Study of Ammonium Sulfide Surface Treatment for Ultrathin Cu(In, Ga)Se$_2$ with Different Cu/(Ga + In) Ratios

Dilara Gokcen Buldu, Jessica de Wild, Thierry Kohl, Guy Brammertz, Gizem Birant, Marc Meuris, Jef Poortmans, and Bart Vermang

In ultrathin Cu(In, Ga)Se$_2$ (CIGS) film solar cells, the CdS/CIGS interface may become one of the limiting factors for efficiency. The first step toward reducing the impact of this problem could be a surface treatment process to improve the quality of the front interface. The purpose of this study is to have a better understanding of the effect of wet chemical surface treatment, using ammonium sulfide ((NH$_4$)$_2$S), on CIGS thin film layers with different Cu/(Ga + In) (CGI) ratios. Herein, photoluminescence (PL) and time-resolved PL (TRPL) studies are conducted on bare CIGS, ammonium sulfide–treated CIGS thin films, and samples with CdS. In bare CIGS, CGI ratio–dependent changes in PL are observed on both a low-energy (defect related transition) and a high-energy peak (band-to-band transition). After the surface treatment, the PL maximum increases by factors ranging from 4 to 11 depending on the CGI ratio, accompanied by a slower decay. Trends with similar improvement as in the PL study are observed in the performance of the solar cells. It is shown that the impact of the surface treatment is beneficial independently of the CGI ratio of the absorber layers. In all cases, the treatment is shown to improve the efficiency.

1. Introduction

Among all thin film photovoltaic (PV) technologies, the Cu(In, Ga)Se$_2$ (CIGS) thin film is one of the most studied materials due to its high conversion efficiencies, beyond 23%. In addition to its high efficiencies, it has high potential for application in building-integrated PV solutions, which makes it an interesting candidate for the new emerging applications on the market. Nevertheless, CIGS is still far away from becoming dominant on the photovoltaic market. For CIGS thin film PV technologies to compete with dominant Si-PV technologies, their production costs will have to be reduced. One of the ways to reduce production costs is to reduce the thickness of CIGS material and, consequently, limit the usage of scarce elements such as In and Ga.

Another way is to use a simple and energy-efficient deposition method such as one-stage coevaporation to deposit the CIGS layers. Because of the one-stage process, there will be no Ga gradient, which will also improve the repeatability of the process. Yet, in the absence of a Ga gradient at the rear surface, when reducing the thickness of the absorber layer, interface recombination may become one of the factors limiting the performance of the solar cells. In addition, when there is no Ga grading toward the front surface, the recombination increases at the buffer/CIGS interface, and thus, the open circuit voltage can be decreased. Therefore, implementing a passivation layer at the front and rear interfaces becomes important to overcome the impact of this limitation. There have been successful studies for rear surface passivation. More recently, new studies have investigated front surface passivation. The first study was based on a metal–insulator–semiconductor device structure where a very thin gallium oxide (GaO$_x$)$_y$ layer was used as a passivation layer. This study showed that the efficiency of the solar cells improved with a very thin (less than 2 nm) passivation layer. Furthermore, the first implementation of a passivation layer with openings on the front interface of CIGS was recently demonstrated. However, no significant improvements to efficiency and open-circuit potential ($V_{oc}$) were observed. As can be seen, front surface passivation of CIGS absorbers is still challenging. In other words, the expected improvement has not yet been achieved. The surface properties of the absorber such as surface roughness, the most common copper selenide secondary...
phases, and impurities at the surface can be a critical factor. For that reason, the CIGS surface must be as clean as possible before further processing steps.

Several studies have reported that wet-chemical surface treatments before the CdS buffer layer deposition are a way to improve the efficiency of CIGS solar cells. Surface treatments lead to improved surface properties by removing secondary phases and undesired oxides and/or passivating the surface. Most commonly, a KCN treatment is used to etch a Cu$_{2-x}$Se secondary phase on Cu-rich CIGS thin films.$^{[7,8]}$ However, KCN is highly toxic, which is why recently ammonium sulfide has been investigated as an alternative and safer solution to KCN.$^{[9]}$ Also, NH$_3$ treatment is well known for eliminating any oxides present on the surface.$^{[10,11]}$ However, despite the apparent advantages of this surface treatment, possible disadvantages also have to be taken into account. For example, by etching In and Ga, the NH$_3$ treatment promotes the creation of a Cu–Se layer and interface defects may be created by using highly concentrated NH$_3$ solutions.$^{[11,12]}$ In addition to these treatments, surface sulfurization is also used to improve the performance of solar cells. Nakada et al. used an aqueous solution for surface sulfurization and reported that cell performance is improved either through the formation of a very thin sulphide layer or because the surface is passivated by sulfur atoms.$^{[13]}$ Another study showed that sulfurization with an Na$_2$S and thiourea solution can replace the surface oxides by sulfides. The O$_{ac}$ acceptor-type defect is replaced with a S$_{ac}$ because of the smaller electronegativity difference between In and S. This substitution may be more efficient to decrease surface recombination.$^{[14]}$ In light of the reported studies, finding optimal parameters of the surface treatments and a suitable surface treatment plays a key role in improving the efficiency of CIGS solar cells.

2. Result and Discussion

2.1. The Effect of Cu/(Ga + In) (CGI) Ratio on the Photoluminescence of Bare CIGS Thin Films

Three different types of CIGS films were used in this part. These samples are named according to their CGI ratio. Samples with different CGI ratios of 0.72 (Cu-poor), 0.8 (Cu-desired), and 0.92 (Cu-rich) were prepared to investigate the effect of the CGI ratio. The photoluminescence (PL) spectra of the as-prepared absorber layer as well as their calculated bandgap value and their peak maximum (dashed line) for each CGI ratio are given in Figure 1. The bandgap was calculated using the following equation$^{[15]}

$$E_g(x) = E_{g}^{CGS}(x) + E_{g}^{cis}(1 - x) - bx(1 - x)$$

(1)

where $x$ is the Ga/(Ga + In) (GGI) ratio, $E_{g}^{CGS} = 1.68$ eV is the bandgap of CuGaSe$_2$, and $E_{g}^{cis} = 1.02$ eV that of CuInSe$_2$. The bowing parameter $b$ is 0.21 eV. The CGI ratios are $x = 0.31$ and $x = 0.34$ for Cu-poor and Cu-rich samples, respectively, and $x = 0.27$ for the Cu-desired sample. As shown in Figure 1, two peaks appear in the PL spectra, one at high and one at low energy. While the peak positions depend on the CGI, the ratio between the low and higher energy peak change with the CGI ratio, similar to what we observed before.$^{[16]}$ The peak at high energy can be identified as band-to-band transition. With an increasing CGI ratio, both the PL peak maximum and its full width at half maximum (FWHM) decrease. One possible reason for this effect could be a reduced presence of copper vacancies with an increasing CGI ratio.$^{[17]}$ On the other hand, the low-energy peak, which is clearly visible in Cu-desired and Cu-rich samples, could be related to a defect. For the Cu-poor sample, a significant energy shift can be observed compared to the calculated bandgap, implying the peak is mainly due to a very intense defect-related transition. The band-to-band transition peak merges with the defect peak, thus forming the broad peak one can see in Figure 1. In their study, Hultqvist et al. showed, by using different buffer layers, that similar PL spectra contain a low-, medium-, and high-energy peak.$^{[18]}$ They suggested that these extra peaks below the bandgap could not be related to the absorber alone, but interface defects as well. In our case, we can tell that this low-energy peak is not due to the CIGS/CdS buffer layer interface as we investigated the bare CIGS absorber (Figure 1). Instead, we think that the low-energy peak is related to the copper vacancies as well, as its PL peak maximum and FWHM show changes with CGI. The Cu-poor samples with a CGI ratio of 0.72 has a 21 at% Cu concentration. Cu-desired and Cu-rich samples are grown with a CGI ratio of 0.8 (22.5 at% Cu) and 0.92 (24.5 at%) respectively. When examining the phase diagram of CI(G)Se, it can be seen that between 16 and 24 at% Cu content, the material has two phases, which are CunGaSe$_2$ and an ordered defect compound (ODC). This ODC defect consists of a Cu vacancy ($V_{Cu}$) and an antisite defect of In on Cu (In$_{Cu}$). The $V_{Cu}$ acceptor and In$_{Cu}$ donor defects easily form a neutral defect pair ($2V_{Cu}$ + In$_{Cu}$.$^{[13,14]}$ This complex defect ($2V_{Cu}$ + In$_{Cu}$) is expected to be electrically inactive.$^{[15,19,20]}$ In the Cu-desired sample, the low-energy peak was observed at around 1.04 eV, which is 110 meV lower than the band-to-band transition (1.15 eV). This peak cannot be related only to an
isolated $V_{\text{Cu}}$ defect because the acceptor-type defect level of $V_{\text{Cu}}$ is reported to be 30 meV.\textsuperscript{[21,22]} As the peak at low energy is significantly deeper than this, it could be related to a defect complex that includes $V_{\text{Cu}}$. We propose that this defect could be related either to the neutral complex defect ($2V_{\text{Cu}} + \text{In}_{\text{Cu}}$) or the acceptor-type defect $O_{\text{Sc}}$, as the difference in the position of the PL peaks matches the reported energies for these defects.\textsuperscript{[23–26]} However, Ishizuka et al. show that the behavior of the acceptor $O_{\text{Sc}}$ defect changes with sodium incorporation.\textsuperscript{[26]}

Thus, this defect cannot be the defect that we observed at low energy, because our samples have all been supplied with the same amount of sodium. Due to this, we conclude that the observed peak at low energy is most probably related to the neutral complex defect ($2V_{\text{Cu}} + \text{In}_{\text{Cu}}$).

### 2.2. The Effect of Ammonium Sulfide (AS) Surface Treatment on the Photoluminescence of CIGS Thin Films

In this section, we study the evolution of the PL and time-resolved photoluminescence (TRPL) responses of our samples after each of the processing steps. For each CGI ratio, we created a set of two absorbers: i) standard process (bare CIGS–CdS) referred to as w/o AS and ii) surface treatment process (bare CIGS–AS treatment–CdS) referred to as w/AS. First, the bare CIGS samples for each set were measured. Then, the measurements were performed after AS (for the AS-treated absorber of each set) and after CdS (for both samples in each set). In this manner, the changes in PL spectra and PL decay time were investigated step by step. The PL intensity change after each step for untreated (w/o AS) and AS-treated (w/ AS) samples is given as a ratio in Figure 2. After the AS treatment, the peak maximum increased 11-, 4-, and 7-fold for Cu-poor, Cu-desired, and Cu-rich samples, respectively. However, the peak maximum decreased slightly after CdS deposition for the Cu-poor and Cu-desired samples. We believe this is because during the chemical bath deposition, the CdS layer forms in a slightly different way on each sample as the formation of the buffer layer is impacted by changes on the sample surface and/or its composition. This could, then, lead to slight changes in the thickness of CdS, which can cause some absorption of the 532 nm laser light of the PL setup. Nevertheless, when comparing the CdS-covered samples with and without AS treatment, it can be clearly seen that the PL intensity is higher for the samples with AS treatment. Therefore, it can be said that AS treatment has a beneficial impact on the CIGS surface and improves the quality of the interface between CIGS and CdS. Figure 3a,b shows the changes in FWHM upon CdS deposition for untreated (w/o AS) and AS-treated (w/ AS) samples. Changes in the high- and low-energy peaks are shown for all three CGI ratios. The FWHM is determined by fitting the PL spectra using Gaussian peaks. Changes after AS treatment only (thus without CdS) are not shown here because the FWHM decreases only minimally. In Figure 3a, the FWHM of the peak at high energy after CdS deposition is shown. As can be seen, the peak at high energy continuously gets sharper with an increasing CGI ratio (the light dashed line in Figure 3a), as we previously discussed in the context of Figure 1. This effect is further amplified by the AS treatment (dark dashed line in Figure 3a). The FWHM change of the low-energy peak after CdS deposition is given in Figure 3b. Here, it is clearly visible that the peak gets broader with AS treatment. This could mean that the defect-related peak is disappearing after surface treatment. These significant changes on high-energy and low-energy peaks could be explained by the fact that sulfur fills the copper vacancies and thus $S_{\text{Cu}}$ forms during the surface treatment.\textsuperscript{[27,28]}

The improvements on the PL maximum and the FWHM of the high-energy peak may be expected as it has been previously shown that CdS has a passivating effect on CIGS by substituting Cd into $V_{\text{Cu}}$.\textsuperscript{[22,29,30]} As the PL maximum and FWHM further change upon AS, this passivation effect of CdS seems to be enhanced by the AS surface treatment. This enhancement could be related to the reduction of copper vacancies by sulfur substitution. Both effects due to the substitution of Cd and S then combine and generate a reduction in availability of copper vacancies. This reduces the overall concentration of ($2V_{\text{Cu}} + \text{In}_{\text{Cu}}$) defects in the material, thereby reducing the defect-related low-energy peak in the PL response. Another option, in the case of the Cu-rich samples, is the removal of any possible Cu$_2$–Se secondary phase.

The PL decay time of the samples for bare CIGS, after AS treatment and after CdS deposition, is given for all three CGI ratios in Figure 4a–c. In the PL decay graph for each ratio, only one curve of the bare CIGS was given for own CGI ratio, as all bare samples have a similar low PL decay time ($\approx\!1$ ns) independent of the CGI ratio. The PL decay time improved significantly after AS treatment for the Cu-poor and Cu-desired samples; however, for the Cu-rich sample, clear improvement on the PL decay time could not be observed. Moreover, the PL decay time of samples without AS treatment was improved after CdS deposition (w/o AS CIGS + CdS). This CdS-related
improvement was further enhanced after AS treatment for all samples, but the most significant change was observed for the Cu-poor and Cu-desired samples (w/ AS CIGS + CdS). Thus, it appears that the passivation effect of AS is more effective in Cu-poor and Cu-desired absorbers. This can be explained by the filling of $V_{\text{Cu}}$ with sulfur, and thus reduction of the complex defect $(2V_{\text{Cu}} + \text{In}_{\text{Cu}})$. For the Cu-rich sample, alongside the possible reduction of the concentration of $(2V_{\text{Cu}} + \text{In}_{\text{Cu}})$, the $\text{Cu}_2\text{Se}$ secondary phases could be removed as well with AS, as is a known etchant for this secondary phase.\[9\]

2.3. The Effect of AS Surface Treatment on Device Performance

In this section, the samples that we used in the PL study were processed into solar cells. An improving trend with AS treatment similar to the one detected in the PL and TRPL measurements was also observed in current-voltage ($I$–$V$) measurements. The solar cell parameters are given in Figure 5. In our measurements, the $V_{\text{oc}}$ improved for the Cu-poor and Cu-desired samples, but decreased for the Cu-rich sample. The fill factor (FF) improved for the Cu-desired and Cu-rich samples, but decreased slightly for the Cu-poor sample, while the current increased or remained constant. When the surface recombination decreases following chemical surface passivation, the open circuit voltage ($V_{\text{oc}}$) and FF are expected to improve.\[31\] An increase in $V_{\text{oc}}$ can be estimated from the PL yield, by transforming the Lasher-Stren-Wurfel equation into\[32\]

$$\Delta\mu_{\text{AS-ref}} = kT \ln \left( \frac{I_{\text{AS}}}{I_{\text{ref}}} \right)$$

\(I_{\text{AS}}\) is the PL peak maximum of the high-energy peak of the AS-treated samples and \(I_{\text{ref}}\) is the PL peak maximum of the high-energy peak of the reference, i.e., the untreated sample. Both intensities are after CdS deposition. $\Delta\mu$ is the quasi-Fermi-level splitting, which is an equivalent measure for the maximum $V_{\text{oc}}$. Thus, changes in $\Delta\mu$ can be directly related to changes in $V_{\text{oc}}$. According to Equation (2), the expected improvement in $V_{\text{oc}}$ was 15, 20, and 35 mV for the Cu-poor, Cu-desired, and Cu-rich samples, respectively. In the case of the Cu-poor and Cu-desired samples, we measured an improvement in the open circuit voltage after AS treatment of 12 and 20 mV, respectively. These values are in good agreement with the improvements predicted by Equation (2). This leads us to conclude that surface treatment with AS has a similar effect on surface passivation in the case of the Cu-desired and Cu-poor samples. The predicted $V_{\text{oc}}$ improvement was not observed for the Cu-rich sample, as the $V_{\text{oc}}$ for the AS-treated sample is lower than that for the untreated sample. This reduction of the $V_{\text{oc}}$ could be related to the duration of the surface treatment. Buffiere et al. showed that for a CIGS sample with CGI:0.9 one can observe a drop in $V_{\text{oc}}$ if the sample is etched with AS for too long. Nevertheless, the performance of their solar cells was improved due to a gain in short circuit current.\[9\] This current gain was also observed for our Cu-rich sample. Thus, it can be said that the improvement in device performance is mostly related to removing possible $\text{Cu}_2\text{Se}$ secondary phases. The external quantum efficiency (EQE)-corrected power conversion efficiency of samples increased with AS treatment from 7.8% to 8%, from 5% to 6%, and from 6.6% to 8.2% for the Cu-poor, Cu-desired, and Cu-rich champion cells, respectively. These results indicate that, during the AS treatment, a combination of different effects takes place. It can be said that the observed improvements are either coming from the passivation of the surface or are possibly due to removal of secondary phases for the Cu-rich sample. Unfortunately, the device performance of

Figure 3. a) The change in FWHM of the high-energy peak after CdS deposition for each sample (w/o AS and w/ AS) for each CGI ratio. The dashed line is a guide to the eye following the evolution of the FWHM of the high-energy peak (dots) and shows that the peak is consistently getting narrower after AS treatment when compared to the untreated samples (w/o AS). b) The trend in FWHM of the low-energy peak (green dots) shows that it is broadening with AS treatment.
our one-stage coevaporated CIGS is still limited by other factors. Typically, the performance of this type of material is lower than for the more conventionally used three-stage coevaporated samples. This is mainly because in our samples there is no Ga grading at the front and back surface. Therefore, the interface recombination at both the front and back interface is more critical and is one of the limiting factors for our device performance.\textsuperscript{[13]} Also, our CIGS has relatively small grains (<100 nm), and thus more grain boundaries.\textsuperscript{[34]} The grain boundaries are generally accepted in their role as recombination centers. The high concentration of them is, thus, another limiting factor for device performance. Due to these limiting factors in the bulk and the back interface, the significant improvements in PL cannot be reflected “as is” to the performance of the devices, as treatment is only affecting the CdS/CIGS front surface. Nevertheless, the AS treatment shows definite improvements for all studied CGI ratios. Therefore, it can be said that AS surface treatment is an easy and promising way to improve the buffer/CIGS interface.

### 3. Conclusion

In this study, first, we investigated the effect of the CGI ratio on CIGS thin films. The PL spectra revealed two peaks, which behaved differently depending on the CGI ratio. A low-energy peak, related to the \((2V_{\text{Cu}} + V_{\text{Cu}})\) transition, decreases in intensity with increasing CGI ratio and a high-energy peak, related to the band-to-band transition, becomes sharper. One possible explanation can be a lowering of the amount of Cu vacancies with increasing Cu content. The reduced availability of Cu vacancies reduces the intensity of the low-energy peak by limiting the formation of the \((2V_{\text{Cu}} + V_{\text{Cu}})\) defect complex and sharpens

![Figure 4](image-url)

**Figure 4.** The PL decay lifetime for bare CIGS, after AS treatment (w/ AS CIGS), and after CdS for both untreated (w/o AS) and AS-treated (w/ AS) for the a) Cu-poor, b) Cu-desired, and c) Cu-rich samples. The black continuous line stands for the bare CIGS absorber; the CIGS absorber after AS-treatment is red. The green line is after CdS deposition for the AS-treated sample and the blue one is for the CdS-deposited sample w/o AS treatment. In all cases, the PL decay time improves after the deposition of the CdS layer. This effect is enhanced if CdS is deposited after treating the sample with AS.
the high-energy peak (band-to-band transition) by reducing band fluctuations.

Then, the effect of AS treatment on these samples with different CGI ratios was investigated. The PL intensity and PL decay time are improved after AS treatment and this improvement is maintained after the CdS deposition. We believe this enhancement could be due, once more, to the reduction in the density of Cu vacancies. This reduction takes place through filling of these vacancies with a sulfur atom during the AS treatment. In addition, for the Cu-rich sample, the removal of the \( \text{Cu}_2 \text{Se} \) secondary phase is possibly a cause for the observed improvements.

Measuring the \( I-V \) characteristic of the samples processed into solar cells, the performance was shown to improve with AS treatment. The improvement of the solar cell parameters such as \( V_{\text{oc}} \) and FF indicates that the AS surface treatment has an effect comparable to surface passivation on the Cu-poor and Cu-desired samples. However, for the Cu-rich sample, the improved performance is mostly due to an increased \( J_{\text{sc}} \), which can be due to the removal of the secondary phases.

In this article, we showed that when the AS treatment is applied to the surface of the CIGS absorber before deposition of the CdS layer, the PL decay time and the performance of the devices are enhanced for all CGI ratios. An absolute improvement of up to 1.16% was observed in the solar cell performance. Combining the AS treatment with a passivation layer may improve the performance of solar cells even further. Our results show that AS surface treatment could be an effective way to passivate the front surface by reducing interface defects and removing the secondary phases, thus improving the interface between CIGS and the CdS buffer layer. Further research is currently being focused on explaining the exact impact of the treatments and different ways to passivate the other factors limiting the efficiency of our solar cells.

4. Experimental Section

**CIGS Absorber Processing:** The CIGS was deposited on SLG/Si(O,N)/Mo/2 nm NaF/substrate by using a one-stage coevaporation process. The evaporation rates of all the sources (Cu, In, Ga, and Se) were kept
constant during the absorber layer deposition until the thickness of 450–500 nm and desired composition were obtained. Thanks to this process a flat and homogenous Ga profile was achieved in the CIGS layer.[12] Three sets with different CGI ratios were created. The sets were named according to the CGI ratio; CGI was 0.72 for the Cu-poor sample, 0.8 for the Cu-desired sample, and 0.92 for the Cu-rich sample. Each set contained two absorbers: i) standard process (bare CIGS–w/ AS) CdS) and ii) surface treatment process (bare CIGS–AS treatment–w/ AS) CdS). The composition and thickness were measured with X-ray fluorescence (XRF) and an XRF map was generated for each sample.

Characterization: PL and TRPL measurements were performed with a Picquant FluoroTime 300 system with an excitation wavelength of 532 nm (25ps, 3 MHz). PL and TRPL measurements were taken before and after AS surface cleaning and after CdS deposition. With the help of the XRF map, PL and TRPL were taken at the same three points for bare CIGS samples (the first set) and four points for the samples that were used as solar cells (the second set). The performance of the solar cells was measured at room temperature by using a solar simulator equipped with an AM 1.5 filter and a Keithley 2401 source meter.

AS Treatment: The AS solution with 6–7.5% sulfur concentration was used for surface treatment. The CIGS samples were dipped into the AS solution for 5 min, which was followed by two times 2 min of rinsing in deionized water before being dried with a nitrogen gun.

Solar Cell Processing: After the AS treatment, a CdS buffer layer (30–40 nm) was deposited on the reference and AS-treated samples by spray deposition. The aqueous solution was prepared with cadmium acetate dihydrate (2.7 × 10^{-5} mol), thiourea (95 × 10^{-5} mol), ammonia (2.2 mol) at 65 °C and the deposition took place in ≈13 min. Solar cells were produced by sputtering an i-ZnO/Al:ZnO window layer and finished with Ni/Al/Ni grids.

Acknowledgements

This work received funding from the European Union’s H2020 research and innovation program under grant agreement No. 715027.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

Cu/(Ga + In) ratio, Cu(In, Ga)Se2, photoluminescence, solar cells, surface treatment, thin film photovoltaics

Received: May 16, 2020  
Revised: July 29, 2020  
Published online: August 26, 2020

[1] M. A. Green, E. D. Dunlop, J. Hohl-Ebinger, M. Yoshita, N. Kip payoff, A. W. Y. Ho-Baillie, J. Poortmans, B. Vermang, in: Conf. Record of the Thirty-First IEEE Photovoltaic Specialists Conf., IEEE, Lake Buena Vista, FL 2005, p. 255.

[2] T. Nakada, K. Matsumoto, M. Okumura, in: Conf. Record of the Twenty-Ninth IEEE Photovoltaic Specialists Conf., IEEE, New Orleans, LA 2002, p. 257.

[3] W. Li, S. R. Cohen, D. Cahan, Sol. Energy Mater. Sol. Cells 2014, 120, 500.

[4] W. N. Shafarman, S. Siebentritt, L. Stolt, Handbook of Photovoltaic Science and Engineering, 2nd ed., John Wiley & Sons, Chichester, West Sussex, UK 2011.

[5] A. Hultqvist, J. V. Li, D. Kuciauskas, E. Bucher, Prog. Photovoltaics Res. Appl. 2014, 22, 1027.

[6] J. Lückinger, S. Nishiwaki, B. Bissig, G. Degutis, Y. E. Romanyuk, S. Buecheler, A. N. Tiwari, Sol. Energy Mater. Sol. Cells 2019, 195, 213.

[7] Y. Hashimoto, N. Kohara, T. Negami, M. Nishitani, T. Wada, Jpn. J. Appl. Phys. 1996, 35, 4760.

[8] H. Marko, L. Arzel, A. Darga, N. Barreau, S. Noël, D. Mencaraglia, J. Kessler, Thin Solid Films 2011, 519, 7228.

[9] M. Buffière, A. A. El Mel, N. Lenaers, G. Brammertz, A. E. Zaghi, M. Meuris, J. Poortmans, Adv. Energy Mater. 2015, 5, 1.

[10] B. Canava, J. Vigneron, A. Etcheberry, D. Guimard, J. Guillemoles, D. Lincot, Thin Solid Films 2002, 403–404, 425.

[11] J. Li, Y. Ma, G. Chen, J. Gong, X. Wang, Y. Kong, X. Ma, K. Wang, W. Li, C. Yang, X. Xiao, Sol. RRL 2019, 3, 1.

[12] C. L. Perkins, F. S. Hasoon, H. A. A-Thani, S. E. Asher, P. Sheldon, in: Conf. Record of the Thirty-First IEEE Photovoltaic Specialists Conf., IEEE, Lake Buena Vista, FL 2005, p. 255.

[13] T. Nakada, K. Murayama, M. Okumura, in: Conf. Record of the Twenty-Ninth IEEE Photovoltaic Specialists Conf., IEEE, New Orleans, LA 2002, p. 257.

[14] A. Hultqvist, J. V. Li, D. Kuciauskas, P. Dippo, M. A. Contreras, D. H. Levi, F. Stacey, Appl. Phys. Lett. 2015, 107, 033906.

[15] S. B. Zhang, S. H. Wei, A. Zunger, Phys. Rev. Lett. 1997, 78, 4059.

[16] S. B. Zhang, S. Wei, A. Zunger, Phys. Rev. B 1998, 57, 5642.

[17] M. H. Wolter, Optical Investigation of Voltage Losses in High-Efficiency Cu(In,Ga)Se2 Thin-Film Solar Cells, Universite Du Luxembourg, Luxembourg 2019.

[18] S. Shirakata, K. Ohkubo, Y. Ishii, T. Nakada, Sol. Energy Mater. Sol. Cells 2009, 93, 988.

[19] J. Parravicini, M. Acciarri, M. Murabito, A. De Lonno, A. Gasparotto, S. Binetti, Appl. Opt. 2018, 57, 1849.

[20] J. H. Schon, C. Kloc, E. Bucher, Thin Solid Films 2009, 362, 411.

[21] J. Yang, H. W. Du, Y. Li, M. Gao, Y. Z. Wan, F. Xu, Z. Q. Ma, AIP Adv. 2016, 6, 085215.

[22] S. Shirakata, M. M. Islam, H. Shibata, P. Fons, P. Furbo, T. Kohl, J. H. Schon, C. Kloc, Mater. Sci. Forum 2015, 801, 347.

[23] J. Parravicini, M. Acciarri, M. Murabito, A. Le Donne, A. Gasparotto, S. Binetti, Appl. Phys. Lett. 2018, 102, 185905.

[24] J. Parravicini, M. Acciarri, A. Le Donne, A. Gasparotto, S. Binetti, Appl. Phys. Lett. 2019, 115, 185905.

[25] J. H. Schon, C. Kloc, E. Bucher, Thin Solid Films 2009, 362, 411.

[26] S. Shirakata, M. M. Islam, H. Shibata, P. Fons, P. Furbo, T. Kohl, J. H. Schon, C. Kloc, Mater. Sci. Forum 2015, 801, 347.

[27] J. Parravicini, M. Acciarri, M. Murabito, A. Le Donne, A. Gasparotto, S. Binetti, Appl. Phys. Lett. 2018, 102, 185905.

[28] S. Shirakata, M. M. Islam, H. Shibata, P. Fons, P. Furbo, T. Kohl, J. H. Schon, C. Kloc, Mater. Sci. Forum 2015, 801, 347.