal nanostructures with tailored geometry is one of the central challenges of nanotechnology because geometrical and material parameters are responsible for the optical, electrical, mechanical, chemical, or magnetic properties of such nanostructured thin films. Engineered artificial sculptured thin films (STFs) with designed anisotropies are potential candidates for applications in various fields such as optics, magneto-optics, as well as chemical and biological sensing and detection. However, in order to utilize metallic nanostructures for novel applications their size-, structure-, and material-driven physical properties have to be understood and quantified.

We utilize glancing angle electron-beam deposition, which exploits physical atomic-scale shadowing and dynamically varying particle flux azimuth for fabrication of three-dimensional highly spatially coherent STFs with different morphologies. Subsequently, nanostructures are individually covered with a thin conformal coating (cladding) by means of atomic layer deposition (ALD).

We will present the anisotropic optical properties of highly anisotropic ALD coated metal STFs determined by generalized spectroscopic ellipsometry in the visible and near-infrared spectral region. The analysis of our multilayer slanted columnar thin films deposited at glancing angle ($\theta_i = 85^\circ$) revealed that such STFs possess monoclinic optical properties, and the optical response may be described by an effective medium dielectric homogenization approach. It will be discussed how the anisotropic Bruggeman effective medium approximation (AB-EMA) allows for determination of structural parameters as well as fractions of individual film constituents. Furthermore, the AB-EMA analysis reveals that the anisotropic dielectric properties of the metal core changes upon deposition of a dielectric cladding.

4:40pm **EL+AS+EM+MS+PS+TF-ThA9 Ellipsometric Characterisation of Porous Aluminium Oxide Supports**, W. Ogieglo, N.E. Benes, H. Wormeester, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

Porous aluminium oxide is widely used as a support material for thin film inorganic micro- and mesoporous membranes. Such membranes are used in energy-efficient gas separation, pervaporation and nanofiltration processes. Ellipsometry can be used to determine material properties of the thin membrane films, as well as the penetrant loading [1]. Interpretation of the ellipsometry data requires a detailed knowledge of the porous aluminium oxide support. This support is made of aluminium oxide particles that are sintered together. In between the particles voids are present that amount to 38% porosity. We have studied the influence of the size of the voids on the optical response of the support material. For this study, voids with a diameter of around 60, 80 and 160 nm were used. We noted a strong decrease of the normal incidence specular reflection with void size and a subsequent increase in off specular reflection. In ellipsometry, only a limited depolarization of the specular reflected light was noted in the wavelength range between 300 and 1750 nm. The angle dependent ellipsometry measurements showed that the optical properties of these

supports can not be obtained from a direct inversion. The reason for this is that at the interface the more or less spherical voids are cut, which leads to a distribution of openings at the surface, i.e., a substrate with a very rough surface. This roughness was modelled with a graded porosity changing from 38% in the bulk to 75% at the outer surface. This measured variation in porosity is very similar to the cumulative height distribution of the surface layer obtained from AFM. The validity of this graded porosity model was verified from the analysis of a sample with a thin polysulfone (PSU) layer deposited on the support. The PSU layer partly fills the open pores at the surface. This results in an interface with a graded variation in aluminium oxide, void and PSU.

The proper treatment of the surface layer also provides the optical properties of the porous aluminium oxide bulk material itself. These optical properties can in a limited wavelength range be modelled with Bruggeman's effective medium approximation. As a consequence of the size of the inclusions, their diameter is no longer negligible with respect to the wavelength of light in the UV part of the spectrum. For the material with the largest pore size, also a large part of the visible range has to be excluded. A more elaborate approach than the standard effective medium approach has to be used in this case.

[1] H. Wormeester, N.E. Benes, G.I. Spijksma, H. Verweij and B. Poelsema Thin Solid Films **455-456**, 747-751 (2004)

5:00pm **EL+AS+EM+MS+PS+TF-ThA10 Optical Properties and Structure of Vanadium Oxide Thin Films**, M.A. Motyka, M.W. Horn, Pennsylvania State University, N.J. Podraza, University of Toledo

Vanadium oxide (VO_x) thin films are common materials used as imaging layers in uncooled microbolometer based thermal imaging devices. These films are used in this application largely due to the controllable resistivity of the film (ρ), the high temperature coefficient of resistance (TCR), and the low electrical noise. One of the main difficulties of this material system relates to the multiple valence states of vanadium, each of which results in materials with different electrical properties. Bolometer quality VO_x may consist of a composite of nanocrystalline face centered cubic (FCC) VO phase and amorphous materials. The thin film oxygen content via Rutherford back scattering (RBS) has suggested that the typical ratio V:O should be near 1:1.7-2.0, significantly higher than the stability window of the FCC phase. This off-stoichiometry ratio suggests that the amorphous material is a mixture of higher oxygen valence states similar to V_2O_5 and VO_2 . The higher quality VO_x thin film material also has been observed via transmission electron microscopy (TEM) to contain $\text{VO}/\text{V}_2\text{O}_5$ nano-twin crystalline domains. The presence of each of these phases impacts the electrical and optical properties of the resulting VO_x film. Films with various oxygen contents and structures were studied with spectroscopic ellipsometry (SE) over a spectral range of 0.05 to 5.15 eV using a multichannel dual rotating compensator near-ultraviolet to near infrared instrument in conjunction with Fourier transform infrared spectroscopic ellipsometry (FTIR-SE). Thus, the complex dielectric function spectra ($\epsilon = \epsilon_1 + i\epsilon_2$) can be obtained for these materials over the full spectral range. Differences in ϵ due to variations in the film structure are observed as functions of processing, indicating that SE is a means of probing the material composition and structure. Specifically, ϵ are compared for various film composites fabricated by unbiased pulsed DC magnetron sputtering as well as composite films prepared by reactive ion beam sputtering and pulsed DC magnetron sputtering with a substrate bias. The microstructure and ϵ are correlated with films exhibiting the desirable device electrical properties. *In situ* real time spectroscopic ellipsometry (RTSE) has shown that environmental conditions alter the as-deposited VO_x thin films grown via pulsed DC-magnetron reactive sputtering of a metallic vanadium target. In order to prevent undesired atmospheric effects to the thin film, it is a common practice to encapsulate the thin film with a more environmentally stable material. In this study, the material chosen was SiO_2 grown in the same deposition chamber, pre-atmospheric exposure, via rf sputtering.

5:20pm **EL+AS+EM+MS+PS+TF-ThA11 Sensitivity of Dielectric Properties of Vanadium Dioxide Thin Films to Growth Conditions**, D.W. Ferrara, R.E. Marvel, J. Nag, R.F. Haglund, Vanderbilt University

Vanadium dioxide (VO_2) is a strongly-correlated electron material with a well-known semiconductor-to-metal transition (SMT) that can be induced thermally ($T_c = 68^\circ\text{C}$), optically, or electrically. Recently, VO_2 films have attracted attention as a component in active metamaterials, especially in conjunction with metal nanostructures. Since these structures are highly sensitive to the dielectric properties of the embedding material, the SMT of VO_2 can be used to tune the optical response of the structure. Accurately modeling the behavior of these structures requires detailed knowledge of the dielectric function of VO_2 as it undergoes the SMT; however, previous measurements of the optical constants of VO_2 reveal significant variations between experiments.

To understand systematic variations due to growth conditions, films of VO₂ were deposited on either silicon, glass, or sapphire substrates by pulsed laser ablation of vanadium metal targets in 10 mTorr oxygen (O₂) background gas, followed by annealing at 450°C in 250 mTorr of O₂. Anneal times were varied from 30 to 90 depending on film thickness; deposition thickness was varied from 20 nm to 200 nm. For each sample, temperature-dependent spectroscopic ellipsometry measurements at optical and near-infrared wavelengths were conducted to determine the dependence of the optical constants on film thickness, substrate and crystallinity, and temperature.

Bruggeman and Maxwell-Garnett effective-medium formulations were used to account for three constituent materials: semiconducting VO₂, metallic VO₂, and vanadium pentoxide (V₂O₅). The effective dielectric functions were modeled using Lorentz and Tauc-Lorentz oscillators. Our results show that the contribution of V₂O₅ to the effective dielectric function increases with annealing time, consistent with previous studies. The results are also substantiated using Rutherford backscattering, X-ray photoelectron spectroscopy and X-ray diffraction.

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