Spectroscopic Ellipsometry Characterization of Thin Film Photovoltaic Materials and Devices

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ABSTRACT -- **One of the biggest challenges in the photovoltaic industry is creating a high efficiency device with low manufacturing and material costs. This challenge can be overcome by accurately characterizing thin film materials and photovoltaic device structures to determine properties such as thickness, absorption coefficient, composition, crystallinity, blend morphology, and phase separation, all of which may be modified to result in a more efficient photovoltaic device. One way to characterize thin film materials and photovoltaic device structures is to use spectroscopic ellipsometry, a non-invasive, non-destructive, and non-contact optical technique which can provide all of the above thin film properties, as well as other information, such as optical properties and band gap values. Spectroscopic ellipsometry works on the basis that linearly polarized light, when reflected off of a sample, becomes elliptically polarized. The resultant elliptical polarization state can be modeled in order to provide information about the sample. Because of the information it can provide, spectroscopic ellipsometry is a very powerful technique for the study of thin film photovoltaic materials and devices. In particular, spectroscopic ellipsometry can be applied to anti-reflection coatings, TCO layers, and organic solar cell devices, as will be demonstrated here.**

Index Terms -- **anti-reflection coatings, ellipsometry, organic solar cells, transparent conducting oxides**

I. INTRODUCTION

Progress in the photovoltaic industry is rapidly accelerating, but the need for a high efficiency device with low manufacturing and material costs still remains. In order to achieve such a device, thin film photovoltaic materials and devices can be studied using techniques designed to provide structural information such as thickness, absorption coefficient, composition, crystallinity, blend morphology, phase separation, and band gap, all of which can be tailored, via the thin film deposition process, to achieve a more efficient device, as well as a device which minimizes material usage. One particularly useful technique is spectroscopic ellipsometry, which provides a non-invasive, non-destructive, and non-contact method for studying thin film photovoltaic materials and devices.

Spectroscopic ellipsometry is an optical technique which measures the change in polarization state of light as it is obliquely reflected off of a thin film sample. This change in polarization is represented, at each wavelength, by two parameters, ψ, which is an amplitude ratio, and Δ, which is a phase difference, both of which are measured using a spectroscopic ellipsometer. Regression analysis can then be applied to model the sample at hand in order to determine its properties such as thickness and optical constants. Further analysis of the optical constants can provide additional information about the sample such as its bandgap.

II. EXPERIMENTAL

All samples presented here were measured with a HORIBA UVISEL phase modulated spectroscopic ellipsometer over a spectral range starting at 0.6 eV and extending to either 5 eV or 6.5 eV. All data were then modeled using the DeltaPsi2 software program, and regression analysis, to obtain thickness values and optical properties.

III. RESULTS AND DISCUSSION

A. Anti-Reflection Coating

The first structure used in photovoltaics that will be studied with spectroscopic ellipsometry is a multiple layer anti-reflection coating consisting of a graded TiO_2 layer sandwiched between two SiO_2 layers. The cross-sectional structure for this sample is given below in Figure 1. Anti-reflection coatings, such as the one being studied here, generally help to optimize light absorption in the solar cell in order to improve conversion efficiency, but the index grading profile must be optimized in order to minimize reflections effectively. Studying this film structure with spectroscopic ellipsometry provides the index grading profile, as shown below in Figure 2 for the graded TiO_2 layer. Here, it is clear that the top of the layer has a lower refractive index, and is less dense than the bottom of the layer, which has a higher refractive index. Hence, the overall refractive index is decreasing when moving from the bottom of the layer to the top of the layer, which is the standard index grading profile for AR coatings [1]-[3]. Ellipsometry can also be used to determine film thicknesses, which can then be optimized for maximum performance. The thicknesses of the SiO_2 and TiO_2 layers for the sample studied, obtained by spectroscopic ellipsometry, are shown below in Figure 1.

B. Transparent Conducting Oxide

The second structure used in photovoltaics that will be studied with spectroscopic ellipsometry is the transparent conducting oxide layer, which acts as a window layer and

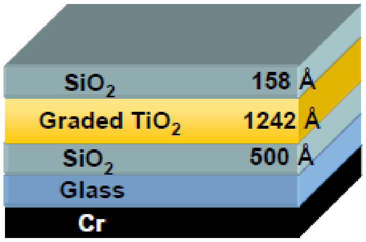

Figure 1: Cross-sectional structure of an anti-reflection coating on a glass/Cr substrate.

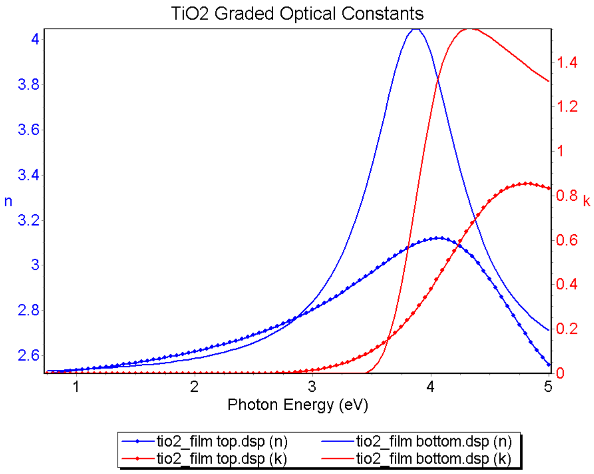

Figure 2: Optical properties, obtained by spectroscopic ellipsometry, for the graded TiO_2 layer contained in the anti-reflection coating structure shown in Figure 1. Dotted lines show the optical properties at the top of the layer and solid lines show the optical properties at the bottom of the layer.

provides electrical contact for electrons to flow through the cell, while also allowing light to pass through to the active solar cell material. The most common material used for a TCO layer is In_2O_3:Sn (ITO), but indium is relatively rare, so ZnO is commonly used as a substitute TCO layer. It is more difficult, however, to tailor the ZnO film to obtain high conductivity and high transparency, as well as a good interface between the TCO layer and the active semiconductor layers. Because of this, a two layer, or oxygen-graded model for the ZnO layer was proposed, in which the oxygen content is varied in order to vary conductivity and refractive index [4]. First, an oxygen-deficient ZnO layer is fabricated in order to provide a good interface match to the active semiconductor layers. Then, a second, thinner, oxygen-rich layer is over-deposited in order to provide high conductivity.

The cross-sectional structure for the sample studied here, consisting of a graded ZnO layer on c-Si, is shown below in Figure 3. Spectroscopic ellipsometry can be used to determine both the thickness of the ZnO layer, as well as that of the surface roughness, as shown in Figure 3. It can also be used to determine optical properties at the top and bottom of the graded ZnO layer, as shown in Figure 4. Here, it is clear that the bottom of the ZnO layer has a lower refractive index which matches closely to the index of refraction of the substrate, and the top of the ZnO layer has a higher refractive index which provides additional conductivity for the TCO layer.

Figure 3: Cross-sectional structure of a graded TCO film on a c-Si wafer.

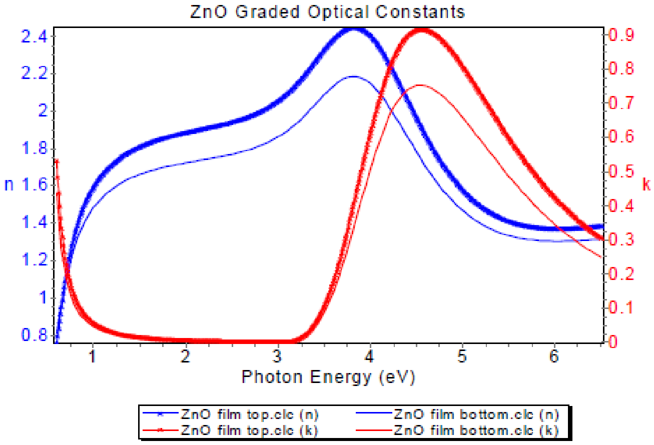

Figure 4: Optical properties, obtained by spectroscopic ellipsometry, for the graded ZnO TCO layer shown in Figure 3. Dotted lines show the optical properties at the top of the layer and solid lines show the optical properties at the bottom of the layer.

C. Organic Solar Cell Devices

The third structure studied with ellipsometry was an organic solar cell device consisting of P3HT and anisotropic PEDOT:PSS, as shown by the cross-sectional structure in Figure 5. Organic solar cells currently have low conversion efficiencies, and hence, they require additional characterization and optimization. Spectroscopic ellipsometry is useful in such situations since it can provide accurate optical properties for each layer in the device, as well as accurate layer thicknesses, as shown in Figures 5-8. More importantly, spectroscopic ellipsometry can be used to study anisotropic thin films, such as the PEDOT:PSS layer. In this case, ellipsometry provides both extraordinary and ordinary optical constants as shown in Figure 6. Spectroscopic ellipsometry can also provide optical properties for the P3HT and ZnO layers, shown in Figures 7 and 8, respectively.

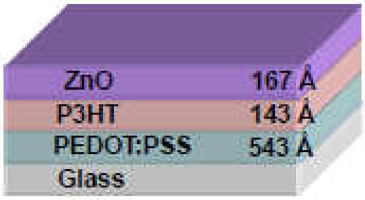

Figure 5: Cross-sectional structure of an organic solar cell.

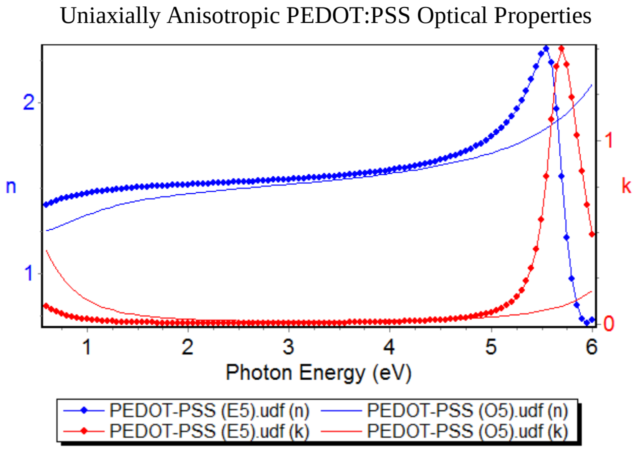

Figure 6: Optical properties, obtained by spectroscopic ellipsometry, for the uniaxially anisotropic PEDOT:PSS layer shown in Figure 5. Dotted lines represent the optical properties for the extraordinary direction and solid lines represent the optical properties for the ordinary direction.

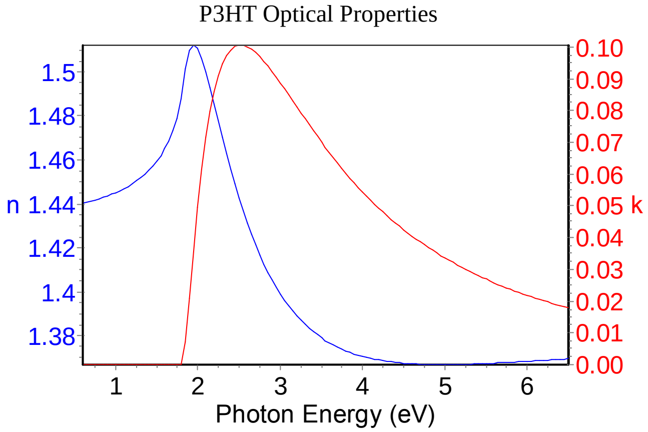

Figure 7: Optical constants, obtained by spectroscopic ellipsometry, for the P3HT layer contained in the structure shown in Figure 5.

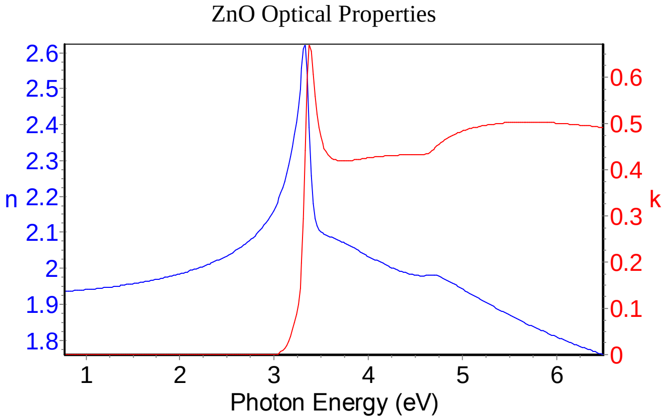

Figure 8: Optical properties of the ZnO layer contained in the structure shown in Figure 5.

IV. CONCLUSION

Spectroscopic ellipsometry is a powerful, non-invasive, non-destructive, and non-contact technique for characterizing thin film photovoltaic materials and devices. Spectroscopic ellipsometry provides a spectral range of ψ and Δ values which can then be modeled in order to obtain film thickness and optical constants. As demonstrated here, spectroscopic ellipsometry is useful for the study of graded anti-reflection coatings, graded transparent conducting oxides, and organic solar cell materials and devices such as PEDOT:PSS and P3HT. Spectroscopic ellipsometry can also provide optical constants and thickness information for anisotropic thin films. After characterizing thin films with spectroscopic ellipsometry, deposition and fabrication parameters can be changed to result in a film more tailored to the needs of the application; in this case, a higher efficiency.

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