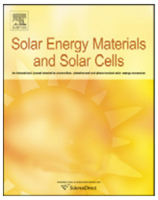
Solar Energy Materials & Solar Cells 93 (2009) 874–878

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat



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

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ARTICLE INFO

Article history:
Received 17 December 2007
Accepted 9 October 2008
Available online 18 November 2008

Keywords:
Optical characterization
Chalcopyrites
Tandem cell
Transparent back contact

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 $E_g = 1.7\,\text{eV}$ $CuGaSe_2$ (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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doi:10.1016/j.solmat.2008.10.008

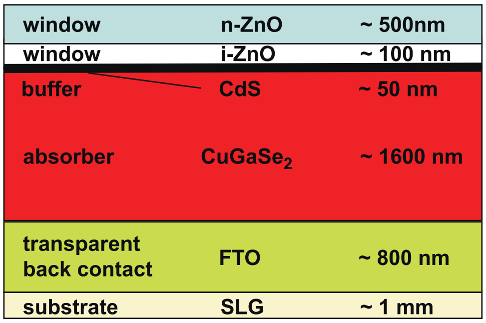

Fig. 1. Layer stack of the transparent chalcopyrite-based top cell. The CuGaSe$_2$ absorber is grown on fluorine-doped tin oxide (FTO) used as transparent back contact. On top of a thin CdS buffer, an i- and n-ZnO layer finish the cell and build the heterojunction with the p-type absorber.

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 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.

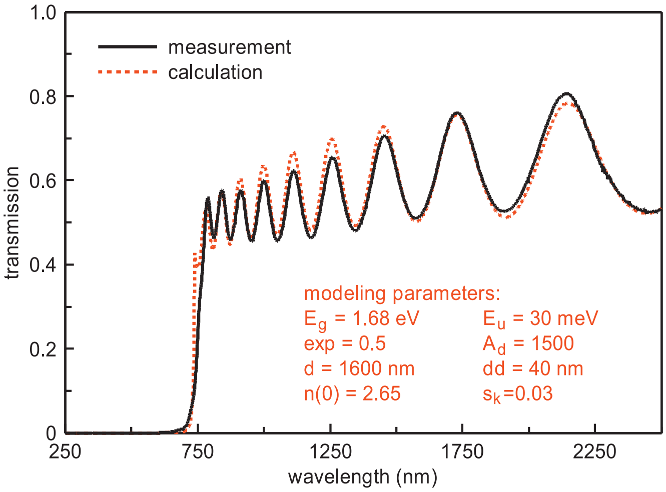

Fig. 2. Transmission of a polycrystalline CuGaSe$_2$ thin film deposited on soda-lime glass. The measured curve is modeled with the program Diplot, values of fitting parameters as described in the text are given in the inset.

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