**Spectroscopic ellipsometry studies of 3-stage deposition of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ on Mo-coated glass
and stainless steel substrates**

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ABSTRACT

In order to achieve proper process monitoring and control for the deposition of thin film photovoltaic absorbers, for example $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS), optical techniques such as spectroscopic reflectometry and polarimetry are advantageous because they can be set up in an unobtrusive manner in the manufacturing line, and collect data in-line and in-situ. The use of these techniques requires accurate optical models that correctly represent the properties of the layers being deposited. In this study, Spectroscopic ellipsometry (SE) has been applied for the characterization of each individual stage of CIGS layers deposited using the three-stage co-evaporation process. Dielectric functions have been determined for the energy range between 0.7 eV and 5.1 eV. As the layers' thicknesses are in the order of 2.5 μm , thickness non-uniformity along with surface roughness has been included in the analysis. A high similarity between the optical models developed for CIGS on glass and on stainless steel substrate was observed. Critical-point line-shape analysis was used in this study to determine the critical point energies of the CIGS based layers. These results can assist in the development of optical process-control tools for the manufacturing of photovoltaic absorbers, increasing the uptime and yield of the production line.

1 INTRODUCTION:

Direct conversion of sunlight into electrical energy (photovoltaic effect) is a cleaner and safer alternative to fossil fuels for energy requirements in the future. Photovoltaics (PV) are promising as they could compete with traditional energy production methods due to expected lower processing costs. The key is to develop large-scale module manufacturing processes while improving conversion efficiencies to reduce the power generation costs and expand the PV power generation market [1].

Low-cost thin-film PV absorber materials currently in the market are amorphous silicon (Si:H), cadmium telluride (CdTe) and copper indium diselenide (CuInSe₂; CIS) and its alloys with Ga and/or sulphur (CIGS). Si:H solar cells have low efficiency (~10 %) due to light induced degradation leading to long term stability issues [2]. Even though CdTe lab-scale cells show high efficiency (~21 %) [3], but the toxicity of Cd and strict environmental regulations make them less attractive. CIGS cells with reported laboratory scale cell efficiency exceeding 20% are promising [4, 5] due to their very high absorption coefficient ($\sim 1 \times 10^5/\text{cm}$) in the visible wavelength range and the fact that they can be deposited in a variety of substrates, both rigid and flexible. [6-9]. CIGS lab-scale cells made on flexible metal substrates reported efficiencies above 17 % [10, 11].

A typical CIGS solar cell structure consists of a molybdenum back contact, a CIGS absorber layer, a thin buffer layer (CdS, ZnS or In₂S₃) and a transparent conducting oxide (TCO) bi-layer made up of intrinsic and aluminum doped zinc oxide which acts as a front contact. This photovoltaic stack is traditionally deposited on a rigid substrate (soda-lime glass), but recent trends show that flexible substrates such as stainless steel and polymer-based materials are also being used. Many

applications such as light photovoltaic (LPV), building integrated photovoltaics (BIPV) and space power generation can be achieved using these flexible substrates which allow roll-to-roll manufacturing leading to substantial cost reductions [12].

CIGS absorber layer can be deposited using various deposition techniques such as co-evaporation [13], selenization [14], sputtering [15], spray pyrolysis [16] and electro-deposition [17]. Laboratory scale CIGS solar cells produced using 3-stage co-evaporation process have demonstrated high efficiencies in the order of $\eta > 21\%$ [4], while commercial modules achieved efficiencies varying between $11\% < \eta < 16\%$. CIGS modules with high efficiency can be achieved if the composition and thickness of the absorber layer are controlled within a particular range.

The critical need for measuring, monitoring, and controlling the thickness, structure, phase, and composition of these solar cell component layers in real time, during their deposition can be fulfilled by real time spectroscopic reflectometry which offers rapid and relatively low cost in-line process control but it requires accurate optical models which represent the main properties (e.g. thickness and composition) of the photovoltaic layers [18].

Spectroscopic Ellipsometry (SE) is a non-destructive linear optical technique that uses polarized light to characterize thin film and bulk materials. The light undergoes a change in polarization as it interacts with the sample structure. Ellipsometry measures the change in polarization as light reflects or transmits from a material structure. The optical constants (complex refractive index) and film thickness of the sample are extracted from the change in the polarization state by light reflection or transmission with the help of appropriate optical models.

Optical models developed for thin CIGS films (<700 nm) can be found in the literature [19-21]. These models are very successful at describing not only the thin CIGS layers, but when combined with models for the full photovoltaic stack, they can very accurately predict the quantum efficiency of the device. However, these models do not properly describe thick samples (between about 1.5 and 2.5 μm) and do not take compositional gradients into account. Spectroscopic Ellipsometry is a powerful tool to develop proper optical models for thick samples, as it is quite sensitive to surfaces/interfaces to characterize the complex dielectric functions precisely [18]. From this dielectric function, characteristics of the bulk layer such as the composition and phase can be determined. All this information can assist in understanding the fabrication process as well as more realistic quantum efficiency modeling [22].

In order to develop the optical models for thick CIGS-based polycrystalline layers, samples grown by the three-stage evaporation process were analyzed using SE, and the thicknesses, roughness and complex dielectric functions were determined. The thickness and surface roughness thus obtained were compared with values measured by other techniques. Optical models developed for samples stopped after each deposition stage, took into consideration thickness non-uniformities and surface roughness.

Standard line-shape analysis has been used in this study to determine the critical point energies in the complex dielectric functions of the CIGS based layers. In this analysis, the theoretical formulas of the dielectric function are fitted to the second derivative of the dielectric functions obtained from the SE data modeling. This method relies upon the observation that prominent features in the optical response are due to inter-band transitions in the vicinity of critical points in the joint density

of states. Thus, inter-band transitions at the critical points were characterized from these dielectric functions by this analysis.

To confirm the validity of resulting SE analysis, optical models developed for CIGS on a glass substrate were applied to the characterization of CIGS on a flexible substrate (stainless steel).

2 EXPERIMENT

The three-stage process, originally developed by researchers at the National Renewable Energy Laboratory (NREL), was used to deposit CIGS. In the first stage In, Ga, and Se are co-evaporated. After an $(\text{In,Ga})_2\text{Se}_3$ precursor film of prescribed thickness is deposited, the second stage is initiated where the substrate temperature is increased to a higher temperature, and Cu and Se are evaporated in the absence of In and Ga fluxes. CIGS is formed as Cu atoms diffuse into the precursor $(\text{In,Ga})_2\text{Se}_3$ film. Excess Cu starts accumulating on the surface as Cu_{2-x}Se as the material becomes stoichiometric. After this Cu-poor to Cu-rich transition, third stage is initiated. In this stage, In and Ga are evaporated in absence of Cu flux at the same temperature. A Cu-rich to Cu-poor transition marks the end of third stage when the source temperatures of In and Ga are reduced to stop co-evaporation. Three-stage CIGS was co-evaporated in a chamber fitted with Indium, Gallium, Copper, and Selenium sources [13]. Soda-lime glass coated with a 300 nm layer of molybdenum, and stainless steel with a metal stack capped by a 500 nm layer of molybdenum, were used as substrates.

A similar process was used to deposit CIGS samples on stainless steel substrates. These samples had the same nominal composition as the samples prepared on glass substrates. For the rest of this work, samples will be referred as 1, 2 and 3 respectively, depending on the stage they were stopped

at, for both glass and stainless steel substrates, indicating the substrate nature wherever it is relevant.

A rotating-compensator multichannel ellipsometer (J.A. Woollam, RC2) was used to collect ellipsometric spectra at 65°, 70° and 75° incident angles in the spectral range of 0.7-5.1 eV with 0.01 eV resolution. The data collected at all three angles were analyzed simultaneously. Depth profiles of the concentration of Cu, In, Ga and Se across the thickness of the samples were obtained by secondary ion mass spectroscopy (SIMS) in “Time-of-flight” (TOF) mode. Samples were analyzed using an ION-TOF V TOF-SIMS instrument in static mode. A 25 keV Bi⁺ beam was used for analysis while in-situ Cs⁺ beam was used for sputtering with a 300 µm raster area and a 50 µm detection area. The thickness of each sample was determined using a stylus profilometer (Dektak M150), and was used for TOF-SIMS depth calibration.

3 RESULTS AND DISCUSSION

Fig. 1 shows Scanning Electron Microscope (SEM) images of the (a) surface and (b) cross section of CIGS after 3-stage deposition process. The surface topography for the samples deposited on glass is clearly different from that on stainless steel, showing apparently larger grain sizes. The samples on different substrates were prepared in separate batches, and the thickness of the CIGS layers on glass were on average 0.5 µm thicker than those on stainless steel.

The results of the TOF-SIMS depth profiles are shown in Fig. 2 for each of the stages of the deposition. Sample 1, stopped after the 1st stage shows uniform concentration of In, Ga and Se

164 along the thickness. Cu is added in the 2nd stage, which reacts with IGS and forms CIGS. As Ga
165 diffusion is slower than Cu diffusion, the Ga depth profile dips moving towards the surface in
166 sample 2, as shown in Fig. 2. In sample 3, the Ga concentration rises moving towards the surface
167 as in 3rd stage Ga and In are co-evaporated under Se flux. It is also noticeable that once Cu is
168 introduced in the second stage, it diffuses to the back of the absorber layer. Samples grown on
169 glass and stainless steel showed similar concentration profiles with minor differences.

171 3.1 Spectroscopic Ellipsometry Analysis

172 Spectroscopic Ellipsometry (SE) data from all three sample types was analyzed to understand the
173 way the dielectric function changes while stepping from one stage of deposition to another in the
174 3-stage deposition process. Ellipsometry measures a change in polarization as light reflects or
175 transmits from a material structure and compares it to a model. Change in polarization is quantified
176 by the amplitude ratio, $\tan(\psi)$, and the phase difference, Δ , expressed as $\tan(\psi)\exp(i\Delta)=r_p/r_s$, where
177 r_p and r_s are the complex electrical field reflection coefficient for the p- and s- polarized light,
178 respectively [18].

181 SE data analysis was performed on the measurements collected at multiple angles (65°, 70°, 75°)
182 to obtain the dielectric function. When there are unknown dielectric functions in a sample,
183 dielectric function modeling for layers is carried out with the help of regression analysis where it
184 is assumed that the dielectric function of an analyzed layer is independent of thickness. In this
185 analysis, we have used a Cauchy model to define the dielectric function in the wavelength region
186 where the CIGS material is transparent i.e <1 eV. This Cauchy model was used as a starting point
187 in the Kramers-Kronig-consistent B-Spline function which was fit to the experimental spectra (ψ ,

Δ) by regression analysis. This fit is based on the Levenberg-Marquardt algorithm to reduce the least-squares difference between experimental and model-generated data. Thickness of the material of interest obtained by ancillary experimental techniques was used as a fixed parameter in the regression analysis while the surface roughness is modeled with Bruggeman Effective Medium Approximation (EMA) where it is assumed a 50 vol.%/50 vol.% mixture of underlying material and free space. We have also considered thickness non-uniformity across the spot size and angle offset due to thick CIGS layers in the analysis. We further parameterized the extracted dielectric function using Tauc-Lorentz oscillators to provide physically meaningful parameters such as energies, broadening parameters, and resonance exponents related to the band structure and excited state relaxation times of the CIGS material under study. From the parameterized dielectric function, we performed the fitting again, to determine the dielectric function more accurately [18].

The generic model used for the SE analysis is shown in Fig. 3. For Stage I (Sample 1) the model is based on an IGS bulk layer with surface roughness. For stages II and III (Samples 2 and 3) the model considers a full CIGS bulk layer, which is formed after the first stage, along with surface roughness. As the Mo layer is opaque in the wavelength range analyzed here, it was treated as a substrate for every sample using the dielectric functions developed by the U. Toledo group [21]. In order to model the IGS and CIGS layers, the optical models incorporated surface roughness and thickness non-uniformities across the spot size. In samples 2 and 3 the Ga concentration varies as a function of thickness, as can be seen in the SIMS plot shown in the Fig. 2. The complex dielectric function obtained for these samples from SE are affected by this variation. An excellent result was obtained when simultaneously fitting the experimental spectra (ψ & Δ) collected at various

incident angles to the optical model, indicating that the SE analysis is valid and appropriate. As an example, in Fig. 4 we show the fit for one incident angle for sample 1 on glass substrate. For clarity only one out of two data points of experimental spectra are shown in Fig.4.

Fig. 5 (a) shows the imaginary part of the complex dielectric function of IGS on glass substrate. Figs. 5 (b) and (c) similarly show the corresponding dielectric functions of the CIGS layer in samples 2 and 3. Fig. 5 (d) shows the evolution of the imaginary part of the dielectric function from one stage of deposition to the next. CIGS material formed in the second stage has few differences with respect to the CIGS formed in the third stage. Given the similarity in the Cu distribution measured by SIMS for both samples, the differences can be attributed to the change in the concentration of Ga.

3.2 Critical Point (CP) Analysis

A standard CP analysis has been performed for the dielectric functions of the CIGS-based layers in order to determine the CP energies of the optical transitions in the energy range 0.7 eV to 5.1 eV. In this analysis, the second derivative spectra of the modeled complex dielectric function are used and the theoretical formulas for second derivative of the dielectric function expressed by:

$$\frac{d^2\epsilon}{dE^2} = n(n-1)A \exp(i\phi) (E - E_p + i\Gamma)^{(n-2)} ; \quad n \neq 0$$

$$\frac{d^2\epsilon}{dE^2} = A \exp(i\phi) (E - E_p + i\Gamma)^{-2} ; \quad n = 0$$

Where A, ϕ , E_p and Γ show the amplitude, phase, position, and width of the peak. CP is classified into one-dimension ($n=-1/2$), two-dimension ($n=0$), and three-dimension ($n=1/2$) according to the

235 wave vector involved in the optical transition and the joint density of state (DOS) around the CP
236 depends on the band structure. Furthermore, when an optical transition exhibits excitonic behavior
237 $n = -1$ is employed in the equation. From the CP analysis using the second derivative spectra, the
238 specific features of the CP were characterized selectively.

239
240 Since the dielectric functions obtained by the analysis were based on B-spline polynomials there
241 was no need to perform smoothening for the differentiation.

242
243 For accurate CP analysis, from the modeled dielectric functions (ϵ_1 & ϵ_2) obtained from SE analysis,
244 second derivative spectra were calculated for the energy range between 0.7 eV and 5.1 eV with
245 uniform data spacing. Fig. 6 (a), (c), (e) show the second derivative of modeled ϵ_2 spectra (circles)
246 for samples 1, 2 and 3 (glass substrate) and the calculated fitted spectra (line) from the CP analysis.
247 An excellent fitting between modeled and calculated spectra was observed when the excitonic
248 transitions ($n = -1$) were assumed for all the critical points in all the samples. Earlier studies have
249 been performed using 2D line shape ($n = 0$) [8, 23, 24].

250
251 Fig. 6 (a), (c), (e) show the fitting procedure from where A , ϕ , E_p and Γ values of each CP are
252 extracted for each sample. In the case of IGS, CP analysis shows a band gap critical point (E_0) at
253 2.315 eV and another peak at 4.7 eV. From the fig. 6 (b) it can be seen that the dielectric function
254 is quite smooth over the measured region while dropping to zero below E_g . This result confirms
255 that the SE analysis utilized produced reasonable dielectric functions. The transition peaks
256 obtained for the IGS layer are in agreement with those reported by Pradhan *et al.* [21].

The structure of the fundamental absorption edge of CIGS is well established [25]. CIGS is a semiconductor with a direct band gap at the Brillouin-zone center Γ . In this material, three transitions called $E_{0(A)}$, $E_{0(B)}$ and $E_{0(C)}$ from lower to higher energy arise from a threefold valence-band maximum which is composed of three non-degenerate states. According to Alonso *et al.* [26], the peak at the lowest energy seen in the ϵ_2 spectra of samples 2 and 3 is composed by the two closer peaks $E_{0(A, B)}$ and the following one corresponds to $E_{0(C)}$. The ordinary polarization $E \perp c$ is expected to dominate the spectra in polycrystals. Hence, the main contribution to the first observed peak comes from the component (A or B) with $E \perp c$. Of the two components, $E_{0(A)}$ corresponds to CIS and $E_{0(B)}$ to CGS-like band arrangement. At room temperature A and B peaks are very close hence we see them as one peak in the fig. 6 (d).

The ϵ_2 spectra from samples 2 and 3 above the direct band gap (E_0) have very similar features. The main transitions that contribute to ϵ_2 have been assigned to critical points at the Brillouin-zone center Γ and edge N and T points according to band-structure calculations by Jaffe and Zunger [27] for ternary compounds (Cu-III-VI_2) and correlating the observed transitions to those of binary zincblende analogues. The transitions are labelled according to the ref. [23] and are related to the standard zincblende notation. The different observed transitions within calculated band structure are listed in Table 1 and labelled in fig. 6 (d) and (f).

$E_{\Gamma X}$ is an indirect transition from $\Gamma_{5v}^{(1)} \rightarrow \Gamma_{3c}$ at 2.2 eV which matches the calculated value. The prominent E_{1A} transition observed in samples 2 and 3 were very close to each other. E_{1B} , having a slightly larger broadening, is observed only in sample 3 and not in sample 2. Crystal-field splitting of the valence band at the N point leads to the energy separation of about 0.8 eV between $E_{1(A)}$ and $E_{1(B)}$ as seen in the Sample 3 spectra. This effect is either small or non-existent in sample 2 where

there is only one observed E_1 transition. The transitions observed around 4 eV in these two samples were identified as $E'_{\Gamma X}$, the gap at the Γ point by comparing with previously calculated values [23, 27]. Transitions seen at higher energy around 5 eV correspond to E_{2B} which is a T-point transition. All the energies observed are close to the theoretical values from ref. [23, 27].

Fig. 7 shows the comparison between dielectric functions determined for the CIGS sample 3 on glass and stainless steel substrates respectively. The dielectric functions of CIGS on both glass and stainless steel substrates coincide, except for a slight difference at the E_0 peak. This may be due to compositional fluctuations caused by the deposition tool leading to changes in the grain size distribution. Change in the grain size effects the lifetime broadening parameter [28]. This confirms that the optical models are robust and can be applied to CIGS of varying thicknesses and roughness over different substrates.

Next step in the development of these optical models for CIGS would be taking the effect of varying Ga concentration along the thickness into consideration. The compositional gradient of Ga across the thickness of the CIGS layer in Sample 3, “double grading”, is a consequence of the 3-stage deposition process. Changes in the Ga concentration cause changes in the dielectric functions. The results shown here are an outcome of the cumulative effect of variation of the Ga concentration in the CIGS layer in sample 2 and 3. In order to determine the effect of Ga concentration on the dielectric function at each energy point, the CIGS layer model needs to be graded as per the Ga concentration variation. This will be a part of future studies.

4 SUMMARY

The dielectric functions of polycrystalline CIGS-based layers formed after each stage of the Cu(In_{1-x}Ga_x)Se₂ three-stage co-evaporation process have been determined by using spectroscopic ellipsometry. An initial model for the dielectric functions was extracted from ellipsometric data of CIGS layers on glass substrates, with a thickness in the order of 1.5 - 2.5 μm, incorporating the surface roughness observed in the thick layers. SE analysis was performed and an excellent fit between the model and the ellipsometric data was obtained for CIGS deposited both on glass and on stainless steel substrates. Thicknesses obtained from SE have been verified by profilometry, SEM and SIMS measurements. To characterize the transition energies in the energy range between 1 and 5.1 eV, critical point line-shape analysis was performed for the dielectric functions obtained. Inter-band transitions have been identified and verified by analogy with previously published work. Spectral dependencies of the optical functions of CIGS on the Ga concentration need to be investigated in order to understand the structural evolution and identify the compositional fingerprints for real-time process control applications.

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6 Tables:

Table 1: Inter-band transitions in Sample 1, 2 & 3 according to the notation used by Alonso et. al. [7]

<u>Label</u>	<u>Energy (eV)</u>		
	<u>Sample 1 (IGS)</u>	<u>Sample 2 (Cu-rich CIGS)</u>	<u>Sample 3 (Cu-poor CIGS)</u>
E_0	2.315	1.315	1.265
$E_{\Gamma X}$	-	2.218	2.216
E_{1A}	4.782	3.073	3.131
E_{1B}			3.848
$E'_{\Gamma X}$	-	4.377	4.323
E_{2B}	-	5.044	5.136

7 Figure Captions

- Figure 1: (a) Surface profile and (b) Cross-section SEM images of CIGS after 3-stage deposition process on Glass and Stainless steel (SS) showing different surface roughness and grain size.
- Figure 2. Depth profiles determined by SIMS (a) Sample 1(stopped after first stage), (b) Sample 2 (stopped after second stage) shows that the concentration of Ga dips as soon as the second stage starts. (c) Sample 3 (stopped after third stage) shows that the concentration of Ga rises back once the third stage deposition begins. The bottom pictures show the structure of (d) Sample 1 consisting of Mo layer topped with IGS layer, (e) Sample 2, Mo layer and Cu-rich CIGS layer and, (f) Sample 3, Mo layer and CIGS layer.
- Figure 3. Sample model showing bulk layer with surface roughness on top opaque Molybdenum layer used for SE analysis
- Figure 4. Fit and experimental data for Sample 1 (IGS) in the energy range 0.7-5.1 eV.
- Figure 5. Complex dielectric function ϵ_2 for samples a) 1, b) 2 and c) 3 on top of an opaque molybdenum layer determined from SE analysis. d) Evolution of ϵ_2 as the deposition progresses.
- Figure 6. Second derivative ϵ_2 spectra calculated from the dielectric function shown in the fig.5 (circles) and the fitted spectra calculated from the CP analysis for (a) Sample 1, (c) Sample 2, (e) Sample 3. (b), (d) & (f) Shows inter-band transitions in dielectric functions of Sample 1 (IGS), Sample 2, and Sample 3 layers.
- Figure 7. Comparison of ϵ_1 and ϵ_2 spectra determined for CIGS after 3rd stage of deposition on Glass substrate vs Stainless steel substrate.

(a)

(b)

First Stage

(a)

Second Stage

(b)

Third Stage

(c)

Sample 1

(d)

Sample 2

(e)

Sample 3

(f)

Figures 3

Figures 4

Figures 5

(a)

(b)

(c)

(d)

Figures 6

(a)

(b)

(c)

(d)

(e)

(f)

Figures 7