

Fluctuations in net doping and lifetime in Cu(In,Ga)Se₂ solar cells

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Abstract — By extracting profiles perpendicular to the substrate from images obtained by electron-beam-induced current measurements on Cu(In,Ga)Se₂ (CIGS) solar cells, fluctuations in the width of the space-charge region as well as in the diffusion length in the quasi-neutral region were studied. Devices with various solution-grown buffer layers as well as different [Ga]/([Ga]+[In]) ratios in the CIGS absorber were investigated. Complementary analyses by means of energy-dispersive X-ray spectrometry, and cathodoluminescence provide additional insight into the local optoelectronic and compositional properties of investigated cells.

Index Terms — CIGS, diffusion length, EBIC, electrostatic fluctuations, space-charge region.

I. INTRODUCTION

Polycrystalline Cu(In,Ga)Se₂ (CIGS)-based thin-film solar cells have achieved power conversion efficiencies of 22.9% [1]. However, this value is still below the theoretical maximum efficiency of 33.3% at the Shockley-Queisser limit [2] for a band-gap energy of 1.15 eV. While the fill factor and the short-circuit current are already close to their maximum values, power-conversion efficiency of the record CIGS solar cells is mainly limited by the open-circuit voltage due to non-radiative recombination [3].

One possible origin for the enhanced recombination can be potential fluctuations in CIGS thin films and buffer/window layers [4]. Excess charge densities at line and planar defects as well as inhomogeneous distribution of the net doping density and difference in the lifetime of electrons between neighboring grains induce electrostatic potential fluctuations [5].

In the present work, electron-beam induced current (EBIC) in a scanning electron microscope (SEM) is used to investigate fluctuations in the net doping and lifetime of polished solar cell cross-sections. We studied CIGS solar cells varying Ga content and solution-grown buffer layers. In addition, cathodoluminescence (CL) and energy dispersive X-ray (EDX) measurements were applied on the same position.

II. EXPERIMENTAL

A. Sample Preparation

Polycrystalline CIGS thin-films (thickness ~2 μm) were co-evaporated on a Mo-coated soda-lime glass by an in-line multi-

stage process [6]. The CdS and Zn(O,S) buffer layers were grown by chemical bath deposition (CBD) as described elsewhere [7]. The solar cells were completed by sputtered ZnO/ZnO:Al bilayer for the devices with CdS buffer layer, and by Zn_{0.75}Mg_{0.25}O/ZnO:Al in the case of the devices with Zn(O,S)-buffer. The [Ga]/([Ga]+[In]) (GGI) ratios in CIGS absorber layers are GGI = 0.30 and GGI = 0.66, as measured by X-ray fluorescence analysis (XRF). Overview of the samples studied in the present work, with the corresponding solar cell parameters are summarized in table 1.

For the high-quality SEM measurements, flat cross-sectional specimens were prepared by gluing two stripes of thin-film solar cells face-to-face. The samples were then mechanically polished. A 4-5 nm thick carbon layer was deposited on top of these cross-sections to protect the surface and reduce surface charging during the measurements.

B. Sample Analysis

EBIC and EDX analyses were performed using a Zeiss UltraPlus SEM, equipped with an Oxford Instruments XMax80 X-ray detector. EBIC measurements were conducted using electron beam energies from 5 to 15 kV and low beam currents, in order to avoid high-injection conditions. To get a good resolution of the X-ray lines, EDX maps were acquired using 10 kV beam energy and 1.5 nA beam current.

CL measurements were performed at room temperature at Zeiss MERLIN SEM, using a DELMIC SPARC CL system, equipped with an iDus InGaAs array as detector. An IR-spectrometer and monochromator grating of 300l/mm blazed at 1200 nm were used. The beam parameters were set to 8 kV for the beam energy and 1 nA for the beam current.

Capacitance-voltage (C-V) and quantum efficiency (QE) measurements were carried out, in order to obtain macroscopic values for the net doping densities in the CIGS absorber and to determine the diffusion lengths in the quasi-neutral region.

Current-voltage measurements were carried out with a WACOM AM1.5G solar simulator at standard testing conditions. Solar cells were measured in the as-grown state without further light-soaking or annealing procedures.

TABLE I

GA CONTENT, BUFFER LAYER AND PHOTOVOLTAIC PARAMETERS OF STUDIED $\text{Cu}(\text{In,Ga})\text{Se}_2$ THIN-FILM SOLAR CELLS

| Sample № | GGI of CIGS | CBD-buffer/high-resistive layer | CBD-buffer thickness (nm) | Eff. (%) | V_{oc} (mV) | FF (%) | J_{sc} (mA/cm ²) |
|----------|-------------|---------------------------------|---------------------------|----------|---------------|--------|--------------------------------|
| 1 | 0.30 | CdS/i-ZnO | 50 | 17.0 | 684 | 78.7 | 31.5 |
| 2 | | Zn(O,S)/i-ZnMgO | 15-20 | 15.8 | 664 | 72.9 | 32.6 |
| 3 | 0.66 | CdS/i-ZnO | 50 | 11.9 | 767 | 68.7 | 22.5 |
| 4 | | Zn(O,S) i-ZnMgO | 15-20 | 7.9 | 688 | 49.8 | 23.0 |

III. RESULTS AND DISCUSSION

A. Electron-beam induced current measurements

Fig.1 shows EBIC maps obtained on the cross-sections of the studied CIGS solar cells at $E_B = 7$ kV. The brightness of the pixel is directly proportional to the measured EBIC current. At the buffer/CIGS interface, the EBIC signal is displayed saturated. This corresponds to the space-charge region (SCR) with following decay in the quasineutral region in the absorber where the diffusion length of the charge carriers plays a dominant role.

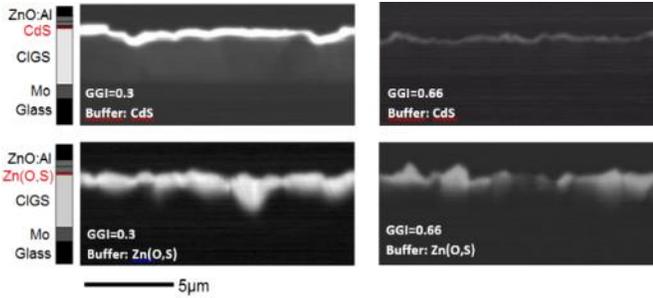


Fig. 1. EBIC images for CIGS solar cells with GGI=0.30, GGI=0.66 and CdS/i-ZnO, Zn(O,S)/i-ZnMgO buffer/window layers at $E_B=7$ kV

In order to avoid high surface recombination, EBIC measurements were conducted at different beam energies ($E_B=5-15$ kV). From the acquired EBIC maps, line profiles perpendicular to the pn-junction were extracted. By fitting experimental and simulated profiles based on the analytical model proposed by Donolato [8], values for the widths of the SCR (w_{SCR}) and for the diffusion length (L_D) were extracted. It is shown that fluctuations of w_{SCR} are much larger for solar cells with Zn(O,S)/i-ZnMgO layers than for CdS/i-ZnO, but they are independent of Ga content in the CIGS layer (see Fig. 2).

Since the w_{SCR} is influenced by the free charge carrier density as described in [9], fluctuations of the net doping N_A in the absorber layer and N_D in buffer/window layer can be estimated. We presume that N_A does not deviate significantly in all investigated samples but mainly N_D attributes to the electrostatic fluctuations in CIGS with Zn(O,S)/i-ZnMgO layers. However further investigation is required to distinguish

the magnitude of N_A and N_D . The amplitude of electrostatic fluctuations was calculated using Poisson equation:

$$\Delta\varphi = \frac{k_B T}{q} \ln\left(\frac{N_{D1}}{N_{D2}}\right) \quad (1)$$

For the cells with CdS/i-ZnO layers $\Delta\varphi$ does not exceed the thermal energy ($E_{th} = 25$ meV) and therefore does not affect the device performance while for the cells with Zn(O,S)/i-ZnMgO layers $\Delta\varphi$ varies from 30 to 50 meV, which would result in the loss of the open-circuit voltage V_{oc} of up to 50 mV.

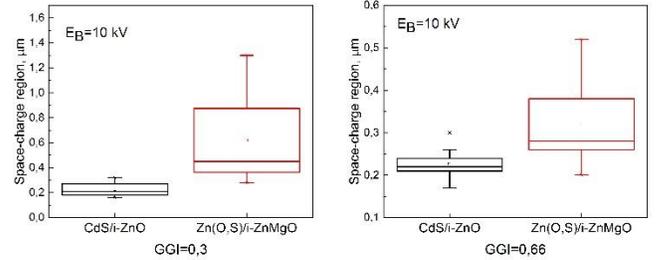


Fig. 2. Variations in the width of the SCR for CIGS solar cells with a) GGI=0.30 b) GGI=0.66

In addition to inhomogeneous distribution of the net doping density, spatial variation in lifetime τ of minority charge carriers can affect the V_{oc} . As the lifetime is linked to the diffusion length L_D by $L_D = \sqrt{D\tau}$, where D is a diffusion constant it was possible to reveal fluctuations in τ by evaluating EBIC profiles.

The average values of w_{SCR} and L_D obtained by EBIC were confirmed by C-V and QE analysis (not shown here).

B. Cathodoluminescence measurements

In order to get a better insight into local electrical and optoelectronic properties CL measurements were conducted. Fig. 3 and 4 show CL maps for CIGS solar cells with GGI=0.66 where (3a, 4a) is the corresponding SEM image, (3b, 4b) CL intensity and (3c, 4c) peak-wavelength distribution.

Obtained maps show local variation of the CL intensity between neighboring grains and even across individual grain. As the local quasi-Fermi level splitting $\Delta\mu$ measured by the CL intensity is proportional to $\ln(p_0, \tau_n)$, the CL images confirm the presence of fluctuation in the net doping N_A and lifetime τ obtained by the EBIC analyses.

Besides, CL measurements provide an access to get a direct distribution of the local band-gap energy. It is shown that the wavelength peak shifts perpendicular to the surface from 850 to 950 nm with respect to the Ga gradient. The results agree well with the Ga distribution obtained by EDX spectrometry.

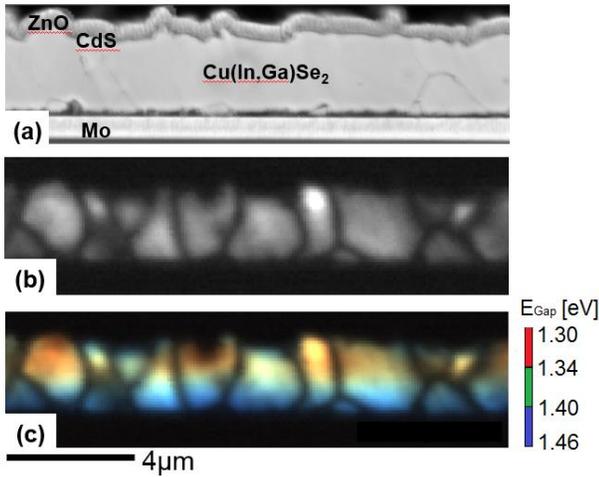


Fig. 3. (a) SEM image; (b) CL intensity; (c) and peak-wavelength distributions for Cu(In,Ga)Se₂ solar cells with GGI=0.66 and CdS/i-ZnO layers

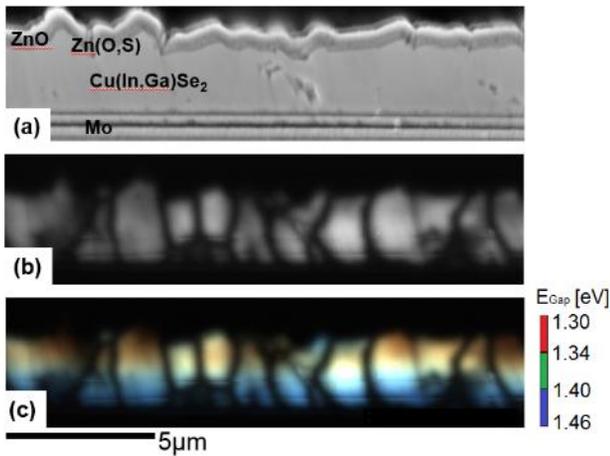


Fig. 4. (a) SEM image; (b) CL intensity; (c) and peak-wavelength distributions for Cu(In,Ga)Se₂ solar cells with GGI=0.66 and Zn(O,S)/i-ZnMgO layers

IV. CONCLUSIONS

The present work reports about the microscopic properties of CIGS solar cells with solution-grown CdS and Zn(O,S) buffer layers and different integral GGI ratios of 0.30 and 0.66 in the CIGS absorbers. The fluctuations in the width of the SCR and therefore in the net doping are affected substantially by the choice of the buffer/window layer. On the other hand, for devices with the same buffer/window layer, a different GGI ratio does not influence the extent of the electrostatic potential

fluctuation. Further evaluation of the data will provide insight into the effect of the buffer/window combination on the magnitude of the fluctuations, which may lead to enhanced recombination and thus to a decrease of the open-circuit voltage.

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REFERENCES

- [1] http://www.solar-frontier.com/eng/news/2017/1220_press.html, Solar Frontier Achieves World Record Thin-Film Solar Cell Efficiency of 22.9%, accessed on January 19, 2018.
- [2] W. Shockley, H. J. Queisser, “Detailed balance limit of efficiency of pn junction solar cells”, *J. Appl. Phys.* 32, pp. 510-519 (1961).
- [3] D. Abou-Ras, S. S. Schmidt, N. Schäfer, J. Kavalakkatt, T. Rissom, T. Unold, R. Mainz, A. Weber, T. Kirchartz, E. Simsek Sanli, P. A. van Aken, Q. M. Ramasse, H.-J. Kleebe, D. Azulay, I. Balberg, O. Millo, O. Cojocar-Miréidin, D. Barragan-Yani, K. Albe, J. Haarstrich, C. Ronning, “Compositional and electrical properties of line and planar defects in Cu(In,Ga)Se₂ thin films for solar cells – a review”, *Phys. Stat. Sol. (RRL)* 10, pp. 363-375 (2016).
- [4] J. H. Werner, J. Mattheis, U. Rau, “Efficiency limitations of polycrystalline thin film solar cells: case of Cu(In,Ga)Se₂”, *Thin Solid Films* 480-481, pp. 399-409 (2005).
- [5] D. Abou-Ras, N. Schäfer, C. J. Hages, S. Levchenko, J. Marquez, T. Unold, *RRL Solar* 2, 1700199 (2018).
- [6] G. Voorwinden, R. Kniese, P. Jackson, M. Powalla, “In-line Cu(In,Ga)Se₂ co-evaporation process on 30 cm × 30 cm substrates with multiple deposition stages”, *Proc. 22 Europ. Photovolt. Sol. En. Conf. Milano*, pp. 2115-2118 (2007).
- [7] D. Hariskos, P. Jackson, W. Hempel, S. Paetel, S. Spiering, R. Menner, W. Wischmann, M. Powalla, “Method for a high-rate solution deposition of Zn(O,S) buffer layer for high-efficiency Cu(In,Ga)Se₂-based solar cells”, *IEEE J. Photovoltaic.*, vol. 3, no. 4, pp. 1321-1326 (2016).
- [8] C. Donolato, “Evaluation of diffusion lengths and surface recombination velocities from electron beam induced current scans”, *Appl. Phys. Lett.* 43(1), pp. 120-122 (1989).
- [9] R. Scheer and H.-W. Schock, *Chalcogenide Photovoltaics*. WILEY-VCH Verlag & Co. KGaA, Weinheim, 2011.