<http://www.diva-portal.org>

Postprint

This is the accepted version of a paper presented at *IEEE 42nd Photovoltaic Specialists Conference, 14-19 June 2015, New Orleans, LA, USA*.

Citation for the original published paper:

Frisk, C., Ren, Y., Li, S-Y., Platzer-Björkman, C. (2015)

CZTS solar cell device simulation with varying absorber thickness.

In: *2015 IEEE 42nd Photovoltaic Specialist Conference (PVSC). Proceedings* IEEE conference proceedings

<http://dx.doi.org/10.1109/PVSC.2015.7355794>

N.B. When citing this work, cite the original published paper.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-268931>

CZTS Solar Cell Device Simulations with Varying Absorber Thickness

Christopher Frisk, Yi Ren, Shuyi Li, Charlotte Platzer-Björkman

Ångström Solar Center, Division of Solid State Electronics, Uppsala University, Ångström Laboratory,
Box 534, SE-751 21, Uppsala, Sweden

Abstract — In this study the influence of absorber layer thickness on the trends of the four current-voltage (J-V) parameters for our CZTS solar cells is studied with simulations and compared with empirical data. In the case of dominating interface recombination we find that open-circuit voltage and fill-factor are largely unaffected by thickness variations 0.5 – 2.0 μm , whereas short-circuit current, and thereby efficiency, saturates (98 % of max) at >1.1 μm absorber thickness, in agreement with measurements. In the case of suppressed interface recombination all four J-V parameters exhibit strong thickness dependence at <0.5 μm due to back contact recombination.

Index Terms — absorber layer, CZTS, device model, photovoltaic cells, simulations

I. INTRODUCTION

Thin film $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) absorber layers are attractive alternatives for future solar cell applications due to the abundancy and availability of their constituent elements, and the electronic properties and high absorption capabilities of the material. Device modeling can be used to bridge theory with empirical data and simulations based on different models can give insight into the opto-electronic properties of solar cells, leading to potential improvements in power conversion efficiency (PCE). In this work we use 1D SCAPS [1] models to simulate the influence of CZTS absorber layer thickness on current-voltage (J-V) characteristics and compare with an empirical data set with similar thickness variations [2]. The models are minor variations to our baseline reference device model [3], built with input parameters from a reference device presented at IEEE PVSC-41 [4]. The aim of this study is to evaluate the trends induced by changing thickness, and to predict the influence of thicknesses variation, for future reference, in the limit of bulk and back contact recombination.

The baseline reference device has a co-sputtered 2 μm CZTS absorber layer, with Cu/Sn ratio 2.0 and Zn/(Cu+Sn) ratio 0.39 – 0.40 as measured from energy dispersive X-ray spectroscopy after anneal, and measured PCE of 6.7 %. For a description of the deposition process and full device structure, see [4]. The composition of the absorber layers in the thickness series varies in Cu/Sn ratio within 1.83 – 1.93, and in Zn/(Cu+Sn) ratio within 0.36 – 0.41, as measured from X-ray fluorescence spectroscopy (XRF). The reference device was characterized with regular J-V and temperature dependent J-V (J-V-T), quantum efficiency (QE), with and without voltage bias, capacitance voltage (C-V), drive-level capacitance profiling (DLCP) and reflectance spectroscopy. The CZTS doping density in the model was set according to the hole concentration ($p = 2 \cdot 10^{16} \text{ cm}^{-3}$) from the analysis of

the C-V and DLCP measurements, and the reflectance was used as an optical filter in the model. Shockley-Read-Hall (SRH) recombination in the model is addressed by comparing simulated and measured J-V and QE data. It is implemented at the contact interfaces, in the bulk materials, as mid-gap defects, and at the absorber/buffer layer interface. Interface recombination is dominating in our model due to interface defects and a cliff-like conduction band alignment [5], and is the main reason for open-circuit voltage (V_{OC}) deficit, which is supported by J-V-T analysis. The electronic bandgap energy (E_g) is lowered from its ideal value, based upon E_g fluctuations due to disorder in the CZTS crystal structure [6], also factoring in on the V_{OC} deficit.

Setting the recombination is important in the model, but of equal importance is addressing the minority carrier generation, a property known to be high, but the exact absorption coefficient as a function of photon wavelength ($\alpha(\lambda)$) differs substantially between studies [7-9]. In this study α is based on a reflectance and transmittance (R-T) measurement on a 500 nm CZTS film deposited on glass. The Cu/Sn and Zn/(Cu+Sn) ratios of this film are 1.84 and 0.36 respectively, as measured from XRF. For wavelength $\lambda > 600 \text{ nm}$ α is modified with a numerical method accordingly: Assuming the expression

$$QE(\lambda) = \frac{\int \alpha(\lambda) \Phi_{in}(\lambda) e^{-\alpha(\lambda)x} f_c(x) dx}{\Phi_{AM1.5}} \quad (1)$$

we iteratively change $\alpha(\lambda)$ until the calculated QE and measured QE match each other within a predetermined error tolerance. In (1); Φ_{in} and $\Phi_{AM1.5}$ are the absorber incident and air mass 1.5 (AM1.5) photon flux respectively, x the distance through the absorber layer, f_c the collection function. The form of f_c is assumed to be unity in the space charge region (SCR) and an exponential decay, with L_e as decay constant, explained further by M. Green [10]. f_c is chosen so that the iteratively changed α asymptotically goes to the R-T measured α , and the overlap occurs at $\lambda \approx 600 \text{ nm}$.

A complete description of the reference model, including the semi-empirical absorption coefficient, can be found in [3].

II. METHOD

A. Thickness variation in Model A

Modeling programs such as SCAPS will require the user to set a plethora of physical parameters, many which in different variable combinations will yield similar simulation results. For

this reason it is important that the model is based on empirical data, and that as many parameters as possible are fixed within the model. This means that quantitative models should be constructed independently for each and every case. In this work, when settling for the trends, most of the parameters are left unchanged from the reference model. V_{OC} deficit due to E_g lowering and interface recombination together constitutes about 510 mV, 50 mV more than in the reference model, and L_e was increased to 500 nm. These changes were done to accommodate the overall higher short-circuit current (J_{SC}), and lower V_{OC} , observed in the thickness series, compared to the reference device. The change of L_e was justified by comparing the two QE measurements of the 750 nm and 1000 nm samples, seeing an increase at long wavelengths in the thicker sample. Full-width-half-maximum of the main characteristic CZTS peak from Raman spectroscopy indicates that crystal quality in the depletion region is similar within the thickness series, indicating that keeping the parameters in the model constant is reasonable [2].

Batch calculations of J-V were performed with and without the changes, varying the thickness 500 – 2000 nm, while recording J_{SC} , V_{OC} , fill-factor (FF), PCE, cumulative recombination and cumulative generation. The model with above mentioned changes to diffusion length and E_g will be referred to as Model A.

B. Thickness variation in Model B

In our baseline model, the V_{OC} deficit is dominated by interface recombination but there is also a contribution from bulk properties; E_g lowering and recombination, and even back contact recombination. In the interest of this study the influence of absorber layer thickness in the case of suppressed interface recombination was investigated, a new model was created with interface defects set to zero. This model is referred to as Model B, in which L_e is a floating value. Batch J-V calculations were performed varying absorber layer thickness 250 – 3000 nm, in this case with L_e varying between 250 nm and 2000 nm. This was accomplished by adjusting the bulk defect concentration.

III. RESULTS AND DISCUSSION

The result of the J-V simulations with thickness variation in Model A and the reference model can be seen in Fig. 1. The simulation data is normalized to the average J-V parameters of the 2000 nm sample. The trends of the empirical data seem to be better captured in Model A than in the reference device model; an almost independent V_{OC} , slightly varying FF, and highly varying J_{SC} , due to collection and generation losses for thin absorber layers, and PCE that follows J_{SC} . The modifications done in Model A are supported by QE measurements and preliminary simulations, however; further

analysis, e.g. of different CZTS defect distribution and optical properties, would be required to conclude these results.

In the reference model, J_{SC} seems to be saturated (98 % of max) at 800 nm, whereas in Model A, the saturation happens for thickness >1100 nm. It is worth to point out that approximately 26 mA cm⁻² and 21 mA cm⁻² worth of current is generated in the 2000 nm and 500 nm thick absorber layers respectively. The main reason V_{OC} remains mostly unaffected of the thickness variation is due to a dominating interface recombination in combination with E_g lowering. The two thinnest samples, with absorber layer thickness of 500 nm and 700 nm respectively, have overall substantially lower J-V parameters compared to the rest of the thickness series. It is likely that detrimental effects such phase segregation, or a distribution of poor quality grains, have a larger impact on thin devices. These 2D effects could be negated with high-resistive layers at either contact interface.

Fig. 1. Empirical and simulated J-V parameters as a function of absorber thickness. The simulated curves of both models have been normalized to the 2000 nm sample of the thickness series.

In Model B, the results are quite different. As can be seen in Fig. 2, when the interface recombination is suppressed, increasing the thickness will increase all four J-V parameters, for moderately high values of L_e , even V_{OC} and FF. The

saturation point for the J_{SC} varies between 750 nm and >2200 nm of absorber layer thickness, depending on L_e , indicating that there is much to be gained if the interface and the collection of minority carriers can be improved for devices with thick absorber layers, i.e. 660 nm [11] might not be enough in terms of J_{SC} yield in good devices. If one wishes to make thin devices still, it is crucial to address the non-ideal back contact, since the overall decrease of all four J-V parameters with decreasing thickness can be attributed to back contact recombination in Model B. In fact, back contact recombination is dominating for all thicknesses when $L_e \geq 1500$ nm. Further empirical studies in this subject are needed to evaluate the real influence of the back contact in CZTS devices [12].

Fig. 2. Simulated J-V parameters in Model B as a function of absorber thickness, with different values of L_e . The curves are not normalized and the relatively high values are a result of suppressed interface recombination and long diffusion lengths.

IV. CONCLUSIONS

In this study, a reference device model and slightly modified model (Model A) is used to simulate the influence absorber layer thickness variation has on the four J-V parameters; J_{SC} ,

V_{OC} , FF and PCE. With a diffusion length of 500 nm, dominating interface recombination, and an absorption coefficient from R-T measurement, numerically modified with QE data at $\lambda > 600$ nm, it is possible to simulate the trend as seen in the empirical J-V data. With the parameter set of our reference model and model A, the efficiency is saturated, following the J_{SC} , at absorber layer thickness between 750 nm and 1000 nm respectively. What exemplifies Model B, where interface recombination is suppressed, is that V_{OC} and FF are heavily dependent on thickness < 500 nm as well. Currently, with dominating interface recombination, CZTS absorber layer thickness will have little effect on FF and V_{OC} . With relatively short diffusion length there is no need to produce >1000 nm layers, however; if interface recombination can be suppressed and CZTS film quality improved absorber layers should be made thicker in order to utilize their full potential.

REFERENCES

- [1] Burgelman M, Nollet P and Degraeve S, "Modelling polycrystalline semiconductor solar cells", *Thin Solid Films*, vol 361, pp. 527-32, 2000
- [2] Ren Y, *et al.*, "Influence of C2ZnSnS4 absorber thickness on thin film solar cells", *In manuscript*, vol 2015
- [3] Frisk C, *et al.*, "Combining strong interface recombination with disorder and short diffusion length in CZTS device modeling", *In manuscript*, vol 2015
- [4] Ericson T, *et al.*, "Zn(O, S) Buffer Layers and Thickness Variations of CdS Buffer for Cu2ZnSnS4 Solar Cells", *Ieee Journal of Photovoltaics*, vol 4, pp. 465-9, 2014
- [5] Bär M, *et al.*, "Cliff-like conduction band offset and KCN-induced recombination barrier enhancement at the CdS/Cu2ZnSnS4 thin-film solar cell heterojunction", *Applied Physics Letters*, vol 99, 2011
- [6] Scragg J J S, *et al.*, "Cu-Zn disorder and band gap fluctuations in Cu2ZnSnS4", *In manuscript*, vol
- [7] Levchenko S, *et al.*, "Optical constants of Cu2ZnSnS4 bulk crystals", *Moldavian Journal of the Physical Sciences*, vol 8, 2009
- [8] Leitao J P, *et al.*, "Study of optical and structural properties of Cu2ZnSnS4 thin films", *Thin Solid Films*, vol 519, pp. 7390-3, 2011
- [9] Persson C, "Electronic and optical properties of Cu2ZnSnS4 and Cu2ZnSnSe4", *Journal of Applied Physics*, vol 107, 2010
- [10] Green M A, *Solar Cells* Englewood Cliffs, N.J., Prentice-Hall, Inc., 1982
- [11] Wang K, *et al.*, "Thermally evaporated Cu2ZnSnS4 solar cells", *Applied Physics Letters*, vol 97, 2010
- [12] B. Vermang *et al.*, "Rear surface optimization of CZTS solar cells by use of passivation layer with nano-sized point openings", in *42nd IEEE Photovoltaic Specialist Conference*, 2015, submitted.