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Real time spectroscopic ellipsometry for analysis and control of thin film polycrystalline semiconductor deposition in photovoltaics

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ABSTRACT

Real time spectroscopic ellipsometry (RTSE) from the near-infrared to ultraviolet has been applied for analysis of the deposition of polycrystalline thin films that form the basis of two key photovoltaic heterojunction configurations, superstrate $\text{SnO}_2/\text{CdS}/\text{CdTe}$ and substrate $\text{Mo}/\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2/\text{CdS}$. The focus of this work is to develop capabilities for monitoring and controlling the key steps in the fabrication of these device structures. Analysis of RTSE data collected during sputter deposition of CdS on a rough SnO_2 transparent top contact provides the time evolution of the CdS effective thickness, or film volume per unit substrate area. This thickness includes interface, bulk, and surface roughness layer components and affects the CdS/CdTe heterojunction performance and the quantum efficiency of the solar cell in the blue region of the solar spectrum. Similarly, analysis of RTSE data collected during co-evaporation of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ (CIGS; $x \sim 0.3$) on a rough Mo back contact provides the evolution of a second phase of Cu_{2-x}Se within the CIGS layer. During the last stage of CIGS deposition, the In, Ga, and Se co-evaporants convert this Cu_{2-x}Se phase to CIGS, and RTSE identifies the endpoint, specifically the time at which complete conversion occurs and single-phase, large-grain CIGS is obtained in this key stage.

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1. Introduction

The most effective thin film solar cell technologies are based on polycrystalline cadmium telluride [CdTe] and copper indium gallium diselenide [$\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ or CIGS] in the superstrate and substrate configurations, respectively [1–4]. These p-type semiconductor absorber layers are incorporated into heterojunction devices with cadmium sulfide (CdS) as the n-type window layer. A critical need exists for measuring, monitoring, and controlling the thickness, structure, phase, and composition of these solar cell component layers in real time during their deposition in the same configuration as is used for solar cell manufacturing. Significant challenges are encountered in applying real time spectroscopic ellipsometry (RTSE) to meet this need.

First, the underlying substrates on which the solar cell component layers are deposited are quite rough. These substrates include the high resistivity transparent (HRT) SnO_2 films on which the CdS/CdTe layers are deposited and the opaque Mo films on which the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2/\text{CdS}$ layers are deposited. RTSE modeling of the initial deposition must simulate a process in which the voids in the surface roughness layer on the substrate film are filled with depositing film material,

thus evolving into a roughness layer at the interface to the growing film. Simultaneously with this process, interfacial reactions and modification of the underlying material may occur, and detection of these effects by RTSE is a key goal as well.

Second, the temperature (T) dependence of the optical properties of the superstrate or substrate component layers is required, since inevitably superstrate/substrate T is a key deposition variable that influences nucleation, coalescence, and the resulting grain structure [5,6]. In the case of the CdTe deposition, this is a significant challenge since the superstrate structure incorporates several optically transmitting layers on soda-lime glass (SLG) – in contrast to CIGS deposition, in which case the top-most substrate layer of Mo is opaque.

Third, the optical properties of the polycrystalline layers may evolve with thickness due to the effects of grain size, strain, and even multiple phases. An important goal is to take such effects into account in order to obtain the highest quality fits and, thus, extraction of maximum information [5–7]. For example, in the optimum three-stage CIGS deposition process, the film evolves a second near-surface phase of Cu_{2-x}Se during two of the stages of the widely-used three stage process [8–11], and this Cu_{2-x}Se phase must be incorporated into the RTSE modeling.

In previous efforts, RTSE has been applied to address such issues in multi-step deposition processes for thin-film hydrogenated silicon photovoltaics technology [12]. The present paper will describe how these issues are in the process of being addressed in the analysis

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of RTSE data collected during thin film polycrystalline CdTe and Cu(In_{1-x}Ga_x)Se₂ solar cell fabrication.

2. Experimental details

In this study of the CdS/CdTe solar cell fabrication, the CdS was deposited by magnetron sputtering at a substrate temperature of 250 °C, a radio frequency (rf) power of 200 W, an Ar pressure of 2.67 Pa, and an Ar flow rate of 23 sccm. The superstrate was NSG-Pilkington TEC-15 glass coated with a SnO₂ high resistivity transparent (HRT) layer. TEC-15 glass is SLG over-deposited with a tri-layer, yielding the structure SLG/SnO₂/SiO₂/SnO₂:F. The deposition time for the CdS layer was 14.5 min for an intended film thickness of 0.12 μm.

The CIGS layers were deposited by the three-stage co-evaporation process onto opaque Mo-coated SLG substrates. In deposition stage I, In, Ga, and Se are co-evaporated at a flux ratio of In:Ga:Se = 7:3:40 [as controlled by electron impact emission spectroscopy (EIES)] onto the SLG/Mo substrate held at $T = 400$ °C. After deposition of a ~0.7 μm thick precursor film of (In_{1-x}Ga_x)₂Se₃ (IGS; $x = 0.30$), the In and Ga evaporation source temperatures are reduced to terminate co-evaporation, which defines the end of stage I. To initiate stage II, conversion of IGS to CIGS, T is increased to 570 °C, and the source temperature of Cu is increased to obtain a flux ratio of Cu:Se = 1:10, as controlled by EIES. After a rapid increase in film emissivity is observed, indicating a rapid increase in free electron concentration near the surface, the source temperature of Cu is reduced to terminate the Cu flux, defining the end stage II. This emissivity increase is identified by a step increase in the substrate heater power needed to maintain a constant $T = 570$ °C. To start stage III, conversion of excess Cu to CIGS, the evaporation source temperatures of In and Ga are again increased for a rate ratio of In:Ga:Se = 7:3:40. Near the end of stage III, as defined by a rapid decrease in film emissivity at $T = 570$ °C, again measured by the substrate heater power, the source temperatures of In and Ga are reduced to terminate co-evaporation.

Real time SE measurements for both the SnO₂/CdS and Mo/CIGS device structures were performed on the growing CdS and CIGS films using a rotating-compensator multichannel spectroscopic ellipsometer [13,14] having a spectral range from 0.75 to 6.5 eV (J.A. Woollam Co., M2000-DI). During CdS deposition, RTSE measurements were taken every 2.4 s, corresponding to a CdS effective thickness increment of ~3 Å. During stages II and III of CIGS deposition, measurements were taken every 3.0 s, corresponding to CIGS effective thickness increments of ~3 and ~13 Å at the transitions to pure phase CIGS near the ends of stages II and III, respectively.

The RTSE data were fit by using a Levenberg–Marquardt method, a non-linear regression algorithm to minimize the square root of the mean square error (MSE) between the experimental and best fit $N = \cos 2\psi$, $C = \sin 2\psi \cos \Delta$, and $S = \sin 2\psi \sin \Delta$ spectra. In these expressions, ψ and Δ are defined as usual by $r_p/r_s = \tan \psi \exp(i\Delta)$, where r_p and r_s are the complex amplitude reflection coefficients for linear p and s polarizations, with planes of vibration parallel (p) and perpendicular (s) to the plane of incidence. A division by $3N - m$ generates the mean, where N is the number of spectral positions and m is the number of fitting parameters.

The data collected during the CdS deposition were analyzed using reference spectra for the complex dielectric function ε at 250 °C for each component of the multilayer stack including SLG, SnO₂ (I), SiO₂, SnO₂:F, SnO₂ (II), and CdS, whereby two different versions of ε are used for SnO₂. The second form (II) is the top-most HRT layer on which the CdS is deposited. The procedures for determining these reference ε spectra are described in Ref. [15]. The data collected during CIGS deposition were analyzed using 570 °C reference ε spectra deduced as components of this study for each material of the device structure including Mo, CIGS ($x = 0.30$), and Cu_{2-x}Se ($x = 0.20$), whereby the two compositions were determined by energy dispersive X-ray analysis. The ε spectra for Mo were obtained in a heating cycle prior to IGS deposition; those for CIGS were obtained from the single-phase bulk layer near the end of

stage II; and those for Cu_{2-x}Se were obtained from a film deposited under conditions identical to the stage II process, but on an oxidized Si wafer substrate using the procedures described in Ref. [16].

3. Results and discussion

3.1. RTSE monitoring of CdS in CdTe solar cell devices

Fig. 1 depicts RTSE analysis results for CdS deposition on the TEC-15/SnO₂ (HRT) superstrate surface. The information extracted in non-linear regression analysis includes the surface roughness on the top-most superstrate layer at $t = 0$ and the time evolution of (a) the CdS bulk layer thickness; (b) the volume fraction of CdS within the roughness modulations of the SnO₂ surface as these modulations are transformed from surface to interface roughness; (c) the CdS volume fraction in the CdS surface roughness layer; and (d) the thickness of CdS surface roughness layer. Also shown in Fig. 1(e) is the time evolution of the square root of the MSE, which can be used in the evaluation of different structural and optical models for describing the growth process.

At $t = 0$, the SnO₂ layer on the superstrate presents a rough surface with a roughness layer thickness given by 450 ± 12 Å. The structural evolution of CdS on this surface, as depicted in Fig. 1, exhibits interface filling ($0 < t < 4.4$ min) and bulk layer growth ($4.4 < t < 14.5$ min) regimes. When the shutter is opened to initiate CdS deposition, the interface filling regime is characterized by two effects that occur simultaneously. First, the voids in the surface roughness layer of the top-most SnO₂ begin to fill with CdS, with a volume percent in the roughness layer given by $f_i(\text{CdS})$. Second, the CdS begins to conformally cover the SnO₂, forming its own roughness layer of thickness $d_s(\text{CdS})$ and CdS volume percent $f_s(\text{CdS})$. The onset of bulk layer growth is observed upon completion of interface filling at $t = 4.4$ min, which occurs when $f_i(\text{void}) \rightarrow 0$. For $t > 4.4$ min, the CdS volume percent in the interface roughness layer is fixed at its final value of $f_i(\text{CdS}) = 30.0 \pm 0.4\%$. During bulk layer growth, $4.4 < t < 14.5$ min, the bulk layer thickness

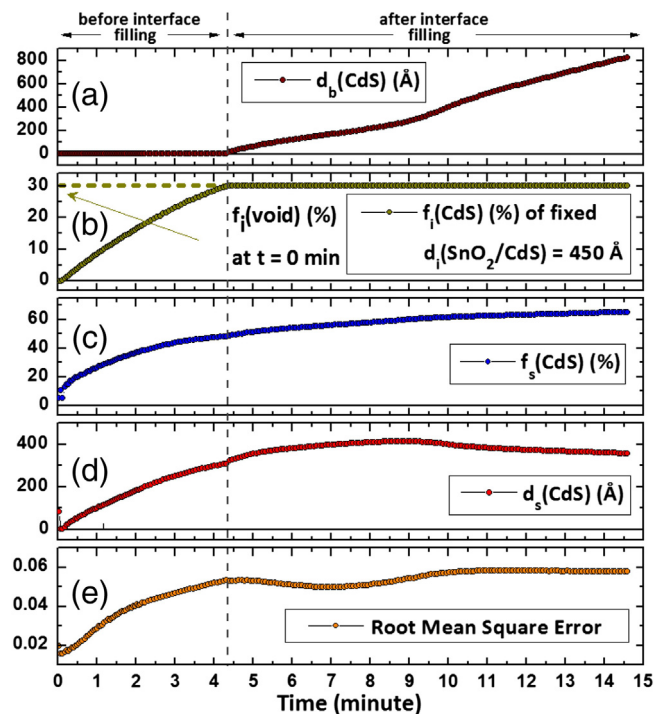


Fig. 1. Structural parameters deduced by RTSE that describe the growth of a 1200 Å CdS film on top of a rough SnO₂ superstrate film, including (a) the CdS bulk layer thickness; (b) the CdS volume percentage in the SnO₂/CdS interface roughness layer; (c) the CdS volume percentage in the CdS surface roughness layer; (d) the CdS surface roughness layer thickness; and (e) a measure of the quality of the fit to the RTSE data given as the square root of the mean square error (MSE).

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