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Quantitative analysis of cell transparency and its implications for the design of chalcopyrite-based tandems

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ABSTRACT

With respect to an efficient tandem construction the transmission of the top cell merits highest attention. For a cell on the basis of $CuGaSe_2$ we present here a detailed optical characterization. The initial focus is on the investigation of the individual layers making up the cell stack, followed by their combination. Results from considerations on light trapping in the $CuGaSe_2$ are shown as well as modifications of the transparent conducting back contact related to the absorber growth. Material parameters obtained in this way serve as input for an optical model. As an outlook we present a loss diagram for the short circuit current density of the bottom cell related to the optical properties of the $CuGaSe_2$ top cell.

1. Introduction

Polycrystalline chalcopyrite thin films are of high interest for low-cost production of efficient photovoltaic modules. The material family covers a wide range of band gaps which makes it also promising for tandem applications. With $E_g = 1.7\,eV$ $CuGaSe_2$ (CGS) is a good candidate to be used as top cell absorber [1,2]. For efficient tandems the top cell ought to be highly transparent below its band gap. Yet, the actual transmission of CGS-based solar cells with transparent conducting oxide (TCO) back contact is only around 60% [3]. In order to increase this value and hence the tandem efficiency, a detailed investigation of the optical properties of the top cell becomes necessary. This analysis then allows the attribution of transmission losses to material properties.

This work presents the result of extensive optical studies of the various layers making up the transparent CGS top cell. Investigations start from the single layers but then take into account possible interactions among them as well. In this way the input for an optical model of the top cell is created which gives access to loss contributions and opens the view on possible improvements.

2. Experimental

Our absorber material is polycrystalline CGS with a thickness of about 1.6 μm, and is grown by physical vapor deposition (PVD) in a three stage process [4]. For a top cell a TCO, in our case fluorine-doped tin oxide (FTO), is needed as back contact. The TCO for the window layer is a combination of an undoped (i-) and an n^+-doped, sputtered ZnO layer of roughly 100 and 500 nm thickness, respectively. It finishes the cell on top of a 50 nm CdS buffer layer deposited from a chemical bath onto the absorber. The setup of our device as investigated here and used in a mechanically stacked tandem is illustrated in Fig. 1. Compared to monolithic integration the stacking offers independent choice of process parameters for top and bottom cell preparations and is therefore the initial approach for tandems. Thus our optical investigations start from an actual TCO/CdS/CGS/FTO/glass cell as a base for the future improvement.

All of the above described layers were first prepared separately on glass substrates (soda-lime glass, SLG, or quartz). In the next step, combinations of the layers were investigated up to the complete cell stack.

Transmission (T) and reflection (R) measurements were carried out using an UV–Vis spectrophotometer with an integrating sphere. The curves were modeled with the program Diplot [5] which uses the transfer matrix formalism suitable for the description of thin film systems. This formalism takes into account coherent propagation of the light (multiple reflections and interference) within individual layers [6]. In addition, the program gives a set of parameters making allowance for basic optical as well as non-ideal material properties. The fundamental variables describe the absorption edge (band gap energy E_g and exponent, i.e. direct or indirect semiconductor, among others) or are related to the interference fringes (layer thickness d and refractive index n, specification of the latter one by $n(E = 0)$ and resonance energy). Material imperfections find consideration in

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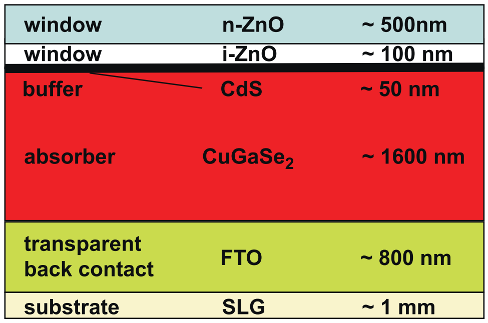

Fig. 1. Layer stack of the transparent chalcopyrite-based top cell. The $CuGaSe_2$ absorber is grown on fluorine-doped tin oxide (FTO) used as transparent back contact. On top of a thin CdS buffer, an i- and n-ZnO layer finish the cell and build the heterojunction with the p-type absorber.

terms of an Urbach tail [7,8] (Urbach energy E_u), defect absorption (in an exponential approach with defect prefactor A_d) and for single layers surface unevenness via scattering coefficient s_k (leading to reduced coherent superimpositions) and thickness variation *dd* (distribution of thicknesses described by averaging). If required free charge carriers can be added in the form of a Drude term [9].

The CGS absorber showing the most uneven surface within the stack was subject to experiments forinvestigating the influence of surface roughness on modeling. Highly textured interfaces may lead to trapping of the light within the layer and hence increase absorption. The model used here does not specifically account for light trapping and misinterpretations of the optical constants might therefore result.

For performing comparative transmission and reflection measurements the CGS was polished by treatment with a 0.08% bromine–methanol solution for 15, 30 or 45 s. It was observed before for materials like $CuInSe_2$ that this kind of chemical etching smoothened the surface [10]. These experiments were carried out for absorber material grown directly on SLG as well as on FTO at the ENSCP in Paris. Characterization was complemented by scanning electron and atomic force microscopy (SEM and AFM).

Concerning the FTO substrate we compared various types and additionally considered the material modification during the process. Optical measurements were performed for FTO samples of type AsahiU [11] before and after the process, the latter one being obtained by etching the absorber from the FTO again. For separating the influence of the temperature to which the FTO is exposed during the CGS growth from the one caused by interactions among the materials, we investigated FTO that was heated at process conditions but without any Cu, Ga or Se deposition.

3. Results

3.1. CGS absorber

A typical transmission curve of a CGS layer grown on SLG is shown in Fig. 2 and values for the essential fitting parameters are given. Modeling of the measured curve was achieved including non-ideal material properties as introduced above.

Only the parameters related to surface roughness (s_k and *dd*) had to be changed in addition to the layer thickness for fitting the optical curves of the polished samples shown in comparison to the untreated case in Fig. 3. The layer thicknesses resulting from the simulation are given in column "d_{sim}" in Table 1. Their decrease corresponds to the frequency change of the interference fringes and is reflected in the increase in transmission as well. This

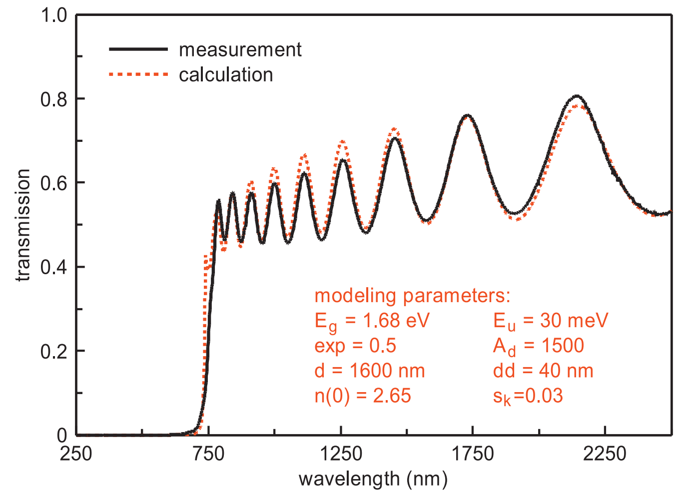

Fig. 2. Transmission of a polycrystalline $CuGaSe_2$ thin film deposited on soda-lime glass. The measured curve is modeled with the program Diplot, values of fitting parameters as described in the text are given in the inset.

latter one is visible in Fig. 3(a) where the transmission of an untreated CGS sample is plotted together with the one of an absorber etched for 30 s. Fig. 3(b) presents the according reflection featuring an absolute gain of about 5%. Including the *T* and *R* measurements of the samples treated for 15 and 45 s in the considerations a tendency of major material loss during the first seconds of etching is observed.

This trend is also visible from direct and hence simulation-independent calculations of layer thicknesses from the distance of neighboring extrema in transmission curves. The underlying relation is

$$n = \frac{1}{4d\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right)},$$

where λ and λ' denote the wavelengths of a pair of minimum and maximum, n is the refractive index of the material and d its layer thickness [12]. Results for the absorber on SLG are given in the last column of Table 1.

To sustain the optical results we performed SEM measurements of cross sections and surfaces. Extracted layer thicknesses are summarized in column "d_{SEM}" of Table 1 and Fig. 4 represents in comparison the top view of a bare (a) and a 30 s etched (b) sample. The smoothing of the surface is obvious.

AFM images (not shown here) reveal this change very well, too, and allow in addition to extract root-mean-square roughnesses. For an example of polished CGS on FTO this value is reduced to about 60% which roughly corresponds to the ratio by which the modeling parameter "scattering coefficient" was changed when adapting the optical curves. Together with a slight adjustment of the "thickness variation", also decreased by polishing, the changes in the curve progression of *T* and *R* could well be followed by the model. This was the case for the sample series grown on FTO as well.

3.2. Transparent conducting oxides

The transmission of the complete top cell stack is profoundly influenced by the optical properties of the transparent back contact. From comparative measurements we found that the net transmission strongly differs from FTO to FTO. Variations in the long wavelength range can partly be attributed to the sheet

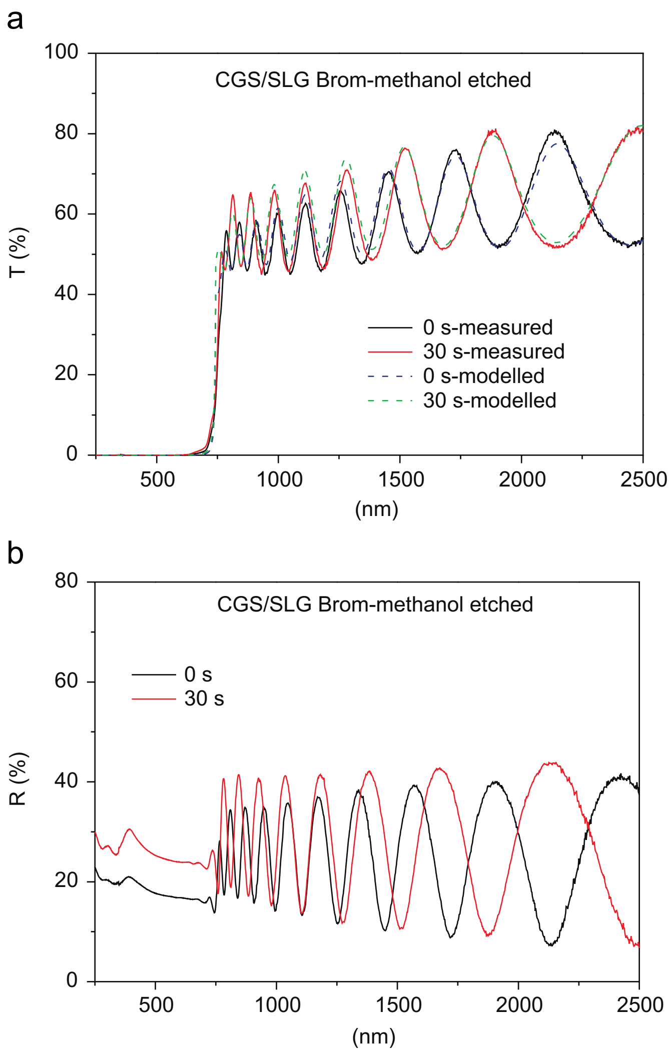

Fig. 3. Comparison of the optical behavior of a $CuGaSe_2$ (CGS) thin film as grown on soda-lime glass (SLG) (black line) to samples etched for 30 s (red/gray) with a bromine solution. The increase in transmission (a) as well as in reflection (b) is obvious. Additionally, simulation results for the transmission curves are included in (a). Starting from the fit of the untreated sample (blue/dark gray dashed) the transmission of the etched absorber could well be modeled by solely changing the parameters describing layer thickness (in good agreement with independently derived values) and surface unevenness (green/light gray dashed).

Table 1
Thicknesses of $CuGaSe_2$ layers grown on soda-lime glass (SLG) as well as on fluorine-doped tin oxide (FTO) and bromine-etched up to 45 s

	t_{etch} (s)	d_{SEM} (μm)	d_{sim} (μm)	d_{calc} (μm)
CGS/SLG	0	1.60	1.60	1.60
CGS/SLG	15	1.33	1.39	1.30
CGS/SLG	30	1.40	1.40	1.46
CGS/SLG	45	1.47	1.27	1.15
CGS/FTO	0	1.60	1.60	
CGS/FTO	15	1.53	1.45	
CGS/FTO	30	1.23	1.33	
CGS/FTO	45	1.23	1.20	

d_{SEM} was obtained from cross sections recorded with electron microscopy, d_{sim} results from simulations of the optical curves and d_{calc} gives additional values calculated from the interference fringes in the transmission measurements.

resistances. Yet, even in our range of interest up to around 1200 nm, which corresponds to the band gap of the bottom cell, strong deviations exist. Differences in layer thickness are one reason, but the type of glass on which the TCO is grown and its transmission also play a crucial role.

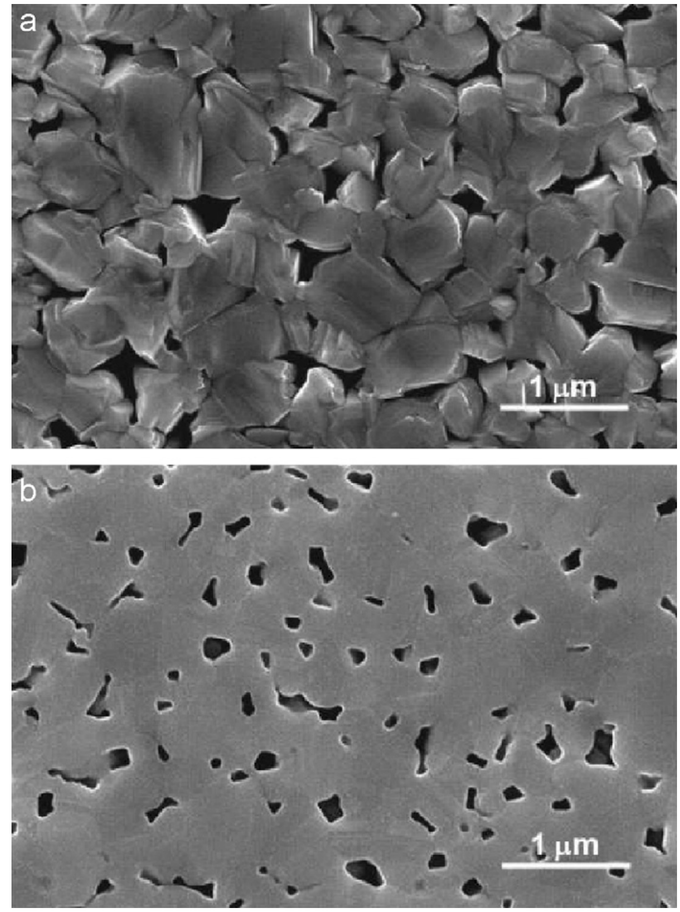

Fig. 4. Electron micrographs of $CuGaSe_2$ absorbers on soda-lime glass. Compared to (a) the sample shown in (b) was bromine–methanol etched for 30 s. The flattening of the surface is clearly visible.

Apart from the properties of the conducting glass as delivered, the behavior in combination with the absorber deposition has to be considered. High substrate temperatures lead to modifications as sustained by our experiments. Fig. 5 illustrates the changes in terms of optical transmission and separates the impact of the high process temperature from the influences of the material deposition and subsequent interactions. Heating only results in a significantly increased transmission in the infrared, which is in accordance with an augmented sheet resistance, as measured after the process by four point probe. A decrease in transmission in the range of the interferences and especially around the band edge occurs however when subjecting the FTO to CGS deposition. Hence, changes in the optical properties of FTO when integrated in the stack have to be taken into account.

Furthermore, variations occur for the front TCO, namely within the ZnO fabrication. In the optical modeling there was made allowance for, so that a description of the complete window system (CdS, i- and n^+-ZnO) was reached. A superimposition of these layers onto the CGS results experimentally as well as theoretically in an increased transmission. This comes along with a grading of refractive indices reducing reflection losses at the interfaces. Thus, we take an optical profit from the window in addition to the electrical one. Finally, judging from the comparison with the measurement, the optical data of the complete top cell stack are modeled accurately when using the input parameters as developed here.

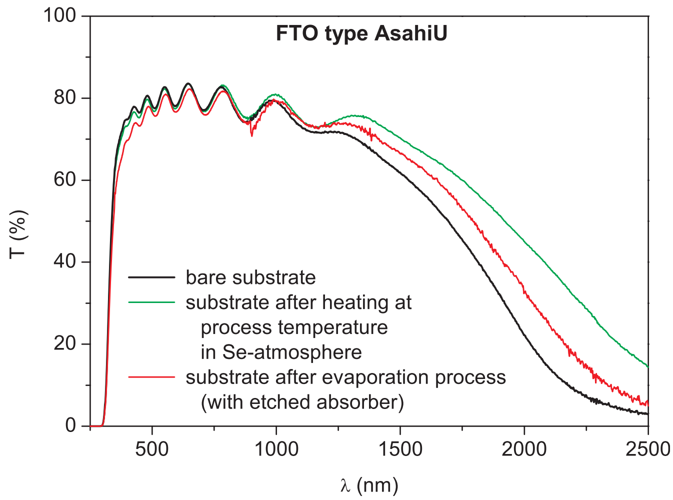

Fig. 5. Degradation of the transparent conducting back contact shown for FTO (fluorine-doped tin oxide) of type AsahiU. The loss in conductivity visible in the increased transmission in the long wavelength Drude region correlates with the high process temperature (green/light gray and red/gray) whereas the decrease in transmission near the band edge was attributed to the absorber growth (red/gray).

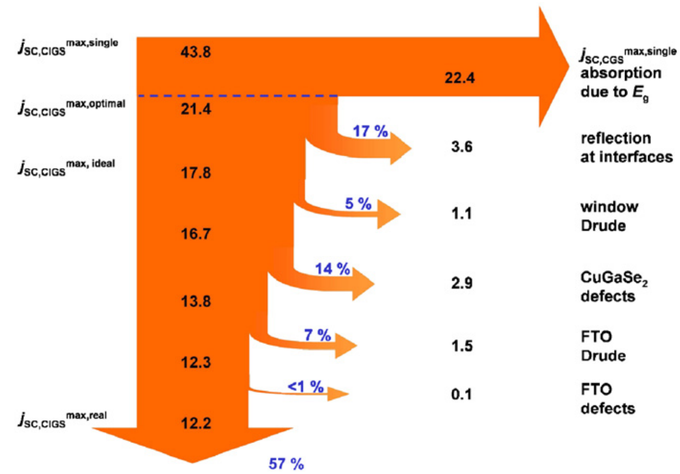

Fig. 6. Diagram of losses in short circuit current density j_{SC} of the bottom cell in a tandem construction due to the reduced transmission of the top cell. Whereas in optimum still 21.4 mA/cm^2 of j_{SC} could remain for a Cu(In,Ga)Se_2 bottom cell the real value is only about 12.2 mA/cm^2. The losses were separated into a part originating from the different refractive indices of the materials and further contributions which could be attributed to certain material properties of the individual top cell layers such as defects and free charge carrier absorption (Drude).

4. Discussion

An optical model can be assembled by extracting parameters for single layers deposited on glass and using those as input to describe the complete stack. The inherent assumption is of course that the layer incorporated in the stack has the same optical properties as the film grown by itself on glass. As shown here, this is not always the case, e.g. when the FTO properties are modified by the subsequent absorber deposition. Hence, the validity of the original assumption has to be checked using the described additional experiments and partial stacks.

The second concern arises from the roughness of the absorber. If this led to significant scattering and light trapping it would be quite challenging to develop an accurate (three-dimensional) model. In our experience it is indeed impossible to model the spectra of individual films without incorporating a certain loss in coherent interference (parameter s_k) and averaging over a thickness distribution (parameter *dd*). We were not able to achieve ideally smooth films by chemical polishing. However, as-grown and polished films can be described by the same set of fundamental parameters. Moreover, the thickness reduction and increased coherent interference in the optical model agrees well with independently derived values. These findings suggest that—at least for the films considered here—light trapping does not hamper the quantitative evaluation.

Using this model of an actual top cell, a quantification of losses and their attribution to material properties becomes feasible by applying the reduced transmission of a top cell to an idealized bottom cell as corresponding to the tandem setup.

At the current development status, the resulting drop in quantum efficiency and hence in short circuit current and efficiency for the bottom cell are very significant. The diagram of losses expressed in terms of short circuit current densities is given in Fig. 6. Starting with a maximum j_{SC} of 43.8 mA/cm^2 for a single cell with a band gap of 1.1 eV, this value is reduced to 21.4 mA/cm^2 when integrated in a tandem with a top cell of $E_g = 1.7$ eV. Even in the case of nearly perfect materials the short circuit current density then is diminished by 3.6 mA/cm^2 due to reflection losses at the interfaces. Additionally, free charge carriers in the window and in the transparent back contact yield a reduction of 1.1 and 1.5 mA/cm^2, respectively. A main contribution comes from defects in the absorber material which cost another 2.9 mA/cm^2, resulting in the end in 12.2 mA/cm^2 short circuit current density of the bottom cell in the tandem.

These losses of about 43% compared to the optimal reachable values are due to the reduced transmission of the top cell and hence should be compensated for by its good electrical properties. However, the electric performance of CGS solar cells is poor, especially on TCO [13]. Consequently improvement from the optical perspective in the form of an enhanced transmission is desirable for following chalcopyrite-based multijunction cells. For this an optical model built upon the comprehensive layer characterization as shown here will be a good starting point.

5. Summary

With regard to a more efficient use of the solar spectrum via tandem constructions we investigated the CGS-based top cell on glass from the optical point of view by measuring and modeling transmission and reflection. The analysis started with an extensive characterization of the individual layers building up the cell stack. For this, the absorber material was, for example, examined with respect to light trapping. Despite a certain surface roughness of the $CuGaSe_2$ which was diminished by polishing, the effect of light trapping is of minor influence and hence optical constants are assumed to be described correctly in the modeling. As for the FTO used as a transparent back contact, its transmission plays a significant role. Additionally, a degradation appears due to the process of absorber growth resulting from the high temperature as well as from material interactions. Hence, the suitability of a given FTO has to be judged from its performance when incorporated in the solar cell rather than from the as-grown properties.

Together with a description of the window system we established a comprehensive set of parameters which serves as input for the optical model of our chalcopyrite top cell. The application of this model to the bottom part of the tandem reveals the existence of losses in j_{sc} as big as 43% compared to optimal values. As this reduction originates from the low transmission of the top cell future work will have to focus on its increase. For this purpose the detailed layer characterization in conjunction with modeling as shown here is the starting point.

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