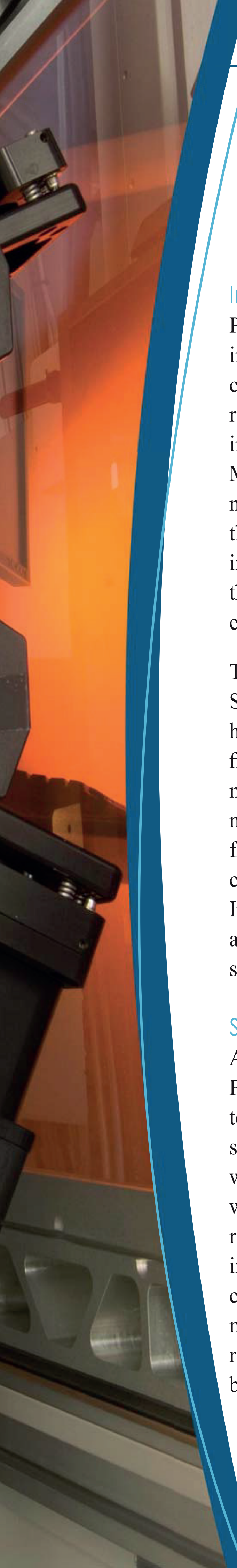

Application Note

Photovoltaics

# Photovoltaic Applications Using Spectroscopic Ellipsometry

## Introduction

Photovoltaic cells (solar cells) are becoming an important source of world electrical energy. Solar cells have been in production for decades, but recent energy price increases have stimulated improved cell design and manufacturability. Many different cell materials and designs are now in production, including second generation thin-film devices. Research continues to investigate next-generation cells, such as organic thin films, that promise low production cost and ease of manufacture.

Thin films are common in most solar cell designs. Spectroscopic ellipsometry (SE) is a natural fit to help study and monitor the performance of these films. Spectroscopic ellipsometry is ideal for measurement of film quality, nanostructure, thickness and optical constants for all types of films; from anti-reflection coatings and transparent conductors to the active semiconductor layers. In this work, we review current and emerging applications of SE to different solar cell films, structures and devices.

## Silicon Solar Cells

At present, crystalline silicon solar cells dominate PV energy conversion world-wide. Silicon technology has been around for decades. The smooth, mirror-like cells of the past have given way to monocrystalline or multicrystalline silicon with textured surfaces. Texturing significantly reduces reflected light. To further capture incoming light, a thin film anti-reflection (AR) coating is commonly added. A popular AR material is silicon nitride (SiNx), as its index of refraction makes a good impedance match between air and the semiconductor. Nitride layer thickness and refractive index determine how effectively reflected light is suppressed.

SE can be used to measure AR coatings on textured silicon, but this requires advanced instrumentation and methods for success. Because of greatly reduced reflection from textured surfaces, the T-Solar™ M-2000® spectroscopic ellipsometer was developed. It includes an intensity optimizer[1], shown in Figure 1, which adjusts to maximize reflected signal from each sample. Even with optimized intensity, rough textured surfaces push measurements to oblique angles above 75°.

Figure 1. Intensity optimizer on an M-2000 spectroscopic ellipsometer allows convenient control of measurement signal to match the ideal range for any sample.

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[1] Patent Pending

Figure 2 shows data collected from textured multicrystalline silicon with a single-layer AR coating. The data are used to determine thickness and refractive index of the coating. The coating refractive index, shown in Figure 2, decreases as the surface becomes rougher. The coating index on this textured surface is 10% lower than values on a smooth, polished silicon surface. Texturing lowers the film density, which can be modeled by mixing the fully dense reference film optical constants with air (void) in an effective medium approximation (EMA). As the surface becomes rougher, the void fraction increases, which lowers the refractive index significantly. Textured silicon itself has a lower optical density, which reduces the substrate index – thus the AR coating is still an effective match.

Multicrystalline silicon surfaces are etched in different ways. An alkaline etch causes texturing along crystal axes (Figure 3a). While this reduces the SE signal on a location-by-location basis, there is enough reflected light for the T-Solar™ system to characterize the coating.

An acidic etch produces very different texturing (Figure 3b), with significantly reduced surface reflection. SE measurements on this surface reveal a greatly reduced index of refraction. As with an alkaline etch, an EMA model determines the index decrease as a mix of ‘void’ with silicon. Thus, an EMA approach works well for characterizing AR coatings on silicon textured by either an alkaline or an acidic etch.

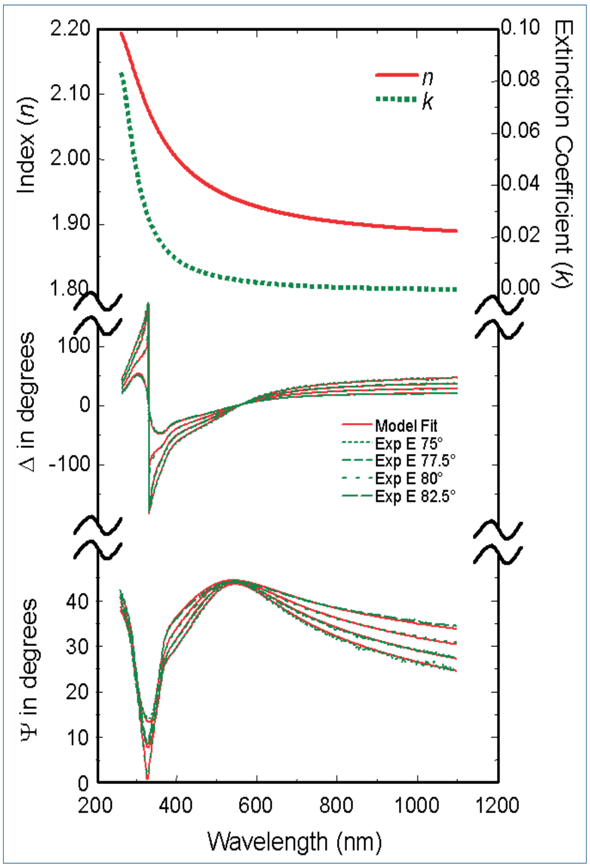
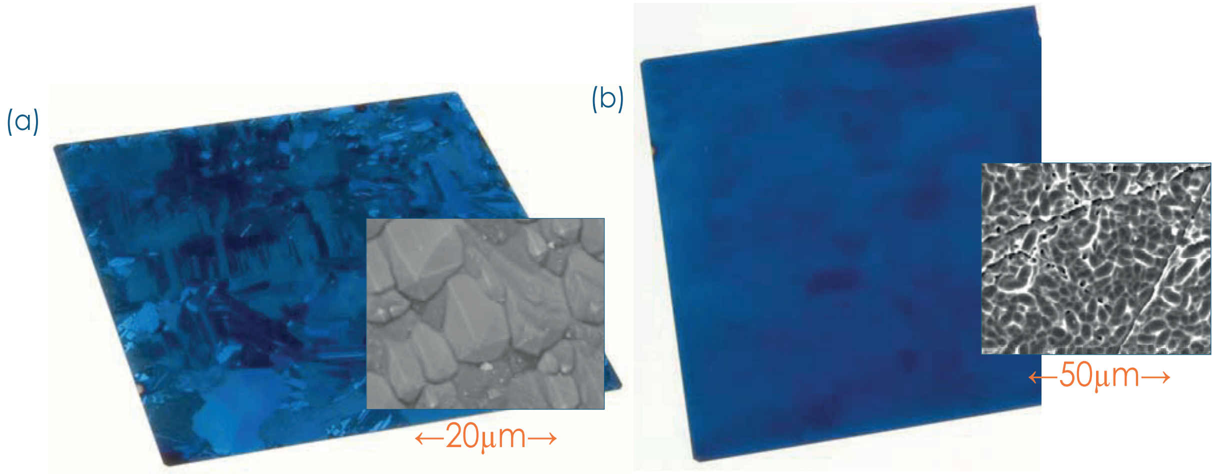


Figure 2. Measured data and corresponding model fit for a single-layer AR coating on multicrystalline silicon. Resulting optical constants for the AR coating are also shown.

Texturing monocrystalline <111> silicon surfaces produces a regular pattern of pyramids as shown in Figure 4 (inset). To measure monocrystalline structures requires special measurement geometries[2,3] as provided by the T-Solar

Figure 3. Images of different multicrystalline silicon solar cells along with Scanning Electron Microscope (SEM) insets for each image. (a) alkaline etched multicrystalline silicon, and (b) acidic etched multicrystalline silicon.



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[2] Patent Pending

[3] M. Saenger, M. Schubert, J. Hilfiker, J. Sun, J. Woollam, “Infrared to Ultraviolet spectroscopic ellipsometry characterization of antireflection layers on textured polycrystalline and monocrystalline silicon solar cells”, IMRC 2008.

system. Accounting for pyramid geometry, the T-Solar ellipsometer can characterize textured monocrystalline surfaces with AR coatings. Figure 4 compares data from coated, textured monocrystalline silicon measured first with the standard SE sample geometry, and second using the T-Solar special geometry. Data oscillations that provide AR coating information are suppressed in a standard SE measurement, but are prominent when pyramidal texturing is accounted for. Thus, T-Solar SE measurement geometry is critical for film characterization on textured monocrystalline silicon. The resulting nitride layer optical constants (Figure 5) are modeled using a Tauc-Lorentz oscillator[4]. This dispersion equation describes both refractive index and UV absorption with only a few free parameters. Again, the refractive index is lower than from films on a smooth surface, due to lower optical densities on textured surfaces.

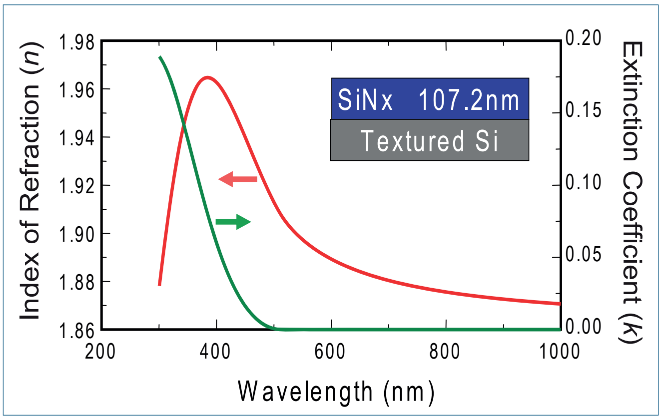

Figure 5. Resulting SiNx optical constants and thickness measured from the textured monocrystalline silicon surface using special T-Solar geometry.

## Thin Film Photovoltaics

Thin film solar cells are increasingly common, as reduced material consumption leads to reduced costs compared to crystalline silicon cells. There are many thin film cell materials and designs being developed for second generation PV. These materials have high optical absorption near the cell surface and shorter minority carrier diffusion lengths compared to crystalline silicon and thus require less material. Materials include amorphous silicon (a-Si), microcrystalline silicon (µc-Si), Cadmium Telluride (CdTe), Copper Indium Gallium di-Selenide (CIGS), dye-sensitized, and organic solar cells. Spectroscopic ellipsometry is well suited to measure optical constants of the various layers, interfacial and surface properties, material uniformity, layer thicknesses, and other parameters needed to improve cell performance.

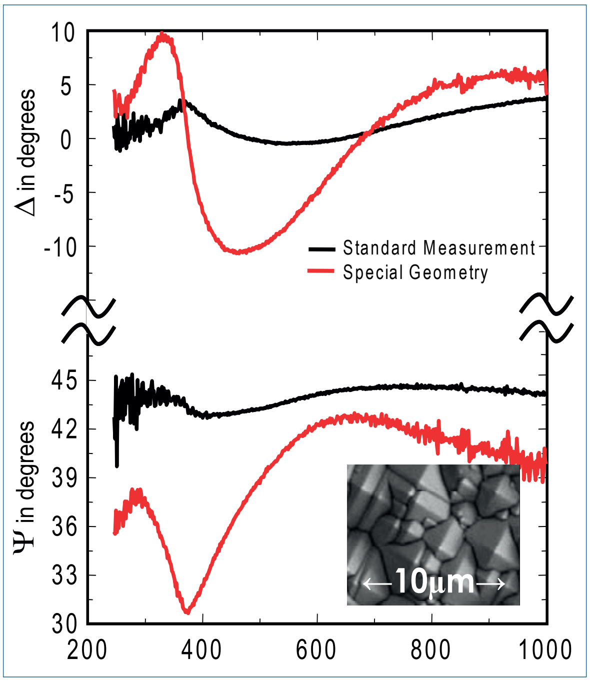

Figure 4. Two data sets from a textured monocrystalline silicon wafer coated with single-layer SiNx film. The first data set uses the standard SE geometry, while the second data set uses the special geometry of our T-Solar system to enhance measurements from the pyramid structures (shown in the inset SEM image). The large increase in oscillations for the T-Solar special geometry allows SE characterization of the SiNx optical constants and thickness.

### Thin Film Silicon

Amorphous (a-Si) and microcrystalline (µc-Si) silicon films are increasingly common in PV applications. SE has measured a-Si and µc-Si layers for many decades, as they are common in semiconductor devices and flat panel displays. SE analysis of these films is well understood, and it is common to see SE used for film-uniformity mapping in PV production environments. Figure 6 shows two large-area mapping tools using a J.A. Woollam M-2000® SE to map large-panel PV film uniformity. The AccuMap-SE® (Figure 6a) accommodates samples up to 1.1 by

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[4] G.E. Jellison, Jr. and F.A. Modine, "Parameterization of the optical functions of amorphous materials in the interband region," Appl. Phys. Lett. 69, 371 (1996), Erratum, Appl. Phys. Lett. 69, 2137 (1996).

1.3 meters, and features high-speed alignment to reduce measurement time per data point to a few seconds. Figure 6b shows a Dai Nippon Screen (DNS) PV mapping tool with integrated M-2000® to measure very large panels. The M-2000 “flies” over the stationary sample during data acquisition. With common dispersion equations, to describe the a-Si layer, it is easy to determine optical constants and thickness uniformity over a panel as shown for p-layer a-Si in Figure 7.

In most single-junction a-Si solar cell structures, the layers differ only in doping density, and visible-light SE has difficulty distinguishing between the differently doped layers (p-, i-, n-). When layers appear optically identical, SE accurately determines total thickness of the structure. However, many a-Si PV panels use multi-junction or hetero-junction structures. These may involve µc-Si and/or a-SiGe films where change in crystallinity or composition provides optical contrast between layers and allows multi-layer analysis. Figure 8 shows silicon-film optical constants varying from amorphous to microcrystalline to polycrystalline. As crystallinity decreases, the sharp, well-defined UV absorptions broaden. This is due to a decrease in long-range order in the material (i.e., films become less crystalline and more amorphous). For reference, Figure 8 also includes optical response for crystalline silicon (c-Si), exhibiting sharp UV absorptions between 3 and 5eV (248-415nm).

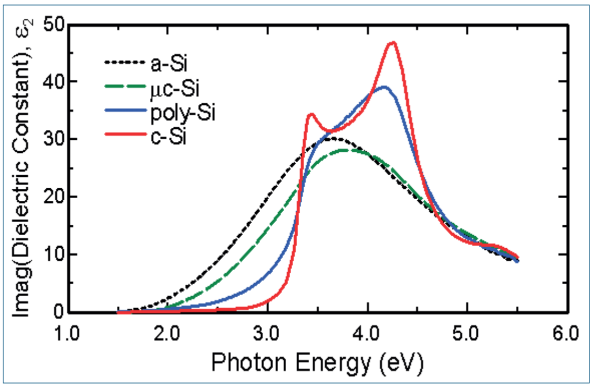


Figure 8. The absorbing region of silicon films can help distinguish between amorphous (a-Si) microcrystalline (µc-Si), polycrystalline (poly-Si) and crystalline (c-Si) films.

Figure 6. Two large-area mapping tools for PV uniformity measurements. Both incorporate our M-2000 spectroscopic ellipsometer for very fast data at hundreds of wavelengths from the ultraviolet to near infrared.
(a) The AccuMap-SE is designed for fast mapping of PV modules up to 1.1 by 1.3 meters.

(b) The latest PV mapping tool from Dai Nippon Screen accommodates very large panels. The M-2000 “flies” over the large, stationary panel.

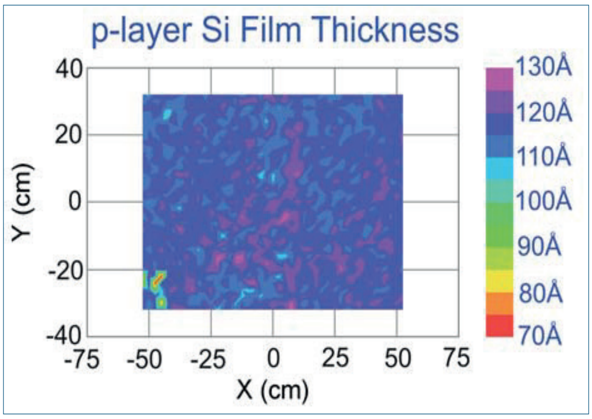
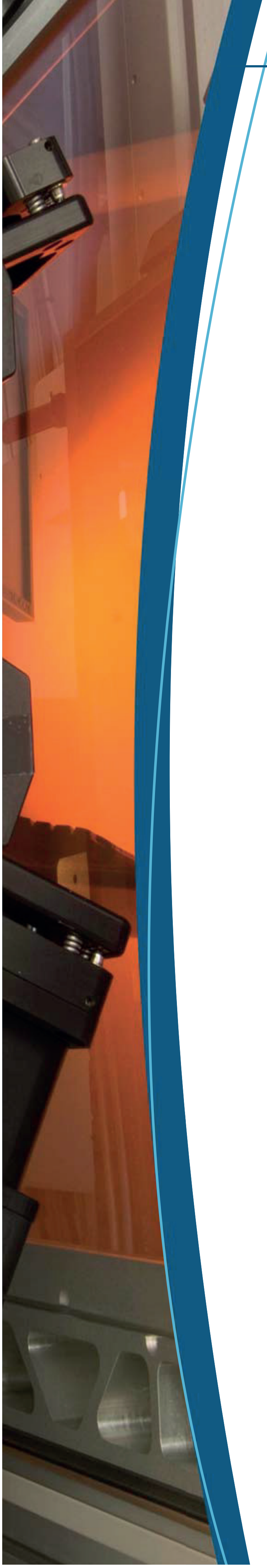


Figure 7. Large-area uniformity map for thin silicon film.



## Transparent Conducting Oxide (TCO) Substrates

Many thin film solar cells are deposited on glass substrates. To provide a conductive surface contact, glass is coated with a TCO layer such as indium tin oxide (ITO), fluorinated tin oxide ($F:SnO_2$) or aluminum-doped zinc oxide (AZO) before addition of the PV films. Conductive films absorb infrared light, due to free carriers in the film. A Drude free-electron dispersion model well-describes near-infrared (NIR) absorption spectra found from SE measurements. This is shown in the ITO k-values in Figure 9. As the film was annealed, conductivity increased, which appears as an increase in NIR absorption (extinction coefficient). Thus NIR-wavelength SE characterizes TCO conductivity, while simultaneously acquired visible-wavelength SE characterizes transparency and film thickness. All TCOs exhibit similar conductivity behavior which can be characterized using this method. TCOs often exhibit strong conductivity variations versus depth into the film. NIR optical constants strongly depend on film conductivity which often needs to be graded in the optical model to best match experimental data.

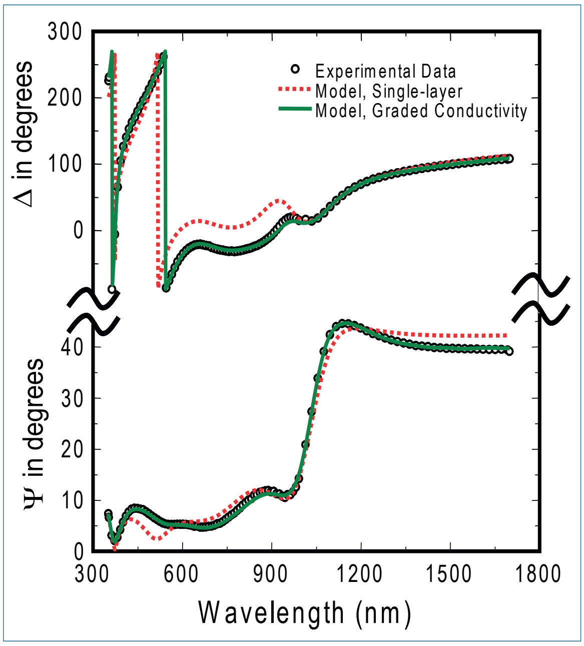


Figure 10. Data from a single-layer ITO film show the strong absorption edge as the film goes from transparent to absorbing (step in Ψ at 1000nm). A single-layer model (red) does not match the data. Data are matched when the conductivity is allowed to a with depth (green).

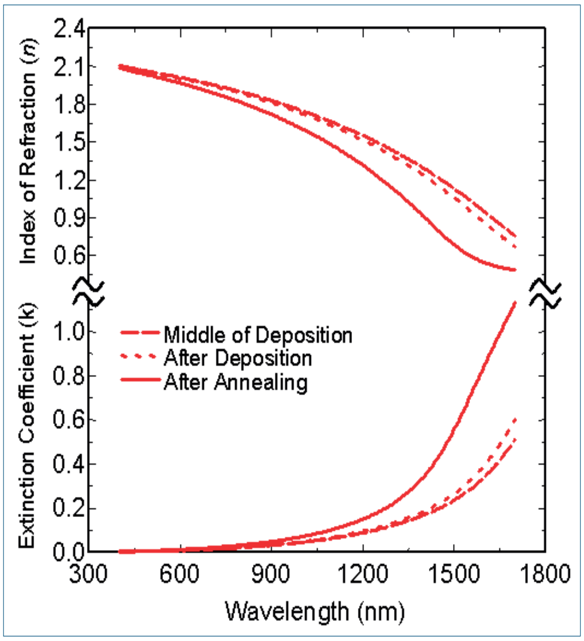


Figure 9. The optical constants of an ITO film were dependent on process conditions. After the film was annealed, the conductivity improved, which results in larger NIR absorption (high-k) from free-carriers in the film.

Figure 10 shows data from a vertically-graded conductivity TCO film. The initial model assumes a single, uniform layer. The second model allows layer conductivity to vary with depth into the film. This model successfully fits the data and provides depth profiles of conductivity. In this example, conductivity was nearly constant through the film. However, the film quickly became non-conductive in the surface region.

For many thin-film solar cells, the TCO is a multi-layered film on glass. Figure 11 shows excellent SE data fits from a commercial TCO coated-glass substrate. The optical model includes three layers. Only the top-layer is conductive[5].

## CdTe/CdS Cells

An increasingly common thin film solar cell structure uses CdTe and CdS layers for light absorption. CdTe has a nearly ideal bandgap (~1.4eV) for PV applications. CdTe-based cells have demonstrated efficiencies above 16%. The CdS layer is generally very thin, yet SE can measure both films. Figure 12 shows optical constants measured from a CdS layer on

commercial TCO glass. Strong absorption above the CdS direct-bandgap insures only the surface region is measured for wavelengths below about 500nm. This is also true of the CdTe layer, although it is generally a few microns thick to provide adequate path-length for optimized light-capture in this layer. The thick CdTe film produces data oscillations above ~1000nm, where the film is transparent and light returning from the film back-surface provides optical interference. It is critical to include surface roughness in the analysis to get good data fits. For some structures, roughness can be too large to collect adequate SE signal, especially at shorter wavelengths. Figure 13 shows an example data set for CdTe/CdS on commercial TCO-coated glass. CdTe is transparent only below about 1.4eV, where thickness can be determined from the interference oscillations.

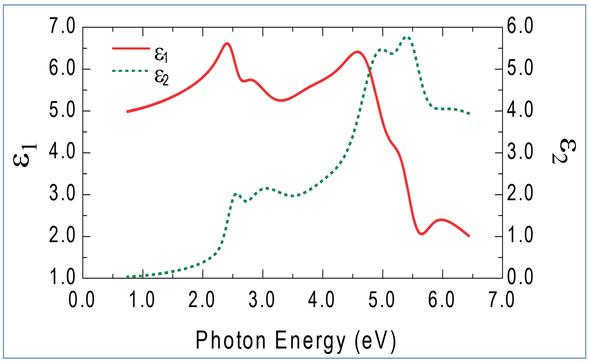
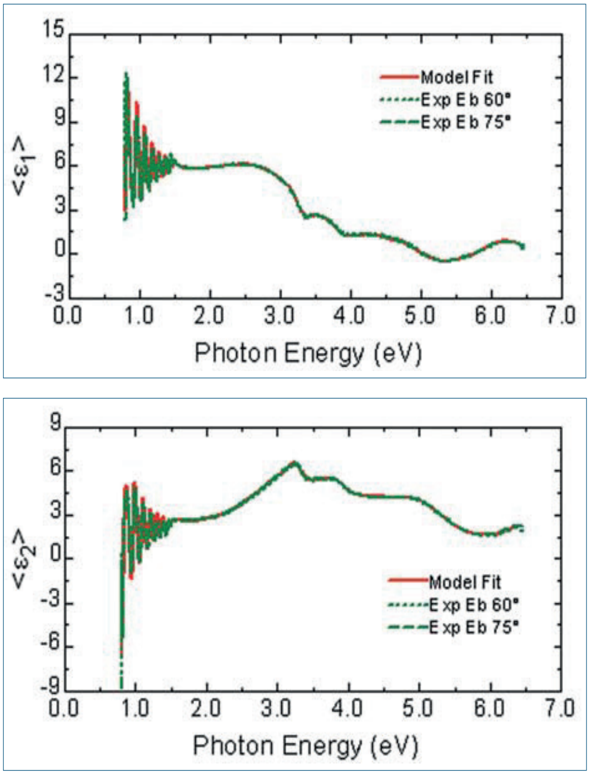


Figure 12. CdS dielectric function measured by SE.



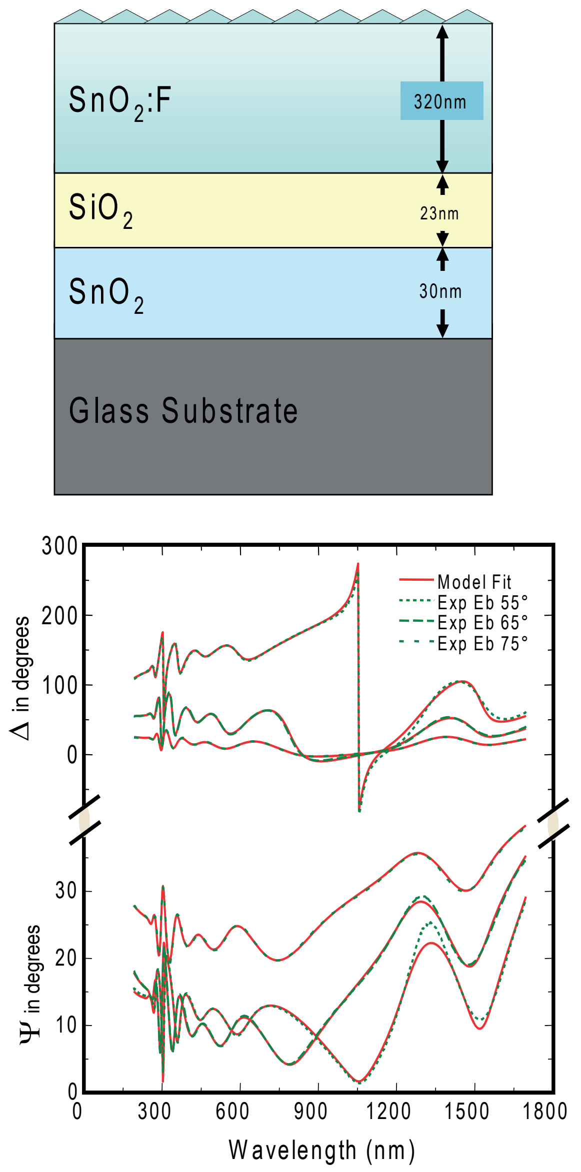


Figure 11. Data and corresponding fits for a commercial TCO coated glass substrate. The model consists of a 3-layer structure where the conductive layer is graded and includes a significant surface layer.

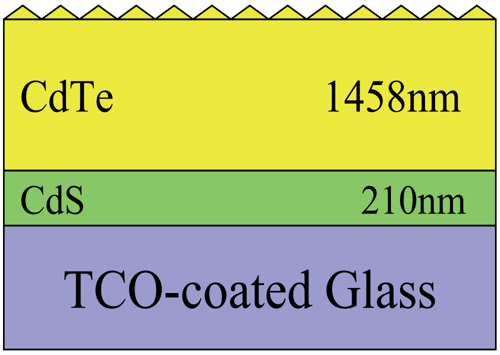


Figure 13. Experimental measurements and corresponding model-fit curves for a CdT/CdS structure on TCO coated glass. The surface-roughness was important to match the data adequately.

## CIGS Cells

Cu(In,Ga)$Se_2$ (CIGS) is another material with strong surface optical absorption and well-matched optical bandgaps to make good thin-film solar cells. The bandgap can be adjusted by varying the indium and gallium material composition. Figure 14 shows optical constants measured by SE for a CIGS film[6].

CIGS layers are also very rough, and it is common to apply anti-reflection (AR) surface coatings to improve cell efficiency. These layers include zinc oxide ($ZnO_x$) and ITO to provide both a conductive surface and an AR coating. Optical constants for $ZnO_x$ and ITO are similar in the visible but differ in the NIR due to conductivity in the TCO layer (as discussed before). Thus, SE data covering both visible and NIR provide details about the CIGS bandgap as well as help differentiate between the $ZnO_x$ and TCO layers.

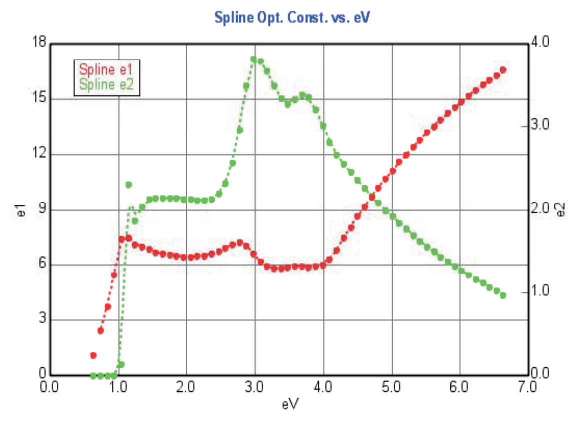


Figure 14. Optical Constants for a CIGS film, measured by spectroscopic ellipsometry.

## Organic PV Cells

Organic-based solar cell efficiencies reached 6% by 2008, whereas 10% is needed to reach commercial viability. Numerous other PV technologies, including those described above, have already reached commercialization. However, thin film organic layers promise light-weight, low-cost, large-area organic cells. Also, it is common to deposit the organic PV layers on glass or plastic substrates; again suggesting low cost, large area manufacturing.

Optical absorption in organics creates excitons with very short lifetimes and diffusion lengths. Collection of photo-generated current is done on a nano-meter scale. Thus current PV research and development involves nano-structured organic materials for separation of electrons and holes to provide electrical energy.

Extensive worldwide research has been done on organic materials for electronics, especially for Organic Light Emitting Device (OLED) display applications. These use materials and structures similar to organics used for PV. Thus considerable expertise exists in materials preparation, characterization, and manufacturing.

Considerable SE expertise has been developed to characterize PV organics and plastic substrates. For example, SE can measure anisotropic optical properties of organic layers.

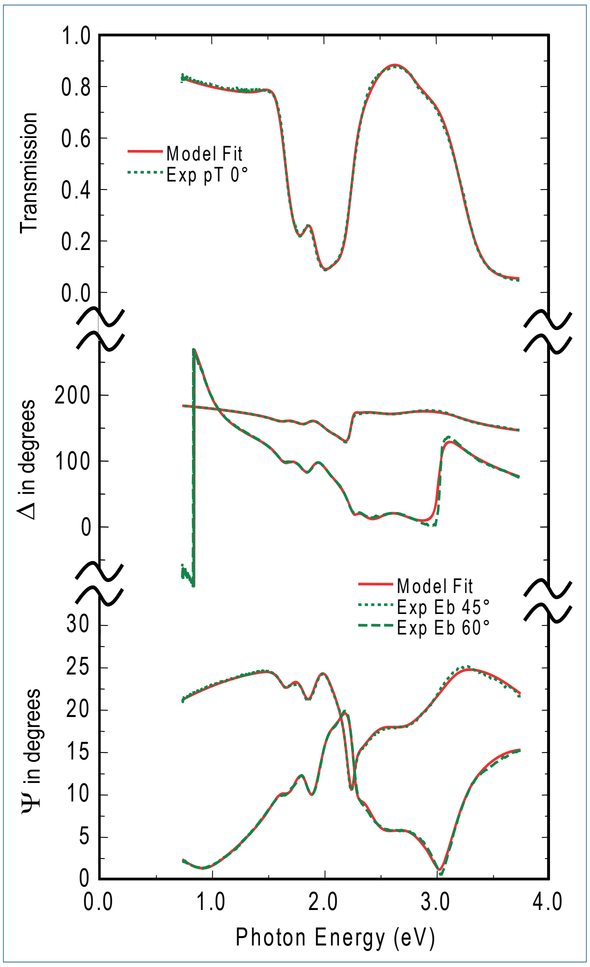


Figure 15. Experimental SE and Transmission data are well-matched by an anisotropic model that allows the in-plane and out-of-plane optical constants to have their own shape.

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[6] A.M. Hermann et al. "Fundamental studies on large area Cu(In,Ga)Se2 films for high efficiency solar cells", *Solar Energy Materials & Solar Cells* **70** (2001) 345.

Analysis of transparent anisotropic materials benefits from simultaneous collection of SE and Transmission (T) data. Combining SE and T measurements helps determine values for many unknown material parameters. Figure 15 shows data from a thin organic film exhibiting mid-visible wavelength absorption. An isotropic model does not match the data very well. A good fit is achieved with an anisotropic layer where in-plane and out-of-plane optical constants are each described by their own oscillators. Figure 15 shows a fit to all data sets simultaneously. The resulting in-plane and out-of-plane optical constants are compared in Figure 16. Organic films are known to be anisotropic due to organized stacking of molecules giving rise to directionally-dependent (anisotropic) optical constants. The degree of anisotropy measured optically in organic films depends on the length scale of short- vs. long-range ordering of molecules compared to the size of the SE light beam. In most cases ordering is long-range, and anisotropy is observed by optical measurements.

An example film used for PV and OLED applications is the polymer PEDOT:PSS. The properties of this film, such as conductivity, change with differing ratios of PEDOT to PSS. To accurately determine the optical properties for this semi-absorbing organic thin film, there are a couple of methods used to improve sensitivity[7]. First, addition of SE + T data provide extra information when the absorbing film is on a transparent substrate. Second, multi-sample analysis is a powerful approach for nominally identical films that have the same optical constants, but different thicknesses. In this case, a single set of optical constants describes the response for multiple films. Figure 17 shows data and corresponding fits to three different films of PEDOT:PSS on which a multi-sample analysis was performed. These polymer films were spun on glass substrates at different rotation speeds to change the film thickness. While each sample has a different thickness, a single-set of optical constants matches data from all

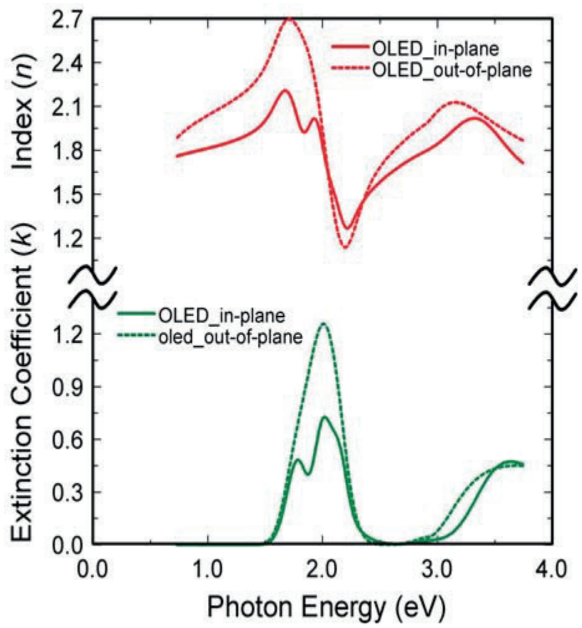

Figure 16. Organic PV film results. Final optical constants for both in-plane and out-of-plane direction used to fit the data in Figure 16. Both sets of optical constants are described by the Kramers-Kronig consistent summation of oscillator terms.

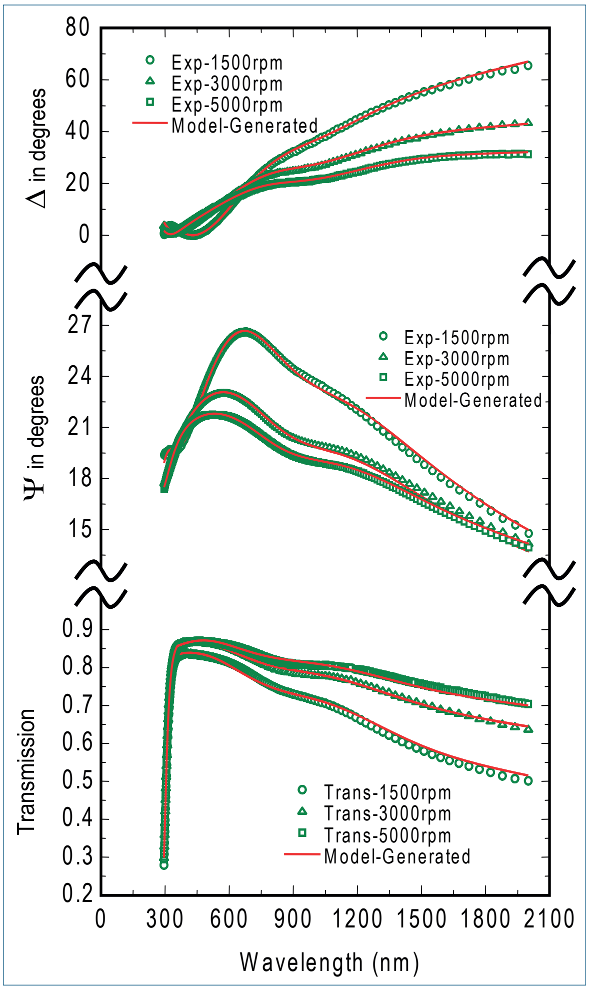

Figure 17. Experimental SE and Transmission data for 3 polymer films spun-on glass at difficult rotation speeds. The model-results come from a single set of anisotropic optical constants where only thickness is different between samples.

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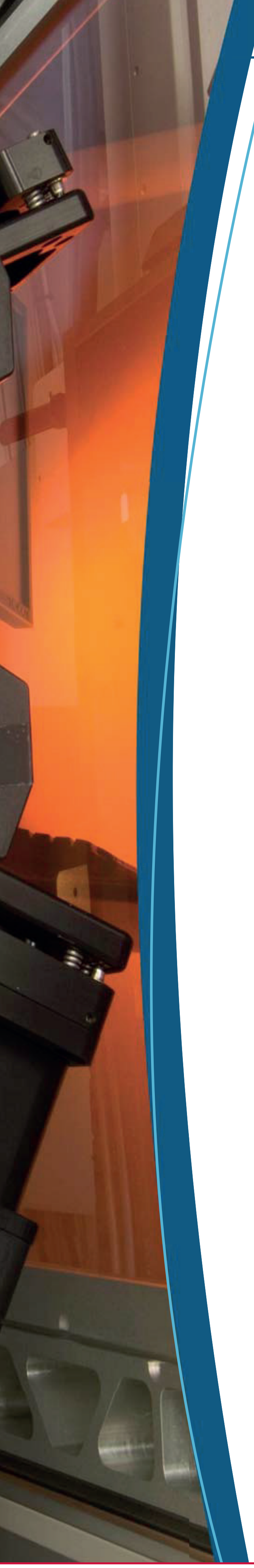
[7] J.N. Hilfiker et al. "Survey of methods to characterize thin absorbing films with spectroscopic ellipsometry" *Thin Solid Films*, (2008) In Press.



samples. For this polymer material, the in-plane and out-of-plane properties differ. That is, the film is uniaxially anisotropic. The resulting anisotropic PEDOT optical constants are shown in Figure 18.

## Conclusion

Spectroscopic ellipsometry is a well established optical technique used to characterize a wide variety of films in photovoltaics research and manufacturing. Applications include measurement of smooth and etch-textured silicon, as well as the silicon nitride anti-reflective coatings used on today's silicon cells.

Next-generation solar cells under development are based on films of compound semiconductor materials such as CIGS, CdTe/CdS; organic films; and transparent conducting oxides such as ITO and AZO. Such films will be deposited on glass and plastic substrates. Spectroscopic ellipsometry has proven effective for measuring all these films and substrates individually and in complex multi-layer stacks.

New hardware innovations such as the AccuMap-SE® with integrated M-2000® ellipsometer allows thickness and optical property uniformity measurements over entire panels, where the ellipsometer "flies" over large panels, making automated measurements at hundreds of points. Another hardware innovation is the T-Solar™ used for SE analysis of AR coatings on textured solar cell surfaces. Additional applications are expected to emerge in the near future, insuring a "bright" future for SE applications in photovoltaics.

If you would like to discuss your photovoltaic applications and how spectroscopic ellipsometry may be beneficial, please call the J.A. Woollam Company at 402-477-7501 and ask for an Applications Engineer. We can also be reached at measurements@jawoollam.com.

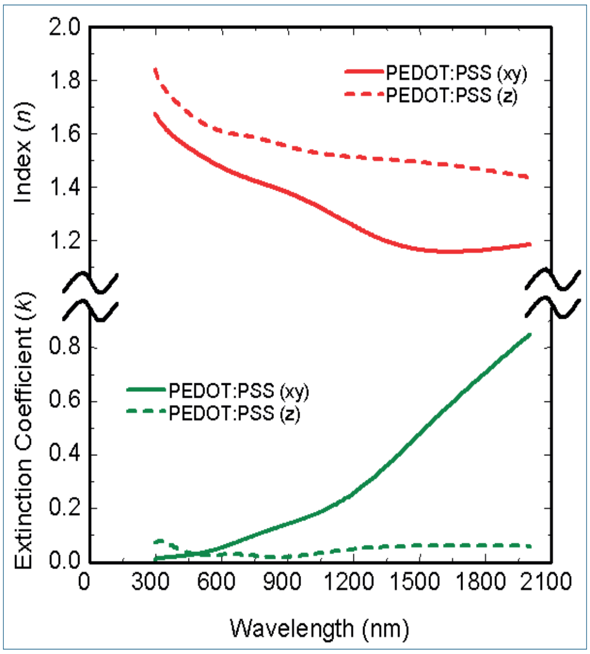


Figure 18. In-plane (xy) and out-of-plane (z) optical constants for anisotropic PEDOT:PSS films deposited on glass.