

© 2017 IEEE. Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, in any current or future media, including reprinting/republishing this material for advertising or promotional purposes, creating new collective works, for resale or redistribution to servers or lists, or reuse of any copyrighted component of this work in other works.

<http://doi.org/10.1109/JPHOTOV.2016.2639347>

Influence of CdS and ZnSnO Buffer Layers on the Photoluminescence of Cu(In,Ga)Se₂ Thin Films

Pedro M. P. Salomé, Jennifer P. Teixeira, Jan Keller, Tobias Törndahl, Sascha Sadewasser, and Joaquim P. Leitão

Abstract—In this work, an optical study by external quantum efficiency and photoluminescence on the influence of different buffer layers on the defect properties of Cu(In,Ga)Se₂ (CIGS) is presented. Chemical bath deposited CdS was compared with atomic layer deposited Zn_{1-x}Sn_xO_y (ZnSnO) coated CIGS samples. For both buffer layers, the CIGS bulk and CIGS/buffer interface are strongly influenced by electrostatic fluctuating potentials, being less pronounced for the sample with the ZnSnO buffer layer which we associate with a lower concentration of donor defects at the CIGS near-interface layer. A change in the bandgap of the CIGS as a consequence of the buffer layer deposition was observed. This study expands the knowledge of defects in the complex quaternary semiconductor CIGS which, as discussed, can be affected even by the choice of buffer layer and its deposition process.

Index Terms—Cu(In,Ga)Se₂, Zn_{1-x}Sn_xO_y buffer layer, CdS buffer layer, photoluminescence, thin film solar cells.

I. INTRODUCTION

THIN film solar cells based on Cu(In,Ga)Se₂ (CIGS) have recently achieved an impressive world record [1] of power conversion efficiency, 22.8%, a value even higher than that of multi-crystalline Si, 21.25%. This achievement has followed a number of recent developments based on improving the surface of the CIGS by an alkali post-deposition treatment [2]. Despite the scarce information on the current world record solar cell from Solar Frontier [1], ZSW achieved similar values of power conversion efficiency, 21.7% for CdS-based devices and 21.0% for Cd-free based devices [3]. These improvements together with the need, for replacing the toxic CdS layer in the CIGS solar cell architecture, emphasize the necessity to study alternatives to CdS and the influence of the buffer layer on the CIGS/buffer layer interface properties. The ideal buffer layer should have better electrical properties than CdS, non-toxic elements, a high bandgap energy (E_{gap}) to allow a high transmission in the visible spectral range, a refraction index between the one of the absorber layer and the one of the optical window layer, a suitable conduction band line-up to the absorber and to the front contact, a low density of recombination defects at the absorber/buffer layer interface, and allow for a deposition by a vacuum

compatible technique [4]. Zinc-compounds are very promising candidates, being non-toxic and highly transparent at short wavelengths due to their high bandgap values [4]. Among the Zn-compounds, the Zn_{1-x}Sn_xO_y (ZnSnO) has demonstrated a great potential as non-toxic Cd-free alternative buffer layer for CIGS thin-film solar cells [5]. ZnSnO has the intrinsic properties required for an ideal buffer layer and can be successfully grown by vacuum compatible techniques, e.g. atomic layer deposition (ALD) [5]. In previous works, it was shown that by changing the Sn fraction and the deposition temperature, it is possible to change the bandgap energy in the range 3.2-3.7 eV, mainly through the position of the conduction band edge [6]–[10]. In this way, ZnSnO can be used to achieve a suitable conduction band alignment with CIGS and i-ZnO [10]. Thus, one of the remaining questions about this buffer layer is its influence on the optical properties of the CIGS and of the CIGS/buffer layer interface.

In this work, we study the influence of the buffer layer on the CIGS by using photoluminescence (PL) as a probing tool for the defects in CIGS and in the CIGS/buffer layer interface. The same CIGS sample was divided to allow for the deposition of different buffer layers, CdS and ZnSnO, and thus these samples were investigated. For both, an influence of a high density of charged defects is observed, being lower for the sample with the ZnSnO buffer layer. The use of ZnSnO allowed a reduction of the charged defect density in the CIGS and/or CIGS/buffer layer interface, compared with the CdS case. This paper is an enhanced version of a manuscript submitted to the 2016 43rd IEEE Photovoltaics Specialist Conference with a similar title [11]. The main improvements are i) the presentation of external quantum efficiency measurements allowing the evaluation of the bandgap of both samples; ii) a deeper discussion of the overall experimental results that address relevant topics for the optical properties like the creation of electrostatic fluctuating potentials in a semiconductor and its influence on the radiative and non-radiative recombination channels, and the influence of the two deposition methods of the buffer layers on the density and types of defects in the CIGS layer.

II. EXPERIMENTAL DETAILS AND METHODS

A CIGS thin film was deposited on Mo coated soda lime glass in a micro-pilot in-line evaporator using a one stage co-evaporation process [5]. A linearly decreasing [Ga]/([Ga]+[In]) ratio from the back contact to the front of the film [12] was obtained. The composition of the CIGS used in this study was [Ga]/([In]+[Ga]) = 0.42 ± 0.03 and [Cu]/([In]+[Ga]) =

P. M. P. Salomé and S. Sadewasser are with the INL - International Iberian Nanotechnology Laboratory, Laboratory for Nanostructured Solar Cells (LaNaSC), Av. Mestre José Veiga, 4715-330 Braga, Portugal

J. Keller and T. Törndahl are with the Ångström Solar Center, Solid State Electronics, Uppsala University, Ångström Laboratory PO Box 534, SE-751 21 Uppsala, Sweden.

J. P. Teixeira and J. P. Leitão are with the Departamento de Física and I3N, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal e-mail: joaquim.leitao@ua.pt.

0.86 ± 0.03 with a thickness of $1.85 \pm 0.25 \mu\text{m}$, measured using a Panalytical Epsilon 5 X-ray fluorescence (XRF) system with a CIGS calibration sample. The CIGS film was split in two pieces to allow for the deposition of different buffer layers: CdS and ZnSnO. The CdS was deposited by conventional chemical bath deposition (CBD) with a solution of 1.1 M ammonia, 0.100 M thiourea, and 0.003 M cadmium acetate, and the solution was heated to 60°C in a water bath. The $\text{Zn}_{0.8}\text{Sn}_{0.2}\text{O}_y$ layer was deposited by ALD at a substrate temperature of 120°C . As precursors, diethyl zinc (DEZn or $\text{Zn}(\text{C}_2\text{H}_5)_2$), tetrakis (dimethylamino) tin (TDMASn or $\text{Sn}(\text{N}(\text{CH}_3)_2)_4$), and deionized water (H_2O) were used together with nitrogen gas (N_2) as both carrier and purge gas. More details on the growth procedure of the two samples can be found elsewhere [10], [13]. For these deposition parameters of the ZnSnO buffer layer, the conduction band offset at the heterointerface CIGS/ $\text{Zn}_{0.8}\text{Sn}_{0.2}\text{O}_y$ should be similar to that of CIGS/CdS [6]. Thus, a similar bandgap alignment for both buffer layers is ensured. EQE measurements of finished solar cells was measured under ambient light, using chopped monochromatic light that was scanned through the wavelength interval of 360-1200 nm.

PL measurements were performed with a Bruker IFS 66v Fourier Transform Infrared spectrometer, equipped with a Ge diode detector cooled at liquid nitrogen temperature, and using as excitation source the 514.5 nm line of an Ar^+ ion laser. A He gas flow cryostat was used to change the temperature of the samples in the range 4-155 K. The correction of the spectral response of the Ge detector was performed for all spectra. In order to deconvolute possible different radiative transitions, a model with Gaussian components was implemented [14]. Similar models were applied for both samples using the lower number of components necessary to describe the luminescence in both temperature (T) and excitation power (P) dependencies.

III. RESULTS

Fig. 1 shows the PL spectra of the two samples measured at 10 K and with an excitation power of $\sim 3.6 \text{ mW}$. For both samples, the emission is a broad and asymmetric band in the range of ~ 0.97 - 1.18 eV , with maximum of intensity at $\sim 1.09 \text{ eV}$. The difference between the relative intensities of the PL spectra should be regarded with caution due to the necessarily different optical alignments for both samples. We note that the incident laser light is not expected to be absorbed in the ZnSnO buffer layer, because the incident photons have a lower energy than the bandgap. However, for the CdS case, the range of bandgap energy values (2.4-2.5 eV) available in the literature [15], includes the incident photon energy ($\sim 2.41 \text{ eV}$). Thus, complementary measurements (not shown) performed with an excitation wavelength of 632.8 nm were performed. They showed no changes in the emission of both samples which proves evidences that the absorption in the buffer layer in the case of CdS is negligible.

The asymmetry of the band can be visually represented by the width at half maximum as displayed in Fig. 1. Each spectrum was fitted with three Gaussian components. The shape of the emission bands was approximately the same

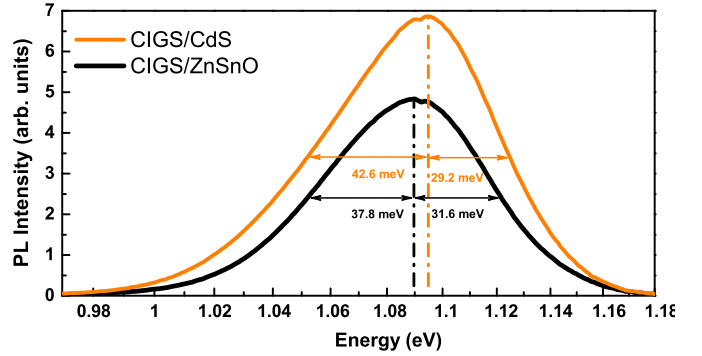


Fig. 1. PL spectra of CIGS/CdS and CIGS/ZnSnO samples measured at 10 K and with an excitation power of $\sim 3.6 \text{ mW}$. The vertical dashed lines indicate the maximum of the luminescence. The width at half maximum calculated in each spectrum shows the asymmetry of each observed band.

for all measured spectra in both dependencies (excitation power and temperature). In fact, the shape is characteristic of electronic transitions occurring in semiconductors with high concentrations of charged defects, as a consequence of a strong compensation level, that create electrostatic fluctuating potentials along the material [14], [16]–[19]. Thus, the three Gaussian components used in the fits describe the asymmetry of the observed luminescence and should not be considered as independent radiative transitions. The following experimental results and their discussion supports this interpretation.

For the sample with the CdS buffer layer, a slight blueshift (4.5 meV) of the luminescence band and a higher asymmetry in the low energy side of the emission are observed when compared with the sample with the ZnSnO layer. A change in the position of the emission can be related with a change of the density of defects or with a change of the bandgap energy. The first case will be addressed in Section IV. Concerning the possibility of a change of the bandgap, EQE measurements were performed and the results are shown in Fig. 2 a). It is well known that $\text{EQE} \propto \alpha \propto (h\nu - E_{\text{gap}})^{1/2}$, being α the absorption coefficient. Therefore, a linear fit of EQE^2 vs. energy around the CIGS bandgap energy can provide us with a rough estimation of the value for the bandgap energy. This is a widely used method in CIGS thin film solar cells and for this material, where the absorption is heavily influenced by bandgap tails, the linear fit should be performed slightly above the bandgap, as shown in Fig. 2 b) [20]. The results of the fit provide a value of 1.178 eV for the CdS sample and a lower value of 1.172 eV for the ZnSnO sample. This difference of $\sim 6 \text{ meV}$ in the bandgap energy of the two samples is compatible with the previous experimental blueshift.

In order to study the influence of the buffer layer on the radiative transitions, and thus on the charged defects density, in CIGS of both samples, we investigated the excitation power and temperature dependencies of the PL. For the first dependency, Fig. 3 shows the results for the peak energy and PL integrated intensity (I) of the band in both samples. By increasing the excitation power, a blueshift of the peak position of 13.5 ± 0.2 and $10.5 \pm 0.5 \text{ meV/decade}$ for the CdS and ZnSnO samples, respectively, is observed. Such high values cannot be understood in the scope of radiative

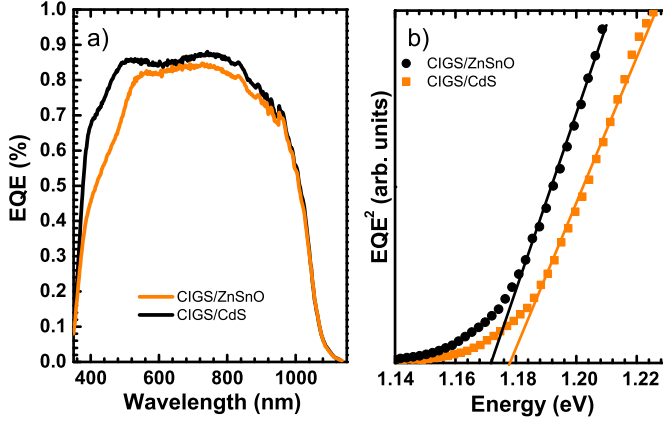


Fig. 2. a) EQE of both devices and b) square values of EQE as function of energy depicting a linear fit for the estimation of the bandgap energy.

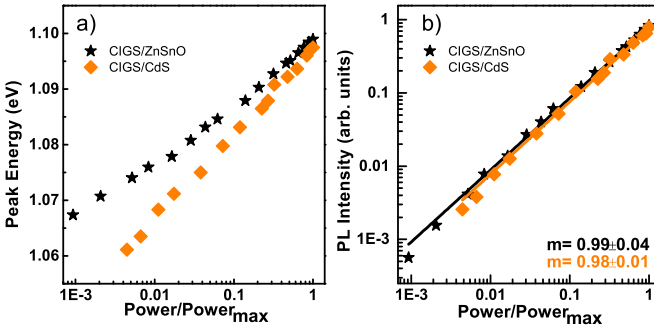


Fig. 3. Dependence on the excitation power of a) peak energy and b) PL integrated intensity of the band in both samples. The solid lines in b) represent the fit to the experimental points by Eq. 1.

transitions involving flat bands, as for example is the case of donor-acceptor pair recombinations [21], [22]. However, these high values of blueshift are easily explained in the scope of the fluctuating potentials model [23], [24]. Concerning the dependence on the excitation power of the PL integrated intensity, the experimental points can be fitted by the power law [25]:

$$I \propto P^m, \quad (1)$$

where m is an adjustable parameter. The estimated values from the fits shown in Fig. 3 b), are 0.98 ± 0.01 and 0.99 ± 0.04 for the CdS and ZnSnO samples, respectively. Values close to one are compatible with some degree of localization of the charge carriers [14].

Fig. 4 shows for both samples, the dependencies with temperature, of the peak energy and of the PL integrated intensity, for an excitation power of ~ 3.6 mW. Increasing the temperature until ~ 90 K, a peak energy redshift of 59 ± 1 and 39 ± 1 meV for the CdS and ZnSnO samples, respectively, is observed. For $T \gtrsim 90$ K, a strong peak energy blueshift (72 ± 1 meV) is observed for the ZnSnO sample. The experimental points suggest a compatible behavior for the CdS sample, however, the thermal quenching of the PL at ~ 100 K (~ 160 K for the ZnSnO sample) prevent its confirmation.

The temperature dependence of the PL integrated intensity was investigated by considering different models for the

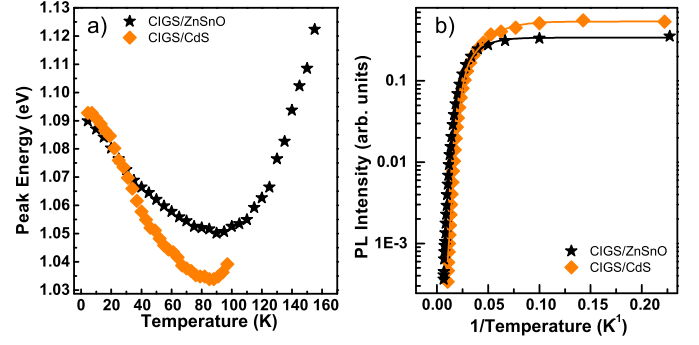


Fig. 4. Dependence on the temperature of a) peak energy and b) PL integrated intensity of the broad band in both samples, under an excitation power of 3.6 mW. The solid lines in b) represent the fit to the experimental points by Eq. 2.

thermal activation of non-radiative de-excitation mechanisms. The same model provides the best fit for both samples. It considers two de-excitation channels, one involving a discrete energy level and another one involving a band, and is described by [26]:

$$I(T) = I_0 \left[1 + c_1 \exp\left(-\frac{E_1}{kT}\right) + c_x T^{\frac{3}{2}} \exp\left(-\frac{E_x}{kT}\right) \right]^{-1}, \quad (2)$$

where I_0 is the PL intensity at $T = 0$ K, the activation energy E_1 represents the energy separation between the radiative state and the discrete high energy non-radiative state, and the activation energy E_x parameterizes the release of the less bound charge carrier from the radiative state to a band. Factor c_1 is proportional to the ratio between the degeneracies of the excited discrete energy level and of the radiative state, whereas $c_x T^{\frac{3}{2}}$ accounts for the effective density of states of the band involved and c_x is a fitting parameter. In the low temperature range (~ 4.5 -22 K), a small quenching of the PL is observed which is interpreted as the thermal activation of a non-radiative channel involving a discrete excited energy level. The estimated activation energies E_1 are 6.6 ± 0.4 meV and 5.2 ± 0.3 meV for the CdS and ZnSnO samples, respectively. These low activation energy values should be related with the presence of defects that create energy levels close to the energy of the radiative states. In the high temperature region, activation energies of 28.9 ± 0.6 and 28.3 ± 0.6 meV for the CdS and ZnSnO samples were estimated, respectively. The similarity of the activation energies for both samples in each non-radiative de-excitation channel suggests that the same mechanisms are responsible for the thermal quenching in both cases. These results support the assumption that the emission in both samples comes mainly from the CIGS layer.

IV. DISCUSSION OF RESULTS

In general, the presence of defects in a semiconductor contributes to the creation of radiative or non-radiative recombination mechanisms of the charge carriers. In the particular case of highly doped and strongly compensated materials, the interaction between defects create fluctuating potentials along the material. This interaction can be described by a well-

known condition: $Na_B^3 \gg 1$, where N is the doping concentration of a particular type of defects, donors or acceptors, and a_B is the corresponding Bohr radius of a donor or acceptor state, respectively [18]. As a consequence of the difference between effective masses of electrons and holes [27], a_B is usually higher for donors than for acceptors. Thus, fluctuating potentials, for the most common semiconductors, are created in first order by donors, despite the intrinsic electrical conductivity type of the semiconductor (p-type in the case of CIGS) [14].

Our results show clear evidence for a strong influence of fluctuating potentials in the recombination channels in both samples and cannot be explained if flat bands are assumed. A few reasons can be pointed out: i) the luminescence of both samples shows an evident asymmetry (see Fig. 1); ii) with the increase of excitation power a strong blueshift of the peak position is observed (see Fig. 3 a)); iii) the dependence of the intensity on the excitation power gave m values close to one; iv) with the increase of temperature, a strong redshift followed by a blueshift is observed (see Fig. 4 a)). In summary, all these experimental results, i)-iv), are strong evidences that support the influence of fluctuating potentials. The experimental results also suggest a higher influence of the electrostatic fluctuating potentials in the CdS sample: the asymmetry and the shifts with excitation power and with temperature are higher for the CdS sample in comparison with the ZnSnO one. Thus, we assume a higher density of defects on the CdS sample in the CIGS near-interface layer probed by the PL (~ 200 nm) [28] and/or the CIGS/buffer layer interface. Additionally, the thermal quenching of the PL in the case of the CdS sample occurs for a lower temperature, which can be explained by the presence of a higher density of defects involved in non-radiative de-excitation channels. The occurrence of a higher influence of fluctuating potentials in the CdS sample cannot explain the observed blueshift of the luminescence in that sample in comparison with the ZnSnO one. Actually, an increase of fluctuating potentials should be reflected in a redshift if the same bandgap is assumed in both CIGS layers. Thus, the observed blueshift is attributed to an increase of the bandgap in the near-interface layer of the CIGS scrutinized by the PL, in accordance with the EQE results of Fig. 2 b).

As discussed in the literature [14], [18], even in the presence of electrostatic fluctuating potentials, acceptor defects can participate on the radiative recombination mechanisms. Our dependence on the temperature of the PL intensity revealed the thermal activation of a de-excitation channel corresponding to the release of a charge carrier from the radiative state to a band. The estimated activation energies (E_x) for both samples is in the range 28-29 meV and is close to the ionization energy calculated theoretically for the Cu vacancy (V_{Cu}), 30 meV, which is vastly assumed as the dominant acceptor defect in Cu-poor CIGS [29], [30]. Thus, the apparently higher PL intensity at low temperatures observed for the CdS sample can be tentatively related with a higher concentration of the V_{Cu} defect since for radiative defects, higher concentrations will lead to higher PL intensity. Concerning the slight blueshift of the luminescence at low temperature, observed for the CdS

sample (see Fig. 1), a higher concentration of the V_{Cu} defect is in perfect agreement with the observation of the slightly higher bandgap energy of the CdS sample since an increase on V_{Cu} concentration leads to higher values of the bandgap [31]. Since the same CIGS piece was used for the two buffer layer depositions, it is safe to say that it was the CdS processing that caused an increase on the V_{Cu} concentration. This is in agreement with reports that during the CBD process there is some Cu-leeching from the CIGS film into the bath [32], [33] providing the CIGS/CdS sample with a higher V_{Cu} defects density than the ZnSnO one, and thus explaining our results.

Having explored the difference in the peak position of the luminescence, we now focus on the influence of fluctuating potentials on the electronic structure. The different behavior of the fluctuating potentials between the two samples could be related to a change in the density and/or type of charged defects and, more specifically, to a change in the compensation level due to a modification of the density of donors at the near-interface layer of the CIGS absorber layer. Indeed, if a diminishing of the density of donors occurs, it will contribute to a reduction of the fluctuating potentials due to a lower compensation level. The properties of the absorber layer and its interface with the buffer layer are critically influenced by the deposition method of the latter and by its chemical composition, as shown previously [34], [35]. Therefore, many different effects can cause a reduction in the donor concentration. A few differences should be analyzed, namely: i) different chemical composition of the buffer layer; ii) different deposition temperatures; and iii) different deposition methods. Concerning the chemical composition of the buffer layer, it is well known that Cd is able to diffuse into the CIGS, where it creates a donor defect, Cd_{Cu} [36], [37]. The creation of donors in the CIGS will contribute to a higher compensation level and to an increase of the density of ionized defects. In the case of the ZnSnO buffer layer, no experimental results are available showing the diffusion of atomic species from the ZnSnO layer to the CIGS. We believe that the formation of the Cd_{Cu} defect is the dominant mechanism that explains the different influence of fluctuating potentials in the two samples. Furthermore, for case ii), a possible contribution could also come from the difference between the deposition temperatures in the two methods, ALD uses a substrate temperature of 120° C which is higher than the CBD one (60° C). Due to the low formation enthalpy of some point defects in CIGS, an increase of the deposition temperature of the buffer layer can promote a significant change of the total density of defects and their types [29], [30]. As an example, it is well known that Cu is a mobile element in CIGS at low temperatures such as 80° C [38]. Other elements, like Na and K, are also extremely mobile and any change in the concentration of an element will cause significant changes to the defect properties of the semiconductor. However, in this case the precise identification of donors would require a detailed XPS analysis comparing both samples. On case iii), the differences to the deposition process, we can highlight that for the CdS deposition the CIGS surface will be directly exposed to the CBD solution, whereas for the ZnSnO the CIGS surface will be exposed to the ALD precursors, DEZn, TDMASn and water vapor. On one hand,

the CBD process is beneficial for the performance of the solar cell [38]–[40] due to restoring the positive defects at the CIGS/buffer interface through the removal of O in the surface In-O bonds [34]. On the other hand during the CBD there is the removal of sodium due to its solubility in water [41]. Subsequently, in the case of the deposition of ZnSnO, there is neither a supply of ammonia to remove surface oxides nor a solution that washes sodium from the surface. With regards to Na, its main effect on the CIGS is the passivation of donor defects [42], [43]. The maintenance of O and Na at the surface contributes to the existence of a lower density of donor defects by passivation of V_{Se} defects and thus to a lower influence of the fluctuating potentials in the ZnSnO sample [38], [39].

In spite of the positive effect attributed to the CBD process on the electrical performance of solar cells, the ALD of ZnSnO reveals to reduce the effect of fluctuating potentials on the CIGS luminescence. In order to test this hypothesis, a water/ammonia dip of the CIGS prior to the ALD deposition would help us to better identify if the O passivation and the removal of Na are critical factors to the differences between the buffer layers or not.

V. SUMMARY

The use of CdS and ZnSnO as buffer layer in CIGS-based solar cells was investigated by EQE and PL. The investigation of the PL dependencies on the excitation power and temperature indicates a strong influence of fluctuating potentials on both samples. A similar non-radiative de-excitation channel was obtained for both samples. By combining the results from the temperature dependence with the EQE analysis, we hypothesize that the CdS sample has a lower concentration of Cu at the CIGS near-interface layer which slightly increases its bandgap energy, shifts the emission to a higher energetic position and increases the luminescence intensity. Thermal quenching of the PL for the sample with the ZnSnO buffer layer was observed for higher temperatures than for the sample with the CdS layer. The study showed a reduction of fluctuating potentials in the CIGS/ZnSnO sample in comparison with the CIGS/CdS one, showing that the choice of the buffer layer, together with its deposition process, changes the properties of the CIGS absorber. Also, it shows that the ZnSnO semiconductor is a promising buffer layer for CIGS based solar cells. The lower influence of the fluctuating potentials in the ZnSnO sample compared with the CdS one was discussed and three major candidates for this difference were identified: i) Cd_{Cu} donor defects present in the CdS sample; ii) increased modification of types and densities of defects, including ion mobility, in the ZnSnO sample due to the higher substrate deposition temperature and iii) effects of exposing the CIGS surface to the aggressive CBD solution in the CdS sample. These conclusions should be kept in mind when designing buffer layer materials and/or choosing their deposition methods.

ACKNOWLEDGMENT

The authors would like to thank the projects RECI/FIS-NAN/0183/2012 (COMPETE: FCOMP-01-0124-FEDER-

027494) and UID/CTM/50025/2013 from the Fundação para a Ciência e a Tecnologia (Portugal).

REFERENCES

- [1] R. Kamada, T. Yagioka, S. Adachi, A. Handa, K. F. Tai, T. Kato, and H. Sugimoto, "New world record Cu(In,Ga)(Se,S)₂ thin film solar cell efficiency beyond 22%," in *Photovoltaic Specialists Conference (PVSC), 2016 43th IEEE*, June 2016, p. 355.
- [2] A. Chirilă, P. Reinhard, F. Pianezzi, P. Bloesch, A. R. Uhl, C. Fella, L. Kranz, D. Keller, C. Gretener, H. Hagendorfer, D. Jaeger, R. Erni, S. Nishiwaki, S. Buecheler, and A. N. Tiwari, "Potassium-induced surface modification of Cu(In,Ga)Se₂ thin films for high-efficiency solar cells," *Nat Mater*, vol. 12, no. 12, pp. 1107–1111, Dec. 2013. [Online]. Available: <http://dx.doi.org/10.1038/nmat3789>
- [3] T. M. Friedlmeier, P. Jackson, A. Bauer, D. Hariskos, O. Kiowski, R. Wuerz, and M. Powalla, "Improved photocurrent in Cu(In,Ga)Se₂ solar cells: From 20.8% to 21.7% efficiency with CdS buffer and 21.0% Cd-free," *IEEE Journal of Photovoltaics*, vol. 5, no. 5, pp. 1487–1491, Sept 2015.
- [4] N. Naghavi, D. Abou-Ras, N. Allsop, N. Barreau, S. Buecheler, A. Ennaoui, C.-H. Fischer, C. Guillen, D. Hariskos, J. Herrero, R. Klenk, K. Kushiya, D. Lincot, R. Menner, T. Nakada, C. Platzer-Björkman, S. Spiering, A. Tiwari, and T. Törndahl, "Buffer layers and transparent conducting oxides for chalcopyrite Cu(In,Ga)(S,Se)₂ based thin film photovoltaics: present status and current developments," *Progress in Photovoltaics: Research and Applications*, vol. 18, no. 6, pp. 411–433, 2010. [Online]. Available: <http://dx.doi.org/10.1002/pip.955>
- [5] J. Lindahl, U. Zimmermann, P. Szaniawski, T. Törndahl, A. Hultqvist, P. Salomé, C. Platzer-Björkman, and M. Edoff, "Inline Cu(In,Ga)Se₂ co-evaporation for high-efficiency solar cells and modules," *IEEE Journal of Photovoltaics*, vol. 3, no. 3, pp. 1100–1105, July 2013.
- [6] M. Kapilashrami, C. X. Kronawitter, T. Törndahl, J. Lindahl, A. Hultqvist, W.-C. Wang, C.-L. Chang, S. S. Mao, and J. Guo, "Soft X-ray characterization of Zn_{1-x}Sn_xO_y electronic structure for thin film photovoltaics," *Phys. Chem. Chem. Phys.*, vol. 14, pp. 10154–10159, 2012. [Online]. Available: <http://dx.doi.org/10.1039/C2CP41394A>
- [7] Y. S. Lee, J. Heo, S. C. Siah, J. P. Mailoa, R. E. Brandt, S. B. Kim, R. G. Gordon, and T. Buonassisi, "Ultrathin amorphous zinc-tin-oxide buffer layer for enhancing heterojunction interface quality in metal-oxide solar cells," *Energy Environ. Sci.*, vol. 6, pp. 2112–2118, 2013. [Online]. Available: <http://dx.doi.org/10.1039/C3EE24461J>
- [8] M. N. Mullings, C. Hägglund, and S. F. Bent, "Tin oxide atomic layer deposition from tetrakis(dimethylamino)tin and water," *Journal of Vacuum Science & Technology A*, vol. 31, no. 6, p. 061503, 2013. [Online]. Available: <http://scitation.aip.org/content/avs/journal/jvsta/31/6/10.1116/1.4812717>
- [9] J. Lindahl, C. Hägglund, J. T. Wätjen, M. Edoff, and T. Törndahl, "The effect of substrate temperature on atomic layer deposited zinc tin oxide," *Thin Solid Films*, vol. 586, pp. 82 – 87, 2015. [Online]. Available: <http://www.sciencedirect.com/science/article/pii/S0040609015003740>
- [10] J. Lindahl, J. Keller, O. Donzel-Gargand, P. Szaniawski, M. Edoff, and T. Törndahl, "Deposition temperature induced conduction band changes in zinc tin oxide buffer layers for Cu(In,Ga)Se₂ solar cells," *Solar Energy Materials and Solar Cells*, vol. 144, pp. 684 – 690, 2016. [Online]. Available: <http://www.sciencedirect.com/science/article/pii/S092702481500481X>
- [11] J. P. Leitão, J. P. Teixeira, J. J. Keller, T. Törndahl, S. Sadewasser, and P. M. P. Salomé, "Influence of CdS and Zn_xSn_{1-x}O_y Buffer Layers on the Photoluminescence of Cu(In,Ga)Se₂ Thin Films," in *Photovoltaic Specialists Conference (PVSC), 2016 43th IEEE*, June 2016, p. 826.
- [12] P. M. Salomé, V. Fjällström, P. Szaniawski, J. P. Leitão, A. Hultqvist, P. A. Fernandes, J. P. Teixeira, B. P. Falcão, U. Zimmermann, A. F. da Cunha, and M. Edoff, "A comparison between thin film solar cells made from co-evaporated CuIn_{1-x}Ga_xSe₂ using a one-stage process versus a three-stage process," *Progress in Photovoltaics: Research and Applications*, vol. 23, no. 4, pp. 470–478, 2015, pIP-13-181.R1. [Online]. Available: <http://dx.doi.org/10.1002/pip.2453>
- [13] P. M. P. Salomé, J. Keller, T. Törndahl, J. P. Teixeira, N. Nicoara, R.-R. Andrade, D. G. Stroppa, J. C. González, M. Edoff, J. P. Leitão, and S. Sadewasser, "CdS and Zn_xSn_yO_z buffer layers in CIGS solar cells," *Solar Energy Materials and Solar Cells*, 2016, submitted.
- [14] J. P. Teixeira, R. A. Sousa, M. G. Sousa, A. F. da Cunha, P. A. Fernandes, P. M. P. Salomé, and J. P. Leitão, "Radiative transitions in highly doped and compensated chalcopyrites and kesterites: The case of Cu₂ZnSnS₄," *Phys. Rev. B*, vol. 90, p. 235202, Dec 2014. [Online]. Available: <http://link.aps.org/doi/10.1103/PhysRevB.90.235202>

- [15] J. M. J. M. Doña and J. Herrero, "Dependence of electro-optical properties on the deposition conditions of chemical bath deposited CdS thin films," *J. Electrochem. Soc.*, vol. 244, pp. 4091–4098, 1997. [Online]. Available: <http://jes.ecsdl.org/content/144/11/4091.short>
- [16] Z. I. Alferov, V. M. Andreev, D. Z. Garbuzov, and M. K. Trukan, "Radiative recombinations in epitaxial compensated gallium arsenide," *Soviet Physics-Semiconductors*, vol. 6, no. 10, p. 1718, 1973.
- [17] P. W. Yu, "Radiative recombination in melt-grown and Cd-implanted CuInSe₂," *Journal of Applied Physics*, vol. 47, no. 2, pp. 677–684, 1976. [Online]. Available: <http://scitation.aip.org/content/aip/journal/jap/47/2/10.1063/1.322633>
- [18] A. P. Levanyuk and V. V. Osipov, "Edge luminescence of direct-gap semiconductors," *Soviet Physics Uspekhi*, vol. 24, no. 3, p. 187, 1981. [Online]. Available: <http://stacks.iop.org/0038-5670/24/i=3/a=R02>
- [19] I. Dirnstorfer, D. M. Hofmann, D. Meister, B. K. Meyer, W. Riedl, and F. Karg, "Postgrowth thermal treatment of CuIn(Ga)Se₂: Characterization of doping levels in In-rich thin films," *Journal of Applied Physics*, vol. 85, no. 3, p. 1423, 1999. [Online]. Available: <http://scitation.aip.org/content/aip/journal/jap/85/3/10.1063/1.369273>
- [20] T. Gokmen, E. Gunawan, T. K. Todorov, and D. B. Mitzi, "Band tailing and efficiency limitation in kesterite solar cells," *Applied Physics Letters*, vol. 103, no. 10, p. 103506, 2013. [Online]. Available: <http://scitation.aip.org/content/aip/journal/apl/103/10/10.1063/1.4820250>
- [21] J. P. Teixeira, R. A. Sousa, M. G. Sousa, A. F. da Cunha, P. A. Fernandes, P. M. P. Salomé, J. C. González, and J. P. Leitão, "Comparison of fluctuating potentials and donor-acceptor pair transitions in a Cu-poor Cu₂ZnSnS₄ based solar cell," *Applied Physics Letters*, vol. 105, no. 16, 2014. [Online]. Available: <http://scitation.aip.org/content/aip/journal/apl/105/16/10.1063/1.4899057>
- [22] —, "Erratum: Comparison of fluctuating potentials and donor-acceptor pair transitions in a Cu-poor Cu₂ZnSnS₄ based solar cell [Appl. Phys. Lett. 105, 163901 (2014)]," *Applied Physics Letters*, vol. 107, no. 4, p. 049903, 2015. [Online]. Available: <http://scitation.aip.org/content/aip/journal/apl/107/4/10.1063/1.4927663>
- [23] I. Dirnstorfer, M. Wagner, D. M. Hofmann, M. D. Lampert, F. Karg, and B. K. Meyer, "Characterization of CuIn(Ga)Se₂ Thin Films," *physica status solidi (a)*, vol. 168, no. 1, pp. 163–175, 1998. [Online]. Available: [http://dx.doi.org/10.1002/\(SICI\)1521-396X\(199807\)168:1<163::AID-PSSA163>3.0.CO;2-T](http://dx.doi.org/10.1002/(SICI)1521-396X(199807)168:1<163::AID-PSSA163>3.0.CO;2-T)
- [24] J. P. Leitão, N. M. Santos, P. A. Fernandes, P. M. P. Salomé, A. F. da Cunha, J. C. González, G. M. Ribeiro, and F. M. Matinaga, "Photoluminescence and electrical study of fluctuating potentials in Cu₂ZnSnS₄-based thin films," *Phys. Rev. B*, vol. 84, p. 024120, Jul 2011. [Online]. Available: <http://link.aps.org/doi/10.1103/PhysRevB.84.024120>
- [25] T. Schmidt, K. Lischka, and W. Zulehner, "Excitation-power dependence of the near-band-edge photoluminescence of semiconductors," *Phys. Rev. B*, vol. 45, pp. 8989–8994, Apr 1992. [Online]. Available: <http://link.aps.org/doi/10.1103/PhysRevB.45.8989>
- [26] J. P. Leitão, A. Carvalho, J. Coutinho, R. N. Pereira, N. M. Santos, A. O. Ankiewicz, N. A. Sobolev, M. Barroso, J. L. Hansen, A. N. Larsen, and P. R. Briddon, "Influence of Ge content on the optical properties of X and W centers in dilute Si-Ge alloys," *Phys. Rev. B*, vol. 84, no. 16, p. 165211, 2011.
- [27] C. Persson, "Anisotropic hole-mass tensor of cuin1xgax(se)2: Presence of free carriers narrows the energy gap," *Applied Physics Letters*, vol. 93, no. 7, p. 072106, 2008. [Online]. Available: <http://scitation.aip.org/content/aip/journal/apl/93/7/10.1063/1.2969467>
- [28] P. M. P. Salomé, P. A. Fernandes, J. P. Leitão, M. G. Sousa, J. P. Teixeira, and A. F. da Cunha, "Secondary crystalline phases identification in Cu₂ZnSnSe₄ thin films: contributions from Raman scattering and photoluminescence," *Journal of Materials Science*, vol. 49, no. 21, pp. 7425–7436, 2014. [Online]. Available: <http://dx.doi.org/10.1007/s10853-014-8446-2>
- [29] S. B. Zhang, S.-H. Wei, A. Zunger, and H. Katayama-Yoshida, "Defect physics of the CuInSe₂ chalcopyrite semiconductor," *Phys. Rev. B*, vol. 57, pp. 9642–9656, Apr 1998. [Online]. Available: <http://link.aps.org/doi/10.1103/PhysRevB.57.9642>
- [30] S.-H. Wei, S. B. Zhang, and A. Zunger, "Effects of Ga addition to CuInSe₂ on its electronic, structural, and defect properties," *Applied Physics Letters*, vol. 72, no. 24, pp. 3199–3201, 1998. [Online]. Available: <http://scitation.aip.org/content/aip/journal/apl/72/24/10.1063/1.121548>
- [31] D. S. Albin, J. J. Carapella, J. R. Tuttle, and R. Noufi, "The Effect of Copper Vacancies on the Optical Bowing of Chalcopyrite Cu(In,Ga)Se₂ Alloys," in *Symposium N Materials for Optical Information Processing*, ser. MRS Online Proceedings Library Archive, vol. 228, 1991, pp. 267–272. [Online]. Available: http://journals.cambridge.org/article_S1946427400386651
- [32] C. Lei, M. Duch, I. M. Robertson, and A. Rockett, "Effects of solution-grown CdS on Cu(In,Ga)Se₂ grain boundaries," *Journal of Applied Physics*, vol. 108, no. 11, p. 114908, 2010. [Online]. Available: <http://scitation.aip.org/content/aip/journal/jap/108/11/10.1063/1.3512966>
- [33] K. Ramanathan, H. Wiesner, S. Asher, D. Niles, R. N. Bhattacharya, J. Keane, M. A. Contreras, and R. Noufi, "High efficiency Cu(In,Ga)Se₂ thin film solar cell without intermediate buffer layers," in *Proc. 2nd World Conference on Photovoltaic Solar Energy Conversion, Vienna 610 July 1998, Austria*, vol. 228, 1998, pp. 477–481. [Online]. Available: www.nrel.gov/docs/legosti/fy98/23898.pdf
- [34] K. Ramanathan, F. Hasoon, S. Smith, D. Young, M. Contreras, P. Johnson, A. Pudov, and J. Sites, "Surface treatment of CuInGaSe₂ thin films and its effect on the photovoltaic properties of solar cells," *Journal of Physics and Chemistry of Solids*, vol. 64, no. 910, pp. 1495 – 1498, 2003, 13th International Conference on Ternary and Multinary Compounds. [Online]. Available: <http://www.sciencedirect.com/science/article/pii/S0022369703001690>
- [35] A. Hultqvist, J. V. Li, D. Kuciauskas, P. Dippo, M. A. Contreras, D. H. Levi, and S. F. Bent, "Reducing interface recombination for Cu(In,Ga)Se₂ by atomic layer deposited buffer layers," *Applied Physics Letters*, vol. 107, no. 3, 2015. [Online]. Available: <http://scitation.aip.org/content/aip/journal/apl/107/3/10.1063/1.4927096>
- [36] D. Liao and A. Rockett, "Cd doping at the CuInSe₂/CdS heterojunction," *Journal of Applied Physics*, vol. 93, no. 11, pp. 9380–9382, 2003. [Online]. Available: <http://scitation.aip.org/content/aip/journal/jap/93/11/10.1063/1.1570500>
- [37] K. Ramanathan, H. Wiesner, S. Asher, D. Niles, J. Webb, J. Keane, and R. Noufi, "A Study of the CdS/CuIn(Ga)Se₂ Interface in Thin Film Solar Cells," in *Symposium G Thin Film Structures for Photovoltaics*, ser. MRS Online Proceedings Library Archive, vol. 485, 1997, pp. 121–127. [Online]. Available: http://journals.cambridge.org/article_S1946427400219398
- [38] U. Rau, D. Braunger, R. Herberholz, H. W. Schock, J.-F. Guillemoles, L. Kronik, and D. Cahen, "Oxygenation and air-annealing effects on the electronic properties of Cu(In,Ga)Se₂ films and devices," *Journal of Applied Physics*, vol. 86, no. 1, pp. 497–505, 1999. [Online]. Available: <http://scitation.aip.org/content/aip/journal/jap/86/1/10.1063/1.370758>
- [39] L. Kronik, U. Rau, J.-F. Guillemoles, D. Braunger, H.-W. Schock, and D. Cahen, "Interface redox engineering of Cu(In,Ga)Se₂ based solar cells: oxygen, sodium, and chemical bath effects," *Thin Solid Films*, vol. 361362, pp. 353 – 359, 2000. [Online]. Available: <http://www.sciencedirect.com/science/article/pii/S0040609099007683>
- [40] U. Rau and M. Schmidt, "Electronic properties of ZnO/CdS/Cu(In,Ga)Se₂ solar cells aspects of heterojunction formation," *Thin Solid Films*, vol. 387, no. 12, pp. 141 – 146, 2001, proceedings of Symposium N on Thin Film Photovoltaic materials of the E-MRS Spring Conference. [Online]. Available: <http://www.sciencedirect.com/science/article/pii/S0040609000017375>
- [41] P. Reinhard, B. Bissig, F. Pianezzi, E. Avancini, H. Hagendorfer, D. Keller, P. Fuchs, M. Döbeli, C. Vigo, P. Crivelli, S. Nishiwaki, S. Buecheler, and A. N. Tiwari, "Features of KF and NaF Postdeposition Treatments of Cu(In,Ga)Se₂ Absorbers for High Efficiency Thin Film Solar Cells," *Chemistry of Materials*, vol. 27, no. 16, pp. 5755–5764, 2015. [Online]. Available: <http://dx.doi.org/10.1021/acs.chemmater.5b02335>
- [42] D. J. Schroeder and A. A. Rockett, "Electronic effects of sodium in epitaxial CuIn_{1-x}Ga_xSe₂," *Journal of Applied Physics*, vol. 82, no. 10, pp. 4982–4985, 1997. [Online]. Available: <http://scitation.aip.org/content/aip/journal/jap/82/10/10.1063/1.366365>
- [43] P. M. P. Salomé, A. Hultqvist, V. Fjällström, M. Edoff, B. Aitken, K. Vaidyanathan, K. Zhang, K. Fuller, and C. K. Williams, "Cu(In,Ga)Se₂ solar cells with varying Na content prepared on nominally alkali-free glass substrates," *IEEE Journal of Photovoltaics*, vol. 3, pp. 852–858, 2013.