Through-the-glass spectroscopic ellipsometry for analysis of the optical structure of CdTe thin-film solar cells in the superstrate configuration

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The polycrystalline CdS/CdTe thin-film solar cell in the superstrate configuration has been studied by spectroscopic ellipsometry (SE) using glass side illumination whereby the reflection from the glass/film interface is collected whereas that from the ambient/glass interface is rejected. The SE data analysis applies dielectric functions (ε) for solar cell component materials obtained by variable-angle and in-situ SE. In the SE analysis of the complete cell, a step-wise procedure ranks the free parameters, including thicknesses and those defining the spectra in ε, according to their ability to reduce the root-mean-square deviation between simulated and measured SE spectra, and the best-fit results compare well with electron microscopy. Combining all SE results, the solar cell quantum efficiency (QE) can be simulated without free parameters, and comparisons with QE measurements enable identification of losses. The capabilities have wide applications in photovoltaic module mapping and in-line monitoring.

[doi: 00000]

A successful, low-cost photovoltaics technology based on CdS/CdTe polycrystalline thin films has emerged for electric power generation with current record solar cell and module efficiencies of 21.0% and 17.0%, respectively.1 Such devices are fabricated in the superstrate configuration such that the solar irradiance first passes through glass, and then through the transparent top contact and n-type window layers, before absorption in the 2-5 μm p-type CdTe layer.2 The solar cells exhibit a complex optical structure; at least six individual stratified media are encountered by the solar irradiance before absorption within the bulk of the CdTe layer. Thus, characterization of the cell structure in terms of optical properties and layer thicknesses is a challenge, yet such a capability is critical for performance evaluations.

Spectroscopic ellipsometry (SE) is promising for this purpose, as it is used widely in the reflection configuration for characterization of multilayered films.3 The relatively large polycrystalline grains of the fully processed CdTe layer in the solar cell lead to considerable surface roughness at the back or film side of the cell and to a weakly-defined specular beam reflected from that side. In addition, after CdTe fabrication, the final device structure is fully coated with an optically opaque metallic back contact layer and further processed.2 Thus, useful SE measurements in reflection from the back of the final device are not possible.

In the first SE studies of CdTe solar cell structures, measurements were performed from the glass superstrate side at a 60° incidence angle by attaching a prism to the glass with index-matching fluid, an optical geometry that suppresses the unwanted ambient/glass reflection and minimizes the undesirable polarization changes that occur in transmission through that interface.4 The thicknesses of the CdS bulk and the CdS/CdTe effective medium interface layer deduced by this method were in good agreement with those obtained destructively using SE from the film side after a Br2-methanol etch that smoothens the CdTe surface. This demonstration, undertaken before application of the metal back contact, indicated that SE could be performed successfully from the glass side of a CdTe solar cell.

In the present study, prism attachment is avoided in the SE measurement by using an aperture to block the ambient/glass reflection, an approach that is inherently non-invasive. Thus, the two polarization changes occurring upon oblique transmission through the ambient/glass and glass/ambient interfaces must be taken into account in data reduction. An example of such an approach for a complete CdTe cell with an opaque Au back contact is presented using a systematic, step-wise analysis.5 A complete description of the cell, including component layer dielectric functions (ε) and a structure corroborated by microscopy, enables simulation of quantum efficiency (QE) with no free parameters. Thus, insights are gained into both optical and electronic losses.

The superstrate used in this study was NSG Pilkington TEC-15™, which is soda-lime glass coated with a tri-layer of [SnO2 (20 nm)]/[SiO2 (30 nm)]/[SnO2:F (300 nm)] (from the glass to film side; nominal thicknesses indicated). This structure was subsequently coated with a highly resistive transparent (HRT) layer of SnO2 having a 100 nm nominal thickness. The complete multilayered structure of the solar cell includes the TEC-15™/HRT superstrate stack coated with magnetron sputtered CdS (~100 nm) and CdTe (~2 μm). The as-deposited stack is subjected to a 30 min CdCl2 treatment at 387°C, and the cell is completed with the evaporation of ~3 nm of Cu and ~30 nm of Au, followed by a 45 min anneal at 150°C for Cu diffusion. Cell measurement under air mass (AM) 1.5 illumination yielded a short-circuit current of 21.7 mA/cm2, open-circuit voltage of 0.815 V, fill factor of 0.702, and efficiency of 12.5%.

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The analogous approach could not be applied to determine $\alpha(E)$ of the CdS layer since $(\psi, \Delta)$ spectra of the final solar cell structure are less sensitive to $\varepsilon$ for CdS. Thus, a simplified CdCl$_2$-treated structure, consisting of glass/CdS/CdTe, was studied with the same CdS thickness of ~100 nm. By eliminating the superstrate layer stack, which exhibits anti-reflection characteristics, greater sensitivity to $\alpha(E)$ spectra of CdS could be obtained, and Eq. (2) could be used with a single CP associated with the E$_0$ transition. The best fit analytically-determined $\alpha(E)$ spectra are compared in Fig. 1 for the CdS in the CdCl$_2$-treated CdS/CdTe structure and as-deposited CdS as a single layer. For the former, modification of CdS occurs throughout its thickness by indiffusion of Te from the overlying CdTe, an effect that is enhanced by CdCl$_2$ treatment. Such modifications include a reduction in bandgap $E_0$ and an increase in broadening $\Gamma_0$.

Based on previous studies of CdS$_{1-x}$Te$_x$, a composition $x = 0.057 \pm 0.007$ is found for the layer in the device structure.

The analysis procedure for through-the-glass SE of the completed CdTe solar cell is designed systematically to identify the best $p$-parameter model while tracking $\sigma_{ECS}$ and the confidence limits on the $p$ parameters. In this way, the parameters are ranked in order according to their ability to reduce $\sigma_{ECS}$. Parameters that can be fixed at their nominal values are also identified, and unnecessary complexities in the model can be eliminated if they do not serve to reduce $\sigma_{ECS}$. The starting point optical model used for $p$-parameter analysis of SE data is based on the assumptions of nominal thicknesses for all layers in the stack: SnO$_2$/SiO$_2$/SnO$_2$/F/ HRT/CdS/CdTe, fixed $\alpha(E)$ spectra from a database, no interface roughness layers, and no optical non-idealities.

The optical modeling performed here tests 24 variable parameters in all. Figure 2 (circles) and Table I show $\sigma_{ECS}$ from Eq. (1) for the best $p$-parameter fits for $p = 1-11$, including only layer thicknesses and the following optical non-idealities: (i) CdTe thickness non-uniformity over the beam area, modeled via $r_p$ and $r_n$ weighted averages, and (ii) the small fraction of ambient/glass reflection collected inadvertently. Also depicted in Fig. 2 (blue squares) are 62 trial fitting steps in order of decreasing $\sigma_{ECS}$. Table I shows that the variable of CdTe thickness yields the best one-parameter model, and addition of the CdS thickness yields the best two-parameter model. For parameters 9 and 10, the best fit thicknesses of the thin SnO$_2$ and SiO$_2$ are so close to nominal values that variations of these values do not reduce $\sigma_{ECS}$. In fact, the error function increases slightly due to the increase in $p$ in Eq. (1). Thus, these two thicknesses can be fixed at nominal values. Introduction of thickness non-uniformity, the $11^{th}$ parameter, is not justified by the Table I results, implying that the CdTe thickness is uniform within the measurement sensitivity. Similarly, an additional 13 parameters describing the component layer $\varepsilon$ spectra are introduced that improve the fit further, as shown in Fig. 2, and detailed elsewhere (see Supplementary Material). These variable parameters include (i) those defining the spectra in $\alpha(E)$, (ii) interface layer volume fractions in the Bruggeman effective medium approximation, and (iii) the coefficients of stress-induced birefringence for the glass.

Figures 3 and 4 show experimental (points) and best fit simulated (lines) spectra in $(N, C, S)$ for the 24 parameter
model of Fig. 2 and the optical model for the device stack with the best fit structural and compositional parameters and confidence limits, respectively. Table II lists deduced dielectric function parameters for the two thickest layers, CdTe and SnO$_2$:F. The band gap $E_0$ and broadening parameter $\beta_0$ for the CdTe in turn provide the in-plane stress and the electron mean free path,$^{9,10}$ and these values are also included in Table II. The resistivity and the effective thickness of the SnO$_2$:F layer provide its sheet resistance.

The 17 best-fit key structural and optical property parameters given in Fig. 4 and Table II, respectively, will be considered next. The effective thicknesses (volume/area) of CdS and CdTe in Fig. 4 are $100 \pm 6$ nm and $1.997 \pm 0.015$ μm, respectively, and these match the intended nominal values. The CdTe band gap and broadening in Table II are close to those of the single crystal,$^{14,15}$ an effect of the CdCl$_2$ treatment which results in low stress and a long mean free path relative to as-deposited CdTe.$^2$ The SnO$_2$:F sheet resistance in Table II is also close to the 15 Ω/sq nominal value for TEC-15/HRT™. Figure 5 shows a cross-sectional electron microscopy (XTEM) image of the solar cell used to corroborate the SE deduced thicknesses. Here, the layers of SnO$_2$ HRT and SnO$_2$:F are indistinguishable. The tabulated thicknesses of the layers in Fig. 4 from XTEM were obtained as an average over an ~4 μm image length and are in reasonable accord with the effective thicknesses from SE. This supports SE as a viable non-invasive method for CdTe solar cell analysis at a single point or in mapping mode.

The cell structure in Fig. 4, along with the component layer $\alpha(E)$ spectra, enable prediction of the QE spectrum and short-circuit current density $J_{sc}$ with no free parameters, based on assumptions regarding the active device layers.$^{16}$ Figure 6 shows the simulation assuming that all electron-hole pairs photogenerated within the CdS/CdTe interface and CdTe bulk layers are collected. The second simulated QE spectrum is designed to fit the experimental result and is based on the assumptions that complete carrier collection

<table>
<thead>
<tr>
<th>Parameter #</th>
<th>Parameter yielding greatest reduction in $\sigma_{\text{SE}}$</th>
<th>$\sigma_{\text{SE}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CdTe bulk layer thickness</td>
<td>157.4</td>
</tr>
<tr>
<td>2</td>
<td>CdS bulk layer thickness</td>
<td>117.7</td>
</tr>
<tr>
<td>3</td>
<td>CdS/CdTe interface layer thickness</td>
<td>90.7</td>
</tr>
<tr>
<td>4</td>
<td>CdTe/Au interface layer thickness</td>
<td>76.3</td>
</tr>
<tr>
<td>5</td>
<td>HRT thickness</td>
<td>61.2</td>
</tr>
<tr>
<td>6</td>
<td>SnO$_2$:F thickness</td>
<td>54.2</td>
</tr>
<tr>
<td>7</td>
<td>Fractional irradiance from top glass reflection</td>
<td>52.3</td>
</tr>
<tr>
<td>8</td>
<td>HRT/CdS interface thickness</td>
<td>51.0</td>
</tr>
<tr>
<td>9</td>
<td>SnO$_2$ thickness</td>
<td>51.1</td>
</tr>
<tr>
<td>10</td>
<td>SnO$_2$:F thickness</td>
<td>51.2</td>
</tr>
<tr>
<td>11</td>
<td>CdTe thickness non-uniformity</td>
<td>51.3</td>
</tr>
</tbody>
</table>

FIG. 2. Step-wise reduction in $\sigma_{\text{SE}}$ of Eq. (1) by adding fitting parameters one by one. Eleven structural parameters have been deduced in 62 fitting steps (squares). Circles indicate the best $p$-parameter fit ($p$ at the top) with the 11-parameter list in Table I. Thirteen optical property parameters were deduced similarly in 88 additional fitting steps that further reduce $\sigma_{\text{SE}}$.  

FIG. 3. Experimental $N = \cos 2\varphi$, $C = \sin 2\varphi \cos \Delta$, $S = \sin 2\varphi \sin \Delta$ spectra and corresponding best fit for a through-the-glass SE measurement of a CdTe solar cell. A list of the thicknesses and non-ideality parameters used in the fit are given in Table I with the best fit values and their confidence limits included in Fig. 4. Best fit compositions in the Bruggeman effective medium approximations are also included in Fig. 4, and the best fit dielectric function parameters of greatest interest are given in Table II.

FIG. 4. Layer stack for the CdTe solar cell identifying the thicknesses and interface layer compositions along with their confidence limits. The second column of SE deduced thicknesses are effective values obtained as the volume of the material per unit area, or the product of the material volume fraction and the thickness summed over all layers that include the material. The third column lists average thicknesses from XTEM for comparison.
Table II. Parameters describing ε and the physical and electrical property parameters derived from them for the CdTe and SnO₂:F layers.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Optical parameters deduced from SE analysis</th>
<th>Physical/electronic parameters deduced from optical parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe</td>
<td>Bandgap, E₀ (eV)</td>
<td>Compressive stress (GPa)</td>
</tr>
<tr>
<td></td>
<td>Broadening, T₀ (eV)</td>
<td>Mean free path (nm)</td>
</tr>
<tr>
<td>In cell</td>
<td>1.496±0.004</td>
<td>0.07±0.06</td>
</tr>
<tr>
<td>Single crystal</td>
<td>1.491</td>
<td>320±130</td>
</tr>
<tr>
<td>SnO₂:F</td>
<td>Resistivity (x10⁴Ω-cm)</td>
<td>Sheet resistance (Ω/sq)</td>
</tr>
<tr>
<td></td>
<td>Scattering time (x10⁻¹⁵ s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.5±0.3</td>
<td>11.5±1.1</td>
</tr>
</tbody>
</table>

occurs from the (i) CdS bulk layer within ~ 10 nm of the CdS/CdTe interface and (ii) CdS/CdTe interface layer; 98% collection occurs from an ~ 1.1 μm thickness of the CdTe bulk layer adjacent to the interface; and 50% collection occurs within another 0.37 μm of CdTe. As a result, ~ 0.35 μm of CdTe adjacent to the back contact is inactive with respect to collection. This simulation yields a QE spectrum and J_sc in close agreement with the experiment. Thus, a complete optical analysis enables evaluation of losses, enabling improvements in optical and carrier collection.

In summary, this study demonstrates the success of through-the-glass SE as a non-invasive optical metrology of CdTe solar cells in the superstrate configuration. The thicknesses deduced from SE analysis agree well with those measured by XTEM, and the deduced optical parameters provide information on the properties of the CdTe and the nature of interfaces. Based on the resulting comprehensive optical and multilayer structural analysis, simulations of the QE spectra can be generated under various assumptions regarding carrier collection. Comparison of QE simulations with data provides insights into the losses. In addition to the single spot capability demonstrated here, the metrology can also be applied to generate maps of film multilayer structure, component film properties, and J_sc predictions due to the high measurement speed of the multichannel ellipsometer (~1 s), enabling metrology in a production line environment.

This research was supported by the DOE/NSF F-PACE Program (Contract DE-EE0005405), Dr. D. Strickler of NSG Pilkington is acknowledged for providing substrates; Dr. J. Lawrence is acknowledged for assistance with XTEM.

![Figure 5](image5.png) FIG. 5. Cross-sectional transmission electron microscopy image of a CdTe solar cell showing six distinct layers (from superstrate): (i) SnO₂; (ii) SiO₂; (iii) SnO₂:F/HRT top contact; (iv) CdS; (v) CdTe; (vi) Cu/Au back contact. Thicknesses averaged over ~ 4 μm image lengths are shown in Fig. 4.

![Figure 6](image6.png) FIG. 6. Quantum efficiency spectrum (QE) measured at 0 V under AM 1.5 (solid line) and simulated QEs based on (i) complete carrier collection from the CdTe bulk and CdS/CdTe interface layers (dashed line); and (ii) 100% collection from 10 nm of the CdS bulk layer and the full 31 nm of the CdS/CdTe interface layer, and 98% and 50% collection from 1.1 μm and 0.37 μm layers of the CdTe bulk, respectively (dot-dashed line); (see inset).
**SUPPLEMENTARY MATERIAL**

A total of 24 variable parameters have been collected into two groups, (i) a group of 11 structural parameters ranked in terms of their ability to reduce σ\textsubscript{NCS} in Fig. 2 and Table I (main text), and (ii) a group of 13 optical property parameters ranked similarly in Fig. S-1 and Table S-I. The second group of parameters include those defining analytical forms for the complex dielectric functions (\(\varepsilon\)) of SnO\textsubscript{2}:F, HRT, and CdTe. Fixed \(\varepsilon\) were used for all other solar cell components. Also included are parameters that describe the interface layer compositions. These in turn define the interface layer optical properties through the Bruggeman effective medium approximation. Finally, the optical parameters include stress-induced birefringence in the glass, modeled as a shift in the ellipsometry angle \(\Delta\) depending on photon energy \(E\) according to \(\Delta[\Delta(E)] = E(c_1 + c_2 E^2)\), where \(c_1\) and \(c_2\) are the variable parameters.

Among the optical property parameters in Table S-I, the resistivity associated with the Drude component of \(\varepsilon\) for SnO\textsubscript{2}:F is most effective in reducing σ\textsubscript{NCS}. The best fit value is (3.5 ± 0.3) \times 10^4 \Omega/cm, which yields a sheet resistance of 11.5 ± 1.1 \Omega/sq, as indicated in Table II (main text). The second and third most effective parameters in Table S-I are those that control the optical properties of the roughness region at the back contact. This region has been separated into two layers according to the analysis of Table I (main text), with the back layer being opaque. Nominal compositions, are 67/33 vol.% CdTe/Au and 33/67 vol.% CdTe/Au for the front and back layers, respectively, as indicated in Table S-I. In the best-fit analysis, these compositions adjust to (88±3)/(12±3) vol.% CdTe/Au and (26±2)/(74±2) vol.% CdTe/Au, respectively, as indicated in Fig. 4 (main text). Thus, the optical nature of the back contact exerts a strong effect on the SE data, and an improved model for this region reduces σ\textsubscript{NCS} from 48 to 37.

The compositional parameters that show the weakest effect and provide no improvement in σ\textsubscript{NCS} over the nominal values of 50/50 vol.% include the contents of CdS in the HRT/CdS and CdS/CdTe interface layers. In fact, Fig. 4 shows that the best fit yields CdS contents of 55 ± 8 vol.% and 48 ± 10 vol.% in the HRT/CdS and CdS/CdTe interface layers, respectively. As suggested by the XTEM image of Fig. 5, the dominant optical effect is due to substrate-induced microscopic roughness since both layer thicknesses, 33 ± 2 nm for the HRT/CdS interface and 31 ± 3 for the CdS/CdTe interface, match the optically-deduced roughness on the uncoated HRT surface. In addition to the two compositional parameters, the electron scattering time \(\tau\) in the Drude component of \(\varepsilon\) for SnO\textsubscript{2}:F also shows a weak effect, meaning that \(\tau\) for the sample measured here matches that of the uncoated SnO\textsubscript{2}:F measured for the reference dielectric function. The result \(\tau = (7.1 ± 0.5) \times 10^{-15}\) s corresponds to a mobility of 50 cm\textsuperscript{2}/V s assuming an electron effective mass for SnO\textsubscript{2} of \(m_e^* = 0.25m_0\).\textsuperscript{51}

Additional optical property parameters deduced in the stepwise analysis of Fig. S-1 and Table S-I include the amplitude \(A_0\), resonance energy \(E_0\), and broadening \(I_0\) that define the \(E_0\) or fundamental bandgap of the dominant CdTe component. \(E_0\) and \(I_0\) have been reported in Table II (main text), and have been used to estimate the stress and excited electron mean free path in the polycrystalline film. The resulting \(\varepsilon\) using the best fit parameters are shown in Fig. S-2 along with \(\varepsilon\) of single crystal CdTe.\textsuperscript{82} Close agreement is found between the spectra with small differences near \(E_0\), as highlighted in the inset. These differences are interpreted in terms of compressive stress and grain boundary scattering, the latter providing a grain size estimate, with both being near the optical detection limits. The optical analysis capability is more powerful for as-deposited CdTe for which the stress is larger and the mean path is shorter, specifically 0.52 ± 0.07 GPa and 26 ± 8 nm, respectively, for the sample of this study.\textsuperscript{53} Finally, it is noted that the ~300 nm mean free path for the CdCl\textsubscript{2} treated sample is consistent with the grain size in the XTEM image of Fig. 5.

![Image](54x114 to 297x303)

**FIG. S-1.** An expansion of Fig. 2 (main text) that includes an additional thirteen parameters defining the optical properties in the SE analysis. The star in the upper left corner represents the end point for step-wise reduction in σ\textsubscript{NCS} for eleven structural parameters. The star in the lower right corner represents σ\textsubscript{NCS} for the total of 24 structural and optical fitting parameters deduced at the end of 152 systematic fitting steps.

<table>
<thead>
<tr>
<th>Parameter #</th>
<th>Parameter yielding greatest reduction in σ\textsubscript{NCS}</th>
<th>σ\textsubscript{NCS}</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>SnO\textsubscript{2}:F: resistivity</td>
<td>48.4</td>
</tr>
<tr>
<td>13</td>
<td>CdTe/Au interface: CdTe vol.% in front</td>
<td>46.3</td>
</tr>
<tr>
<td></td>
<td>CdTe/Au = 67/33 vol.% (nominal) layer</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>CdTe/Au interface: CdTe vol.% in back</td>
<td>37.3</td>
</tr>
<tr>
<td></td>
<td>CdTe/Au = 33/67 vol.% (nominal) layer</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>CdTe: E\textsubscript{0} CP energy (bandgap)</td>
<td>36.2</td>
</tr>
<tr>
<td>16</td>
<td>Glass superstrate: birefringence coefficient, (c_1)</td>
<td>35.3</td>
</tr>
<tr>
<td>17</td>
<td>Glass superstrate: birefringence coefficient, (c_2)</td>
<td>34.8</td>
</tr>
<tr>
<td>18</td>
<td>CdTe: E\textsubscript{0} CP amplitude</td>
<td>34.3</td>
</tr>
<tr>
<td>19</td>
<td>CdTe: E\textsubscript{0} CP broadening</td>
<td>34.1</td>
</tr>
<tr>
<td>20</td>
<td>HRT: (\varepsilon_1) constant offset, (\varepsilon_0)</td>
<td>33.8</td>
</tr>
<tr>
<td>21</td>
<td>SnO\textsubscript{2}:F: (\varepsilon_1) constant offset, (\varepsilon_0)</td>
<td>32.4</td>
</tr>
<tr>
<td>22</td>
<td>CdS/CdTe interface: CdS vol. % in layer</td>
<td>30.5</td>
</tr>
<tr>
<td>23</td>
<td>SnO\textsubscript{2}:F: electron scattering time</td>
<td>30.5</td>
</tr>
<tr>
<td>24</td>
<td>HRT/CdS interface: CdS vol. % in layer</td>
<td>30.5</td>
</tr>
</tbody>
</table>

Table S-I. Optical property parameters added step-wise in order to generate the \(p\)-parameter model with the minimum error function σ\textsubscript{NCS}. The structural and optical property parameters are separated into two groups with the structural parameters considered first (see Table I, main text).
In addition to the SnO$_2$:F Drude parameters whose best fit values are provided in Table II, the constant contribution to the real part of $\varepsilon$ is varied for both the SnO$_2$:F and the HRT layers. The purpose of this variation is to account for small differences in the interband electron concentration in the material. Figure S-3 shows a comparison of the SnO$_2$:F and SnO$_2$ HRT dielectric functions determined by using the best fit parameters. The differences that decrease with increasing photon energy are due to the expected differences in resistivity of the two layers.

REFERENCES