Electrostatic potential fluctuations and light-soaking effects in Cu(In,Ga)Se₂ solar cells

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Abstract
In Cu(In,Ga)Se₂ (CIGS) thin-film solar cells, laterally inhomogeneous distributions of point defects may induce electrostatic potential fluctuations and thus reduce the open-circuit voltage (Voc). In the present work, we investigate possible origins of fluctuating potentials and estimate the amplitude of fluctuations and Voc losses in solar cells with various [Ga] in the CIGS absorber, with different buffer layers and with different durations of an RbF postdeposition treatment (PDT). Electron-beam-induced current measurements were employed to study the local difference in the width of the space-charge region (wSCR). It is shown that the amplitude of fluctuations in the wSCR depends significantly on the choice of buffer system and on the duration of the RbF PDT. In addition, energy-dispersive X-ray spectroscopy and cathodoluminescence measurements reveal that band-gap fluctuations do not have substantial impact on the device performance. Finally, some of the investigated cells were exposed to light soaking, which was found to be a means to reduce the detected electrostatic potential fluctuations and also to increase the effective electron diffusion length in the CIGS absorber for a part of the investigated cells.

KEYWORDS
Cu(In,Ga)Se₂, electron-beam-induced current, electrostatic potential fluctuations, light soaking, space-charge region

1 | INTRODUCTION

Thin-film solar cells based on polycrystalline Cu(In,Ga)Se₂ (CIGS) or Cu(In,Ga)(S,Se)₂ absorber layers have made significant progress in the recent years achieving power conversion efficiencies of up to 23.4%.¹ Various methods were implemented in order to improve the performance including alkali postdeposition treatments (PDTs),² composition grading,⁴ and improvement of the buffer layer.⁵ However, even the record devices are limited in their open-circuit voltages, Voc, and fill factors, FF, as compared with theoretical values of the Shockley–Queisser limit,⁶ primarily due to non-radiative recombination.

It was reported by several authors⁷⁻¹⁰ that inhomogeneities in CIGS thin films may lead to the occurrence of potential fluctuations, which may enhance recombination and thus decrease the Voc of the corresponding device. Three different types of inhomogeneities can be considered within the solar cell: band-gap fluctuations due to local variations in composition (i), as well as net...
doping (ii) and lifetime fluctuations (iii) due to inhomogeneous distributions of (charged) point defects and corresponding redistribution of free charge carriers.\(^\text{11}\) While compositional inhomogeneities have already been studied extensively,\(^\text{9,12}\) only a few reports are discussing possible origins of net doping and lifetime fluctuations in CIGS solar cells. In particular, it was suggested that the choice of a buffer layer\(^\text{13}\) has an impact on electrostatic potential fluctuations, assuming a high density of defects at the CIGS/buffer interface. It was also proposed that the increase in \(V_{oc}\) after PDT is due to reduction of electronic potential fluctuations.\(^\text{14}\)

In the course of the present work, electron-beam-induced current (EBIC) and cathodoluminescence (CL) measurements in scanning electron microscopy (SEM) were employed to investigate the extent of fluctuations in CIGS solar cells. Applying these techniques in a correlative manner on cross-sectional samples of completed solar cell devices provided the means to estimate in homogeneities in local band-gap energies (CL) and charge distributions (EBIC) on the submicrometer scale and allowed for making a quantitative analysis of present potential fluctuations as well as of their impact on the device performance. Band-gap and electrostatic potential fluctuations in CIGS solar cells with various [Ga] in the CIGS layers, buffer system combinations, and durations of the RbF PDT were studied. First, we show that fluctuations of the CL peak energy measured in CIGS layers are not substantial. Then, we will discuss the origins of net-doping variations and their impact on the \(V_{oc}\). Also, microscopic effects of light soaking (LS) and its influence on electrostatic potential fluctuations will be shown. We will compare the LS effects in solar cells with CdS and Zn(O,S) buffer layers, demonstrate that these effects are particularly strongly pronounced in cells with Zn(O,S) buffers, as already reported by various authors,\(^\text{15,16}\) and propose a model on the basis of changes in charge states at the CIGS/buffer interface.

## 2 | EXPERIMENTAL DETAILS

### 2.1 | Solar-cell production and cross-sectional specimen preparation for electron microscopy

#### 2.1.1 | Fabrication of CIGS solar cells with CdS and Zn(O,S) buffer layers and [Ga]/([Ga] + [In]) ratios of 0.30 and 0.66

CIGS absorbers were deposited at ZSW with an in-line multistage coevaporation process on Mo-coated soda-lime glass (SLG) substrates.\(^\text{17}\) No alkali PDT processes were used, and Na (partially K) was only provided from SLG during CIGS deposition at elevated temperatures. Averaged [Ga]/([Ga] + [In]) (GGI) ratios of 0.30 and 0.66 were realized by adapting the Ga and In evaporation rates on different substrate carriers in the same deposition run. Subsequently, CdS or Zn(O,S) buffer layers were grown on the polycrystalline CIGS films by chemical bath deposition (CBD) with thiourea-based processes for both buffer materials.\(^\text{18}\) RF-sputtered i-ZnO was deposited as highly resistive (HR) layer on CdS-buffered samples and for cells with Zn(O,S) RF-sputtered Zn(Mg)O with a [Mg]/([Mg] + [Zn]) of 0.25. DC-sputtered ZnO:Al was used for all stacking sequences as front contact. Solar cells with an area of 0.5 cm² were completed with Ni/Al/Ni grid fingers on top without antireflective coating. An overview of the studied samples with corresponding solar cell parameters is given in Table 1 corresponding to Sample Nos. 1-4.

#### 2.1.2 | Fabrication of CIGS solar cells with CdS and CdIn\(_2\)S\(_4\) buffer layers

CIGS thin films deposited at IMN were grown onto SLG/Mo substrates following a bithermal (380–580°C), static, three-stage process. The overall composition of the 2.2-μm-thick absorber corresponds to GGI = 0.25 and [Cu]/([Ga] + [In]) = 0.85 (CGI). These absorbers were covered with either 50-nm-thick CBD-CdS or CdIn\(_2\)S\(_4\) by physical vapor deposition (PVD).\(^\text{19}\) This latter buffer layer was grown in a sulfide dedicated chamber coevaporating CdS, elemental In, and sulfur; the temperature of the SLG/Mo/CIGS stack was set to 200°C during CdIn\(_2\)S\(_4\) coevaporation. The total thickness of the buffer layer is about 25 nm. All devices were completed with 50-nm-thick i-ZnO and 200-nm-thick conductive ZnO:Al. The solar-cell parameters for these samples (Nos. 5 and 6) are provided in Table 1.

#### 2.1.3 | Fabrication of CIGS solar cells with RbF-PDT

The samples for the experiment regarding the RbF-PDT were prepared at HZB on 2-mm-thick glass substrates coated with 800-nm-thick molybdenum (deposited by DC-sputtering). On top of this back contact, the CIGS absorber was deposited using an adapted static three-stage coevaporation process as described in detail in Heinemann et al.\(^\text{20}\) The maximum substrate temperature during growth was kept at 530°C. The final layers exhibited a Cu-poor (CGI < 1) composition with molar fraction ratios of CGI = 0.9 and GGI = 0.3.

In case of samples with an RbF-PDT, the substrates were cooled down to 280°C after the deposition of the absorber layer and kept at this temperature for the PDT. The PDT was performed for 1 min in one run and 10 min in a separate run. Since all other parameters of the PDT were kept constant, this variation of the duration equals a variation of the amount of RbF deposited on the CIGS. More details on the RbF-PDT can be found in Kodalle et al.\(^\text{21}\) After cool-down, the absorber layers were transferred to our chemical lab in air. Subsequently, they were rinsed in NH\(_3\) (aq), and an approximately 50-nm-thick CdS buffer layer was deposited by CBD. Finally, a bilayer of approximately 180-nm-thick i-ZnO/ZnO:Al was deposited by radio-frequency sputtering before Ni/Al/Ni finger grids were evaporated onto this window layer. The solar-cell parameters for these samples (Nos. 7–9) are given in Table 1.
TABLE 1  GGI ratios, buffer systems layers, and photovoltaic parameters of studied CIGS thin-film solar cells

| Institute | Sample no. | GGI | Buffer system | PDT | Eff. (%) | $V_{oc}$ (mV) | FF (%) | $J_{sc}$ (mA/cm$^2$) |
|-----------|------------|-----|---------------|-----|----------|--------------|-------|-------------------|
| ZSW       | 1          | 0.30| CBD-CdS/i-ZnO | No  | 17.0     | 684          | 79    | 31.5              |
|           | 2          |     | CBD-Zn(O,S)/Zn$_{0.75}$Mg$_{0.25}$O | No  | 15.8     | 664          | 73    | 32.6              |
|           | 3          | 0.66| CBD-CdS/i-ZnO | No  | 11.9     | 767          | 69    | 22.5              |
|           | 4          |     | CBD-Zn(O,S)/Zn$_{0.75}$Mg$_{0.25}$O | No  | 7.9      | 688          | 50    | 23.0              |
| IMN       | 5          | 0.25| CBD-CdS/i-ZnO | No  | 15.4     | 625          | 74    | 33.4              |
|           | 6          |     | PVD-CdIn$_2$S$_3$/i-ZnO | No  | 13.0     | 590          | 67    | 33.0              |
| PVcomB    | 7          | 0.30| CBD-CdS/i-ZnO | No  | 16.2     | 634          | 73    | 35.0              |
|           | 8          |     | CBD-CdS/i-ZnO | 1-min RbF | 13.7     | 618          | 63    | 35.1              |
|           | 9          |     | CBD-CdS/i-ZnO | 10-min RbF | 16.6     | 669          | 70    | 35.4              |

Abbreviations: CBD, chemical bath deposition; PDT, postdeposition treatment.

2.1.4  Cross-sectional specimen preparation

The cross-sectional samples for the SEM measurements were prepared by gluing two stripes of CIGS solar cells face-to-face together, in a way that one stripe was shorter than the other, which provided areas to contact the back and front contacts of one cell for EBIC measurements. Flat cross-sectional surfaces were obtained by mechanical polishing. On top of the cross section, a 4- to 5-nm-thick carbon layer was evaporated in order to protect the surface and reduce charging of specimens during irradiation by the electron beam.

2.2  Characterization of the solar cells

Chemical composition and thickness of CIGS absorbers were determined by means of X-ray fluorescence and glow-discharge optical emission spectroscopy. Current–voltage (I–V) measurements for solar cells were measured with a simulated AM1.5G spectrum at standard testing conditions in the as-grown state, that is, without additional LS or postannealing procedures.

EBIC and energy-dispersive X-ray spectrometry (EDX) data were acquired using a Zeiss UltraPlus SEM, equipped with a beam blanker, an EMax amplifier by point electronic GmbH, and an Oxford Instruments XMax 80 X-ray detector. EBIC measurements were performed at low beam current in order to avoid high injection conditions and varying beam energies from 5 to 15 keV. The frequency of the beam blanker was 5 kHz. EDX elemental distribution maps were acquired at 10-keV beam energy and 1.5-nA beam current.

Capacitance–voltage (C–V) measurements were conducted at room temperature using an HP4284 LCR-Meter and frequencies of 100 kHz. The capacitance values were calculated assuming a simple parallel RC circuit. LS was performed for 30 min in air with an AM1.5 spectrum at 100 mW/cm$^2$. The stage was cooled down to 300 K. Samples were exposed to light through the transparent conductive oxide (TCO) front contact. Red and blue illumination were performed using band pass filters with the center wavelength of (950 ± 2) nm and (450 ± 2) nm, respectively. The full width at half maximum (FWHM) for both filters is (10 ± 2) nm. I–V measurements were carried out before and after LS in order to detect corresponding changes of the photovoltaic parameters.

2.3  Estimation of electrostatic fluctuations by means of EBIC

EBIC measurements are used to characterize local electrical properties of solar cells on a microscopic scale. By applying EBIC in cross section configuration and extracting current profiles from EBIC images perpendicular to the $p$-$n$ junction, the width of the space-charge region ($w_{SCR}$) and the diffusion length of minority charge carriers ($L_D$) in the quasineutral region can be extracted.\textsuperscript{22,23} The simulations of the EBIC profiles were carried out based on a one-dimensional, analytical model proposed by Donolato.\textsuperscript{24} The detailed description of the model and evaluation of EBIC data can be found in Nichterwitz and Unold.\textsuperscript{25}

As the $w_{SCR}$ is influenced by the redistribution of the free charge carriers, the net-doping densities in the $p$-type and $n$-type parts of the $p$-$n$ junction (expressed by $N_A$ and $N_D$) and the charge density at the CIGS/buffer interface, $N_{IF}$, can be calculated. For a heterojunction, the width of the SCR is given by the following equation:\textsuperscript{26}:

$$w_{SCR}(V = 0) = z_{eA}N_{IF}/\Omega + \left(\varepsilon_i\varepsilon_0\sigma_{IF}\frac{2\Omega V_{bi}}{q - N_{IF}^2}/N_D\Omega^2\right)^{0.5},$$

where $\Omega = \varepsilon_i\varepsilon_A + \varepsilon_i\varepsilon_D$. Here, $N_A$ and $N_D$ are the net-doping densities for the $p$-type absorber layer, and for the $n$-type buffer/window stack, $\varepsilon_A$ and $\varepsilon_D$ are the corresponding dielectric susceptibilities, $V_{bi}$ is the built-in potential, and $q$ the elemental charge. The interface charge $N_{IF}$ is the charge density of defects at the CIGS/buffer interface, which
can be positively \( z = +1 \) or negatively \( z = -1 \) charged\(^{26} \); in the course of the present work, \( z = +1 \) was used. The interface defects introduce additional states in the band-gap, which may trap charges and thus influence the potential distribution.\(^{27} \)

3 | RESULTS

3.1 | CIGS solar cells with solution-grown CdS or Zn(O,S) buffer layers as well as different GGI in the absorbers

3.1.1 | CL analysis

Figure 1 shows CL maps for CIGS solar cells with CdS/i-ZnO and Zn(O,S)/(Zn,Mg)O CBD-buffer systems and GGI = 0.66 (Sample Nos. 3 and 4), where Figure 1A,D is the corresponding SEM images, Figure 1B,E the CL intensity, and Figure 1C,F the peak-wavelength distributions. It can be seen that the CL intensity is substantially decreased at grain boundaries owing to a higher density of defects than in the grain interiors, leading to enhanced nonradiative recombination.\(^{28} \) The panchromatic images (Figure 1B,E) show that neighboring grains exhibit only slight fluctuations in intensity. However, the order of magnitude of these variations is about the same for CIGS with CdS and Zn(O,S) buffer layers. As the local quasi-Fermi level splitting \( \Delta \mu \) is proportional to \( \ln(p_0 \tau_n) \) (\( p_0 \) is the local net-doping density and \( \tau_n \) is the local lifetime of the minority charge carriers\(^{29} \)) and to the logarithm of the luminescence flux, the evaluation of the spatial distribution of the CL intensity across the CIGS layers (not shown here) suggests that fluctuations of the product \( \Delta \mu \Delta \Sigma \alpha \) are negligible.

In addition, when applied on a cross section, CL measurements feature the peak emission wavelength, which can be taken as a rough estimate of the local band-gap energy (the real band-gap energy may deviate substantially from this CL peak energy, since the CL maximum may exhibit contributions mainly by transition between defect states in the band gap, instead of band-band transitions).\(^{30} \) From Figure 1C,F, it is apparent that the CL peak shifts perpendicular to the substrate from 840 to 900 nm, which corresponds to a shift in the band-gap energy ranging from 1.38 to 1.48 eV. Extracted CL line scans are in a good agreement with the corresponding GGI distribution obtained from EDX measurements (Figure 2).

Lateral variations in composition within the CIGS alloy need to be in the order of 1 at.% to be relevant for the device performance,\(^{11} \) which has not been detected in the cells studied in the present work by means of EDX (other than the in-depth GGI gradient). In addition, from the extracted CL line scans parallel to the junction (Figure 3), the standard deviation of peak emission energy variations \( \sigma \) does not exceed 25 meV for the CIGS sample with Zn(O,S) buffer layer (at least down to a length scale corresponding to the spatial resolution of the CL maps, about 50 nm); this small deviation results in very small \( V_{oc} \) losses less than about 15 mV (determined using Equation 6). Moreover, lifetime fluctuations in high-efficiency devices were shown to be negligible for the photovoltaic performance based on results from device simulation.\(^{31} \) Therefore, in the course of the present work, we will concentrate on electrostatic potential fluctuations.

3.1.2 | EBIC analysis

EBIC images obtained at a beam energy of \( E_b = 10 \) keV on cross-sectional specimens of CIGS solar cells with CdS/i-ZnO and Zn(O,S)/(Zn,Mg)O CBD-buffer/HR-layer for low (GGI = 0.30) and high (GGI = 0.66) Ga contents (Sample Nos. 1–4) are given in Figures 4 and 5. The EBIC signals appear saturated in the area of the \( p-n \) junction

**FIGURE 1**  Scanning electron microscopy (SEM) images (A,D), corresponding cathodoluminescence (CL) intensities (B,E), and peak-wavelength distributions (C,F) for cross-sectional CIGS solar cells with GGI = 0.66 (Sample Nos. 3 and 4). Acc. intensity is the accumulated CL intensity [Colour figure can be viewed at wileyonlinelibrary.com]
and indicate a high current. This area corresponds to the space-charge region (SCR) while the exponential decay of the signal in the quasineutral region towards the Mo back contact contains information on the diffusion length.22

It can be seen that in case of specimen with Zn(O,S) buffer layer, the width of the SCR exhibits pronounced fluctuations, while with CdS-buffered cells, it appears rather homogeneous. In order to evaluate the magnitude of present fluctuations, profiles perpendicular to the p-n junction were extracted from the acquired EBIC images (10 for each EBIC image). By fitting experimental and simulated profiles,32 values for $w_{\text{SCR}}$ and for the effective diffusion length $L_{\text{eff}}$ can be extracted. $L_{\text{eff}}$, which is strongly influenced by the recombination of charge carriers at the cross-sectional surface, is determined by fitting the decrease of the EBIC intensity from the edge of the SCR to the Mo back contact, as described in Nichterwitz and Unold.25 By extracting $L_{\text{eff}}$ at different beam energies and using a fit described in Nichterwitz and Unold,25 the diffusion length values $L_D$ can be obtained. However, in the present section, we will concentrate only on the evaluation of $w_{\text{SCR}}$ and return to the evaluation of $L_D$ later in Section 3.4. The average values of $w_{\text{SCR}}$ obtained by EBIC are shown

**FIGURE 2** Distribution of GGI ratio determined from energy-dispersive X-ray spectrometry (EDX) analyses (black) and distribution of cathodoluminescence (CL) peak energy (red) extracted perpendicular to the p-n junction from the same position for CIGS with Zn(O,S)/(Zn,Mg)O buffer system and GGI = 0.66 (Sample No. 4) in Figure 1F [Colour figure can be viewed at wileyonlinelibrary.com]

**FIGURE 3** Distribution of cathodoluminescence (CL) peak energies parallel to the p-n junction extracted from Figure 1F for CIGS with GGI = 0.66 and Zn(O,S)/(Zn,Mg) OCBD-buffer systems (Sample No. 4). The pixel size of the CL map was 50 nm [Colour figure can be viewed at wileyonlinelibrary.com]

**FIGURE 4** Scanning electron microscopy (SEM) (top) and corresponding electron-beam-induced current (EBIC) images (bottom) acquired on cross-sectional specimens of CIGS solar cells with GGI = 0.30 and CdS/i-ZnO (A) and Zn(O,S)/(Zn,Mg)O (B) buffer systems (Sample Nos. 1 and 2) at a beam energy $E_b$ of 10 keV [Colour figure can be viewed at wileyonlinelibrary.com]
Table 3. The order of magnitude of the average values of $w_{\text{SCR}}$ were confirmed by C-V measurements (not shown here).

In order to elucidate the contribution of each variable from Equation 1 to the fluctuation of $w_{\text{SCR}}$, the dependence of $w_{\text{SCR}}$ of the net-doping densities $N_A$ and $N_D$ as well as of the interface-charge density $N_{\text{IF}}$ (Equation 1) has to be considered. We estimated the standard deviations $\Delta N_A$, $\Delta N_D$, and $\Delta N_{\text{IF}}$ by applying Gaussian error propagation to Equation 1.

$$\Delta w_{\text{SCR}} = \sqrt{(\partial w_{\text{SCR}}/\partial N_{\text{IF}})^2 \Delta N_{\text{IF}}^2 + (\partial w_{\text{SCR}}/\partial N_A)^2 \Delta N_A^2 + (\partial w_{\text{SCR}}/\partial N_D)^2 \Delta N_D^2}$$

where $\Delta w_{\text{SCR}}$ is the difference in the SCR width between two neighboring points.

The fact that for solar cells with identical CIGS layer but different buffer layers, the fluctuations are substantially different (Figures 4 and 5) suggests that they are related to $N_{\text{IF}}$ and $N_D$ and that the fluctuations in $N_A$ are not relevant. Thus, we set $\Delta N_A = 0$ from now on. The remaining variables needed for the calculation of $\Delta N_D$ and $\Delta N_{\text{IF}}$ were taken from Scheer and Schock26 and Abou-Ras et al.33

They are provided in Table 2. We note that these values may vary strongly for devices with different buffer layers and PDT treatment.

The net-doping density in the CdS buffer layer was reported to be lower than that of Zn(O,S) by at least one order of magnitude.26,34

We calculated the changes in $\Delta N_D$ and $\Delta N_{\text{IF}}$ as well as in amplitude of fluctuations, $\Delta \phi$, using various combinations of $N_D$ and $N_{\text{IF}}$ (shown in the Appendix A). It can be seen that $\Delta N_D$ and $\Delta N_{\text{IF}}$ values become larger with higher doping of a buffer layer. However, for the simple estimations we applied, similar values for all solar cells studied in the present work were obtained.

For the sake of simplicity, we assume two cases.

I. $\Delta N_D = 0$:

Only variations in the interface state density $N_{\text{IF}}$ contributes to the fluctuations in $w_{\text{SCR}}$. Hence, Equation 2 reduces to

$$\Delta w_{\text{SCR}} = \sqrt{(\partial w_{\text{SCR}}/\partial N_{\text{IF}})^2 \Delta N_{\text{IF}}^2}$$

Table 3. Average values for $w_{\text{SCR}}$, $\Delta w_{\text{SCR}}$, $\Delta N_{\text{IF}}$, $\Delta N_D$, and $\sigma$ (estimated by using Equations 1–5) for CIGS with CdS and Zn(O,S) buffer layers and different GGI (Sample Nos. 1–4) at $E_b = 10$ keV

| GGI ratio | Buffer  | $w_{\text{SCR}}$ (nm) | $\Delta w_{\text{SCR}}$ (nm) | $\Delta N_{\text{IF}}$ in $10^{10}$ (cm$^{-2}$) | $\sigma$ (meV) | $\Delta N_D$ in $10^{16}$ (cm$^{-3}$) | $\sigma$ (meV) |
|-----------|---------|------------------------|-------------------------------|-----------------------------------------------|--------------|-------------------------------------|--------------|
| 0.30       | CdS     | 215                    | 35                            | 1.4                                           | 20           | 0.3                                 | 2            |
|           | Zn(O,S) | 340                    | 130                           | 5                                             | 44           | 1.1                                 | 5            |
| 0.66       | CdS     | 235                    | 35                            | 1.4                                           | 18           | 0.3                                 | 2            |
|           | Zn(O,S) | 270                    | 145                           | 5.8                                           | 47           | 1.3                                 | 6            |
II. $\Delta N_{IF} = 0$:

In this case, we estimate only fluctuations in $N_{D}$:

$$\Delta W_{SCR} = \sqrt{\left(\partial W_{SCR}/\partial N_{D}\right)^2 \Delta N_{D}^2}.$$  \hspace{1cm} (4)

It is noteworthy that in real solar-cell devices, we have to assume that both, $N_{IF}$ and $N_{D}$, contribute to the fluctuations in $W_{SCR}$ detected in the EBIC images. However, in the present work, we will consider and discuss cases I and II separately.

Electrostatic potential fluctuations may be considered to stem from deviations in charge densities, $N_1$ and $N_2$, between two neighboring positions. The amplitudes of these fluctuations, $\Delta \varphi$, can be estimated using the expression:

$$\Delta \varphi = k_B T/\text{q} \ln(N_1/N_2).$$  \hspace{1cm} (5)

In Werner et al.\textsuperscript{7} electrostatic potential fluctuations are described by Gaussian distributions of the conduction and valence band energies. The standard deviations of these Gaussian distributions, $\sigma$ (in eV), can be related to $V_{oc}$ losses, $V_{oc,loss}$, via the following equation:\textsuperscript{35}

$$V_{oc,loss} = \sigma^2/2k_B T q.$$  \hspace{1cm} (6)

The effect of the electrostatic potential fluctuations on the $V_{oc}$ is attributed to the fact\textsuperscript{7,35} that they reduce the radiative limit of the $V_{oc}$ compared with the Shockley–Queisser limit. In our case, we approximate the quantity $\sigma$ as the average of the determined amplitudes of fluctuations, $\Delta \varphi$, calculated using Equations 1–5.

Figure 6 displays the range of fluctuations in the $W_{SCR}$ for all studied specimen at $E_b = 10$ keV. The $W_{SCR}$ values for the cell with CdS buffer and GGI = 0.30 are around 170–250 nm and $W_{SCR} = 200–280$ nm for GGI = 0.66, while for Zn(O,S) cells, the $W_{SCR}$ exhibits larger variations in the range of 160–430 nm for GGI = 0.30 and 170–380 nm for GGI = 0.66. The average difference in the SCR width between two neighboring points, $\Delta W_{SCR}$, is less than 50 nm for cell with CdS buffer; however, for cells with Zn(O,S) buffer, the values became $\Delta W_{SCR}$=130–145 nm.

By using Equation 5, we determined the amplitude of fluctuations $\Delta \varphi$ and the corresponding $\sigma$ values for lateral variation in either $N_{D}$ or $N_{IF}$ (Case I or II). Our estimations suggest that fluctuations in $N_{IF}$ have a higher contribution to the $\sigma$ value compared with fluctuations in $N_{D}$. The average values for $W_{SCR}$, $\Delta W_{SCR}$, $\Delta N_{IF}$, $\Delta N_{D}$, and $\sigma$ are summarized in Table 3. It can be seen that the fluctuations in $N_{IF}$ and $N_{D}$ are stronger for CIGS with Zn(O,S) buffer layer. Corresponding average amplitudes of the electrostatic fluctuations in this case are about 44–47 meV.

3.2 | Characterization of CIGS solar cells with CdS or CdIn$2$S$_4$ buffer layers

The results in Section 3.1 exhibited a substantial difference in the EBIC signals when comparing results obtained on CIGS solar cells with CBD-CdS and CBD-Zn(O,S) buffer layers. The EBIC measurements performed on CIGS cells with CBD-CdS (Sample No. 5) and alternative PVD-CdIn$2$S$_4$ (Sample No. 6) confirm the dependence of fluctuations in the $W_{SCR}$ on the applied buffer layer. The CIGS absorber layers were deposited in the same production process. EBIC images for cells studied at $E_b = 7$ keV are shown in Figure 7. Despite the fact that the EBIC images were obtained at a lower beam energy as compared with the analyses presented in Section 3.1.2, the presence of fluctuations in the $W_{SCR}$ are still visible.

The CIGS solar cell with CdIn$2$S$_4$ buffer layer exhibits significant fluctuations in $W_{SCR}$ ranging from 100 to 450 nm. The average $\Delta W_{SCR}$ in this case is around 150 nm. For the CdS-buffered cell, $W_{SCR} = 110–160$ nm was determined with $\Delta W_{SCR} = 20$ nm. Assuming the two cases as described in Section 3.1, local variations in the doping density $N_{D}$ and interface charge $\Delta N_{IF}$ as well as corresponding $\sigma$ values were estimated (here, $\Delta N_{A} = 0$ as in Section 3.1). The fluctuations in $N_{IF}$ and $N_{D}$ appear stronger in case of CIGS with CdIn$2$S$_4$ buffer layer with $\sigma = 50$ meV as the upper limit. The average values for $W_{SCR}$, $\Delta W_{SCR}$, $\Delta N_{IF}$, and $\Delta N_{D}$, as well as values for $\sigma$, are presented in Table 4.

3.3 | Characterization of CIGS solar cells with RbF PDT

To gain insight into the effect of an RbF PDT, an EBIC analysis on CIGS with short (1 min) and completed (10 min) RbF treatment was carried out, with an RbF-free sample as reference. All samples contain

**FIGURE 6** Fluctuations in the width of the space-charge region (SCR) for CIGS solar cells with GGI = 0.30 (A) and GGI = 0.66 (B) (Sample Nos. 1–4) at $E_b = 10$ keV [Colour figure can be viewed at wileyonlinelibrary.com]
a CBD-CdS/i-ZnO/ZnO:Al buffer window layer stack. The comparison of photovoltaic parameters for RbF-treated samples with the reference cell can be found in Table 1. Figure 8 gives EBIC images obtained at $E_b = 7$ keV.

Without RbF PDT, the width of the SCR does not exhibit substantial fluctuations (Figure 8A), as found also for the CdS-buffered solar cells in Sections 3.1 and 3.2. However, after the short RbF treatment (1 min), very strong lateral variations of $w_{\text{SCR}}$ are visible in the EBIC signal (Figure 8B). These strong fluctuations are again substantially reduced in case of a longer duration (10 min) of the RbF PDT (Figure 8C). The average values of $w_{\text{SCR}}$ and $\Delta w_{\text{SCR}}$ are shown in Table 5.

Plan-view SEM images of CIGS absorbers after 1-min (Figure 9A) and 10-min (Figure 9B) RbF PDT show that the surface of CIGS is covered with islands in both cases. Compositional analysis has shown that these islands contain Rb, F, and O.\cite{21} It can be seen that after 1 min of PDT, the islands are very small with the size of around 10–40 nm, while in case of longer treatment, the coverage is more homogeneous with islands in size of 50–100 nm.

The evaluation of fluctuations $\Delta N_{\text{IF}}$ and $\Delta N_{\text{D}}$ is summarized in Table 5. While lateral variations in $N_{\text{IF}}$ are relatively small after 10-min RbF with $\sigma = 26$ meV, for the 1-min PDT cell, $\Delta N_{\text{IF}}$ value increases significantly, resulting in a large $\sigma$ value of 50 meV.

### Table 4
Average values for $w_{\text{SCR}}$, $\Delta w_{\text{SCR}}$, $\Delta N_{\text{IF}}$, and $\Delta N_{\text{D}}$ (estimated by using Equations 1–5), as well as values for $\sigma$, for CIGS with CdS or CdIn$_2$S$_4$ buffer layers (Sample Nos. 5 and 6) at $E_b = 7$ keV

| Buffer     | $w_{\text{SCR}}$ (nm) | $\Delta w_{\text{SCR}}$ (nm) | Case 1 | Case 2 |
|------------|------------------------|-------------------------------|--------|--------|
|            |                        |                               | $\Delta N_{\text{IF}}$ in $10^{10}$ (cm$^{-2}$) | $\sigma$ (meV) | $\Delta N_{\text{D}}$ in $10^{16}$ (cm$^{-3}$) | $\sigma$ (meV) |
| CdS        | 140                    | 20                            | 0.8    | 15     | 0.2    | 1 |
| CdIn$_2$S$_4$ | 230            | 150                           | 6      | 50     | 1.4    | 6 |

Abbreviation: PDT, postdeposition treatment.
3.4 LS experiments performed on solar cells with CdS or Zn(O,S) buffer layers

3.4.1 LS with white light

In this section, we studied effects of LS on CIGS solar cells with CdS and Zn(O,S) buffer layers and different GGI ratios without PDT (Sample Nos. 1–4). In the previous sections, it became apparent that lateral fluctuations in \( w_{\text{SCR}} \) were pronounced particularly for specific CIGS/buffer combinations or for specific conditions of PDT processes after the CIGS deposition. We related these fluctuations in \( w_{\text{SCR}} \) to substantial decreases in \( V_{\text{oc}} \), according to Equations 1–6.

White LS of CIGS solar cells (typically for at least 30 min under AM1.5G conditions) has been shown to improve the \( V_{\text{oc}} \) of the device, especially for solar cells with CBD-Zn(O,S) buffer layers.\(^\text{15,16}\) for CIGS with CBD-CdS buffer layers, the LS effect is less pronounced or can even be detrimental.\(^\text{36}\) Our aim was to find out whether LS can be a means to reduce the electrostatic potential fluctuations detected in the present work and thus, to improve the \( V_{\text{oc}} \) of the CIGS solar cell.

To confirm the beneficial effect of LS on the \( V_{\text{oc}} \), CIGS solar cells with the Zn(O,S)/(Zn,Mg)O buffer system (Sample No. 4) were exposed to the white-light illumination. Table 6 shows that the \( V_{\text{oc}} \) increases by at least about 25 mV after LS for all cells.

To investigate the changes of fluctuations in \( w_{\text{SCR}} \) after LS, EBIC measurements were performed on the solar cells with both, GGI = 0.30 and 0.66 in the CIGS absorbers, and with Zn(O,S) buffer layers (see Section 3.1). The measurements were carried out only a few minutes after the LS, and the exposure of the specimens to the electron beam was kept to a minimum in order to exclude additional effects on the EBIC signals. The EBIC measurements were repeated after 1 week during which the cells were kept in darkness after the LS process. We note that during the LS process, the stage was cooled down to 300 K; however, the samples were placed on specimen holders used for the electron-microscopy investigations, and the cooling might not have been sufficient to eliminate the influence of heat from the lamp.

Figure 10 shows variations in the \( w_{\text{SCR}} \) in CIGS solar cells as grown state, after LS for 30 min, and after 1 week in darkness. It can be seen that cells with both, GGI = 0.30 and 0.66 in the CIGS absorber layers, exhibit similar trends concerning the fluctuations in \( w_{\text{SCR}} \). The range of variations in \( w_{\text{SCR}} \) is slightly decreased right after the illumination for 30 min. However, after keeping the samples in the dark for 1 week, fluctuations in \( w_{\text{SCR}} \) are significantly reduced in both cases (average \( \Delta w_{\text{SCR}} \) value of 50–70 nm). The average values for \( w_{\text{SCR}}, \Delta w_{\text{SCR}}, \Delta N_D, \) and \( \Delta N_F \) are summarized in Table 7.

Our studies reveal a decrease of fluctuations in the \( w_{\text{SCR}} \) SCR for CIGS with Zn(O,S) after white-light illumination. The \( \sigma \) value hence became decreased from 44 (before LS) to 37 meV after 30 min of LS procedure and even to 29 meV after keeping the solar cell for 1 week in the dark after the LS (Figure 11) in case of CIGS with GGI = 0.30. The effect was reproducible on CIGS with GGI = 0.66, for which \( \sigma \) decreased from 47 to 28 meV after the LS procedure and keeping cells in the dark.

In addition to the reduction of fluctuations in \( w_{\text{SCR}} \), also, one further effect of the LS was detected in the studied solar cells. Figure 12 shows EBIC profiles extracted perpendicular to the \( p-n \) junction from the same position at \( E_b = 10 \) kV for CIGS with CdS and Zn(O,S) buffer layers and GGI = 0.30 (A,B) and GGI = 0.66 (C,D). After the LS treatment, these extracted profiles exhibit an increased decay length in the quasineutral regions after LS in all cases, except for the device with CdS buffer and with low [Ga] (GGI = 0.30) in the absorber. This decay length in an ideal model can be interpreted as an effective minority diffusion length, \( L_{\text{eff}} \), although it has also been shown to be influenced by artifacts, such as generation-dependent collection, and recombination at the cross-sectional surface.\(^\text{25,37}\) Values for the effective diffusion lengths before and after LS are summarized in Table 8.

We note that \( L_{\text{eff}} \) values obtained from EBIC analyses are always much smaller (typically one order of magnitude) than the real electron diffusion lengths, owing to a substantial influence of recombination of charge carriers at the cross-sectional surface and the limitation imposed by applying a simplified collection model.
3.4.2 Effects of blue and red illumination

Under white-light illumination, substantial changes were detected in \( \Delta w_{SCR} \) and \( L_D \). In order to confirm whether the n-type part of the junction or the CIGS/buffer interface region is responsible for the reduction of electrostatic fluctuations, we illuminated Sample No. 2 (CIGS solar cell with Zn(O,S) buffer and GGI = 0.30) with blue light for 30 min. The blue-light illumination was conducted using a band-pass filter with a center wavelength of \((450 \pm 2)\) nm and an FWHM of \((10 \pm 2)\) nm. Indeed, from EBIC measurements performed before and after illumination with blue light, it can be seen that fluctuations in the SCR are reduced (Figure 13). The average difference in the SCR values between two neighboring positions \( \Delta w_{SCR} \) decreases from 200 to 90 nm after blue LS.

Red-light illumination is mainly absorbed in the CIGS layer, absorption in the buffer/window layer can be neglected. We performed red LS for 30 min using a band filter with the center wavelength of \((950 \pm 2)\) nm and FWHM of \((10 \pm 2)\) nm. Figure 14 shows EBIC profiles extracted before any illumination (black line), after blue LS (blue line) and after red LS (red line). After red LS treatment, the extracted profiles show an increase in the effective electron diffusion length \( L_{eff} \). On the other hand, illumination with blue light does not have an influence on \( L_{eff} \).

4 DISCUSSION

4.1 Possible origins of electrostatic fluctuations

The EBIC measurements reveal the presence of strong fluctuations in the widths of the SCR for some of the investigated CIGS solar cells, which are substantially affected by the choice of the buffer layer or the conditioning of the CIGS/buffer interface, such as duration of the PDT. We note that the fluctuations are substantial for the CIGS solar

**TABLE 7** Average values for \( w_{SCR} \), \( \Delta w_{SCR} \), \( \Delta N_D \), and \( \Delta N_{IF} \) (estimated by using Equations 1-3) for CIGS with Zn(O,S) buffer layers (Sample Nos. 2 and 4) at \( E_b = 10\) keV

|                | GGI = 0.3 |                  | GGI = 0.66 |                  |
|----------------|-----------|------------------|------------|------------------|
|                | \( w_{SCR} \) (nm) | \( \Delta w_{SCR} \) (nm) | Case 1: \( \Delta N_{IF} \) in \( 10^{10} \) (cm\(^{-2}\)) | Case 2: \( \Delta N_D \) in \( 10^{16} \) (cm\(^{-3}\)) | Case 1: \( \Delta N_{IF} \) in \( 10^{10} \) (cm\(^{-2}\)) | Case 2: \( \Delta N_D \) in \( 10^{16} \) (cm\(^{-3}\)) |
| As-grown state | 340       | 130              | 5          | 1.1              | 270           | 145              | 5.8          | 1.3          |
| LS 30 min      | 350       | 100              | 3.9        | 0.9              | 290           | 110              | 4.4          | 1           |
| 1 week in dark | 380       | 55               | 2.2        | 0.5              | 280           | 70               | 2.8          | 0.6          |

Abbreviation: LS, light soaking.

**FIGURE 11** Decrease of electrostatic fluctuations represented by \( \sigma \) values after light soaking (LS), for CIGS solar cells with CBD-Zn(O,S)/(Zn,Mg)O buffer system and GGI = 0.30 (Sample No. 2) or 0.66 (Sample No. 4) in the CIGS absorber [Colour figure can be viewed at wileyonlinelibrary.com]

**FIGURE 10** Fluctuations in the width of the space-charge region (SCR) before and after light soaking (LS) for CIGS solar cells with Zn(O,S) buffer layer and (A) GGI = 0.30 (Sample No. 2) and (B) GGI = 0.66 (Sample No. 4) at \( E_b = 10\) keV [Colour figure can be viewed at wileyonlinelibrary.com]
cells with chemical-bath-deposited Zn\((O,S)\) (containing two anions, see Section 3.1) and with evaporated CdIn\(_2\)S\(_4\) (containing two cations, see Section 3.2) buffer layers. Also, such fluctuations were found for a CIGS cell of which the CIGS surface underwent a short (and incomplete) RbF PDT (see Section 3.3).

**Figure 15** depicts the proposed scenario schematically in the thin-film stack of a CIGS solar cell with Zn\((O,S)\) buffer layer. From our results, we presume that the inhomogeneous distribution of point defects is more likely to happen in devices with more than one cation or anion in the buffer layer. Transmission electron microscopy (TEM)

| Table 8 | Extracted \(L_{\text{eff}}\) (\(\mu\)m) values for CIGS solar cells with CdS or Zn\((O,S)\) buffer layers (Sample Nos. 1–4) before and after LS at \(E_b = 10\) keV |
|---------|---------------------------------------------------------------|
| \(L_{\text{eff}}\) (\(\mu\)m) | GGI = 0.30 | GGI = 0.66 | GGI = 0.30 | GGI = 0.66 |
| As-grown state | CdS | Zn\((O,S)\) | CdS | Zn\((O,S)\) |
| LS 30 min | 0.2–0.6 | 0.3–1.4 | 0.3–0.5 | 0.4–1.4 |
| 1 week in darkness | 0.2–0.4 | 1–4 | 0.4–1 | 1.2–1.4 |

Abbreviation: LS, light soaking.

**Figure 12** Extracted electron-beam-induced current (EBIC) profiles (at \(E_b = 10\) keV) perpendicular to the \(p-n\) junction for CIGS with GGI = 0.30 CdS (A) and Zn\((O,S)\) (B), GGI = 0.66 CdS (C), Zn\((O,S)\) (D) before the light soaking (LS), after the LS for 30 min and 11 week recovery in darkness (Sample Nos. 1–4) [Colour figure can be viewed at wileyonlinelibrary.com]

**Figure 13** Scanning electron microscopy (SEM) and electron-beam-induced current (EBIC) images obtained at \(E_b = 10\) keV for a CIGS solar cell with Zn\((O,S)/(Zn,Mg)O\) buffer system and GGI = 0.3 (Sample No. 2): A, SEM image; B, EBIC image of the cell before illumination; C, EBIC image on the same position after 30 min of blue light soaking (LS) [Colour figure can be viewed at wileyonlinelibrary.com]
Studies show the presence of structural and compositional inhomogeneities in CBD-grown Zn(O,S) and Inx(O,S)y buffer layers. Small particles, often observed on CBD-Zn(O,S) surfaces, could result from the reaction of free zinc ions with OH\(^-\) and S\(^-\) ions in the solution.\(^{39}\) These studies also showed that the LS effect is minimized for cells with reduced amount of particles in CBD-Zn(O,S) buffer. However, the deposition method can also affect the inhomogeneous distribution of point defects. For a CIGS solar cell with sputtered Zn(O,S) layer, no substantial fluctuations in \(w_{SCR}\) were detected (data not shown here). This could originate from no or less amount of OH\(^-\) ions compared with the CBD process.

Strong fluctuations in \(w_{SCR}\) were also detected in CIGS solar cells with PVD-CdIn\(_2\)S\(_4\) buffer layer. The proposed scenario represented in Figure 15 can be applied to explain lower \(V_{oc}\) values compared with CdS-buffered cells (Table 1). However, the studies on PVD-CdIn\(_2\)S\(_4\) buffer are limited, and the origins of variations in \(N_D\) and \(N_{IF}\) are not clear.

Based on the results presented above and by using Equation 6, we are able to determine \(V_{oc}\) losses for studied CIGS solar cells with different buffer layers and duration of RbF PDT (Table 9). To calculate \(V_{oc}\) losses, we use \(\sigma\) values at the upper limit from corresponding fluctuations in \(N_{IF}\). While electrostatic fluctuations in CIGS with CdS buffer layer can be neglected, in cells with Zn(O,S) and CdIn\(_2\)S\(_4\) buffer layers, the average \(\sigma\) values of 45–50 meV would lead to \(V_{oc}\) losses of about 40–50 mV. This loss can be linked to the lower \(V_{oc}\) values of devices with Zn(O,S) and CdIn\(_2\)S\(_4\) buffer layers as compared with CdS-buffered cells (Table 1). The presence of strong fluctuations exhibiting \(\sigma\) of 50 meV was detected in the RbF-treated sample with the short PDT (1 min). As can be seen in Table 1, this cell indeed features a deteriorated \(V_{oc}\).

The SEM images of the CIGS surface after RbF PDT (Figure 9) demonstrate that the coverage of the CIGS surface by a presumable Rb-containing compound is not contiguous. Indeed, by using TEM imaging of RbF-treated CIGS solar cells, Taguchi et al.\(^{40}\) found RblnSe\(_2\) islands formed at the CIGS/CdS interface. It may be assumed that with incorporation of Rb into the CIGS lattice at the CIGS surface, the corresponding (charged) point defects are not homogeneously distributed at the interface between CIGS and the buffer layer. Consequently, strong fluctuations in \(w_{SCR}\) may occur, depending on the grade of the coverage of RblnSe\(_2\) islands on the CIGS surface. For 1-min PDT duration, the surface is covered with small islands of around 10–40 nm in size. However, for longer durations of the RbF PDT (10 min), the coverage is more homogeneous with islands in size of 50–100 nm. Hence, the fluctuations become less pronounced and similar as for the reference cell.

### Table 9

| Buffer layer | CdS | Zn(O,S) | CdIn\(_2\)S\(_4\) |
|--------------|-----|---------|------------------|
| \(\sigma\) (meV) | 20  | 45      | 50               |
| \(V_{oc}\) loss (mV) | 8   | 40      | 50               |
| RbF PDT Ref. | 28  | 50      | 26               |
| 1-min PDT | 15  | 50      | 13               |
| 10-min PDT |      |         |                  |

Abbreviation: PDT, postdeposition treatment.
4.2 | Light soaking

4.2.1 | Effects on charge states of point defects and on the open-circuit voltage

It was shown that a reduction of fluctuations in \( N_{IF} \) and/or \( N_D \) are mechanisms induced by the LS, leading to increased \( V_{oc} \) values (Table 6). Based on the results presented in Section 3.4.1, we determined \( V_{oc} \) losses before and after LS by using Equation 6. The calculated losses decrease from 37 to 16 mV for CIGS with GGI = 0.30 and from 42 to 15 mV for devices with GGI = 0.66. This difference of about 20–25 mV is in good agreement with the \( V_{oc} \) gain of 25–30 mV after white LS, as determined from \( j-V \) measurements (Table 6). In the following, we will discuss two possible scenarios (a and b) that can lead to this improvement.

(a) Figures 16 and 17 display the first proposed scenario of the LS effect. Initially, the lateral distributions of point defects and free charge carriers at the absorber/buffer interface are highly inhomogeneous (depicted as red dots on Figure 15), especially in CIGS solar cells with Zn(O,S) buffer layers. Upon illumination, the photo-excited electrons occupy donor states or leave acceptor states and, thus, change their charge states. Consequently, changes in the charge states of point defects cause redistribution of free electrons and holes, which changes the electrostatic potential distribution. However, this process is not finished yet when the illumination is cut off (after 30 min), but continues when keeping the solar cell in the dark. Assuming that the changes induced by LS are such that the charge states of point defects and thus the free electrons and holes are distributed more homogeneously, this mechanism would result in a more homogeneous distribution of \( w_{SCR} \) and therefore in a reduction of the amplitude of the electrostatic potential fluctuations.

Our proposed mechanism for the positive effect of LS can be linked directly to the one proposed by Lany and Zunger,41 involving metastable Se–Cu divacancy complexes (VSe–VCu) located at the surface of the CIGS that trap charge carriers. Upon illumination, these divacancy complexes change their charge states from negative to positive, leading to an increase in the net-doping density within the CIGS layer, which ultimately increases the \( V_{oc} \) of the solar-cell device.

It was already mentioned in Section 2 that the investigated specimens could possibly undergo superimposed effects of light and heat. According to the model of Lany and Zunger,41 elevated temperatures induce the same defect configuration as illumination, changing the net-doping density and with that the Fermi energy level. Above \( T = 340 \) K, most VSe–VCu complexes are converted to the acceptor configuration. We suggest that additional heating can contribute to the further conversion of defects deeper in the bandgap.

(b) There can be a second line of explanation of the LS effect, which is related to the interface charge density \( N_{IF} \). If \( N_{IF} \) between CIGS and the buffer layer decreased owing to LS, for example, by a mechanism described in (a) as well as in Figures 15 and 16, it would imply a reduction in interface recombination (since the recombination velocity is proportional to \( N_{IF} \)). Indeed, Ruberto and Rothwarf42 proposed that an increase in the \( V_{oc} \) and \( FF \) upon LS treatment originates from reduction of interface recombination at the CdS/CIGS.

Experiments with blue LS (Section 3.4.2) showed the decrease of fluctuations in the width of the SCR, confirming that the effect takes place in the buffer material or at the CIGS/buffer interface. The blue light is known to improve \( FF \) by removing a kink from the \( j-V \) curve.43 The suggested model in Eisgruber et al.43 implied that initially, the buffer layer exhibits a high concentration of deep states, which are
getting occupied with holes during blue-light illumination. Besides, a long relaxation duration was observed, which was attributed to the slow discharging of deep defects. This could also explain the strong effect of LS on electrostatic fluctuations, found in the present work, even after keeping the cells in the dark.

4.2.2 Effects on the trapping of charge carriers and on the electron diffusion length

As a second consequence of the LS, a significant increase of the diffusion lengths in the quasineutral regions for CIGS solar cells with CdS (GGI = 0.66) and Zn(O,S) buffer layers (GGI = 0.30 and 0.66) after white-light illumination was found. Comparing samples before and after LS for 30 min, the diffusion length increases by almost 2 times in case of the cell with CdS and by about 1.5 times in the case of cells with Zn(O,S). Kedemetal.44 observed similar effect of light-induced increase in diffusion length for a perovskite solar cell with a MAPbBr3 absorber layer.

Figure 18 illustrates a possible origin of the increased L_D after LS. If the light illumination leads to the (partial) occupation of donor states/emptying of acceptor states, the trapping of free charge carriers is reduced, which should increase the electron lifetime and with that the diffusion length. The experiment with red light that is absorbed in the CIGS layer confirmed the increase of the diffusion length after illumination.

5 CONCLUSIONS

The present work discusses electrostatic potential fluctuations in CIGS solar cells as one of possible origins limiting the open-circuit voltage. It was shown that the dominant effect for these fluctuations can be attributed to local variations in the width of the SCR and therefore in the net-doping density N_D and/or in the interface-charge density N_IF, introduced via buffer-layer deposition or PDT. The average amplitude of electrostatic fluctuations, σ, obtained from EBIC measurements for CIGS solar cells with CBD-Zn(O,S) and PVD-CdIn2S4 buffers was around 45–50 meV, which can lead to the losses in V_OC of up to 50 mV. However, for CIGS solar cells with CBD-CdS buffer, σ remains small, and thus, the corresponding V_OC loss is not substantial. In addition, it was revealed that incomplete RbFPDT may introduce strong fluctuations in the w_SCR and thus may lead to the deterioration of the device performance.

Furthermore, LS can decrease significantly the amplitudes of electrostatic fluctuations after 30 min of illumination and 1 week in the dark, which was related to increases in V_OC. As a second effect of the LS treatment, we also detected increased effective electron–diffusion lengths for various CIGS/buffer layer combinations. We explain the improvements of V_OC after LS procedures via the occupation of defect states (proposedly) close to the CIGS/buffer interface, which changes their charge states, leading to more homogeneously distributed charge densities along the CIGS/buffer interface.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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REFERENCES

1. Nakamura M, Yamaguchi K, Kimoto Y, Yasaki Y, Kato T, Sugimoto H. Cd-Free Cu(In,Ga)(Se,S)2 thin-film solar cell with record efficiency of 23.35%. IEEE Journal of Photovoltaics. 2019;9(6):1863-1867.
2. Jackson P, Wuerz R, Hariskos D, Lotter E, Witte W, Powalla M. Effects of heavy alkali elements in Cu(In,Ga)Se2 solar cells with efficiencies up to 22.6%. Phys. Status Solidi RRL. 2016;10(8):583-586.
3. Avancini E, Carron R, Weiss TP, et al. Effects of rubidium fluoride and potassium fluoride postdeposition treatments on CuInxGa1-xSe2 thin films and solar cell performance. Chem Mater. 2017;29(22):9695-9704.
4. Witte W, Abou-Ras D, Albe K, et al. Gallium gradients in Cu(In,Ga)Se2 thin-film solar cells. Prog. Photovolt: Res. Appl. 2015;23(6):717-733.
5. Kamada R, Yagioka T, Adachi S, Handa A, Tai KF, Kato T, Sugimoto H. “New world record Cu(In,Ga)Se2 thin film solar cell efficiency..."
11. Abou-Ras D, Schäfer N, Hages CJ, Levcenko S, Márquez J, Unold T.
14. Jensen SA, Glynn S, Kanevce A, et al. Beneficial effect of post-
22. Nichterwitz M, Abou-Ras D, Sakurai K, et al. Influence of grain
67. Nichterwitz M, Unold T. Numerical simulation of cross
8. Siebentritt S. What limits the efficiency of chalcopyrite solar cells?
13. Salomé PM, Teixeira JP, Keller J, Törndahl T, Sadewasser S, Leitao JP.
16. Witte W, Hariskos D, Powalla M. Comparison of charge distributions
134. Abou-Ras D, Kirchartz T. Electron-beam-induced current measurements
15. Barreau N, Frelon A, Lepetit T, et al. High efficiency solar cell based
20. Rau U, Werner JH. Radiative efficiency limits of solar cells with lateral
22. Shockley W, Queisser HJ. Detailed balance limit of efficiency of p-n
26. Scheer R, Schock HW. Chalcogenide Photovoltaics. Weinheim, Germany: Wiley-VCH; 2011.
27. Nelsen J. The Physics of Solar Cells. Imperial College Press; 2003.
28. Mendis BG, Bowen L, Jiang QZ. A contactless method for measuring the recombinant velocity of an individual grain boundary in thin-film photovoltaics. Appl Phys Lett. 2010;97(9):1-3.
29. Unold T, Güttay L. In: Abou-Ras D, Kirchartz T, Rau U, eds. Photoluminescence Analysis of Thin-film Solar Cells, ch. 11, in: Advanced Characterization Techniques for Thin-film Solar Cells. Wiley-VCH; 2016.
30. Abou-Ras D, Niechertwitz M, Romero MJ, Schmidt SS. Electron microscopy on thin films for solar cells, ch. 14. In: Abou-Ras D, Kirchartz T, Rau U, eds. Advanced Characterization Techniques for Thin-film Solar Cells. Wiley-VCH; 2016.
31. Krause M, Nikolaeva A, Malberg M, Jackson P, Hariskos D, Witte W, Márquez JA, Levcenco S, Unold T, Scheer R, Abou-Ras D, ‘Microscopical analysis of a high-efficiency Cu(In, Ga)Se2 solar cell—a case study,’ to be published.
32. Abou-Ras D, Kirchartz T. Electron-beam-induced current measurements of thin-film solar cells. ACS Appl Energy Mater. 2019;2(9): 6127-6139.
33. Abou-Ras D, Schäfer N, Baldaz N, Brunken S, Boit C. Electron-beam-induced current measurements with applied bias provide insight to locally resolved acceptor concentrations at p-n junctions. AIP Advances. 2015;5(7):077191.1–7.
34. Sharbati S, Keshmish H, McGoffin JT, Geithardt R. Improvement of CIGS thin-film solar cell performance by optimization of Zn(O,S) buffer layer parameters. Appl Phys. A. 2015:118(4):1259-1265.
35. Rau U, Werner JH. Radiative efficiency limits of solar cells with lateral band-gap fluctuations. Appl Phys. Lett. 2004;84(19):3735-3737.
36. Chen S, Jarmar T, Südergren S, et al. Light soaking induced doping increase and sodium redistribution in Cu(In,Ga)Se2-based thin film solar cells. Thin Solid Films. 2015;582:35-38.
37. Nichterwitz M, Caballero R, Kaufmann CA, Schock HW, Unold T. Generation-dependent charge carrier transport in Cu(In,Ga)Se2/CdS/ZnO thin-film solar-cells. J Appl Phys. 2013;113(4):044515.1-16.
38. Jin X, Popescu R, Pasha A, et al. Structural and microchemical characterization of Cu(In,Ga)Se2 solar cells with solution-grown CdS, Zn(O,S), and In(O,S)2 buffers. Thin Solid Films. 2019:671:133-138.
39. Yeh TH, Hsu CH, Ho HW, Wei SY, Cai CH, Lai CH. An ammonia-free chemical-bath-deposited Zn(O,S,OH) buffer layer for flexible Cu(In,Ga)Se2 solar cell application: an eco-friendly approach to achieving improved stability. Green Chem. 2016;18(19):5212-5218.
40. Taguchi N, Tanaka S, Ishizuka S. Direct insights into RbInSe2 formation at Cu(In,Ga)Se2 thin film surface with RbF postdeposition treatment. Appl Phys. Lett. 2018;113(11):113903-1–113903-4.
41. Lany S, Zunger A. Light- and bias-induced metastabilities in Cu(In,Ga)Se2 based solar cells caused by the (Vse–Vinc) vacancy complex. J. Appl. Phys. 2006;100(11):113725-1–113725-15.
42. Ruberto MN, Rothwarf A. Time-dependent open-circuit voltage in Cu(In,Ga)Se2/CdS solar cells: theory and experiment. J. Appl. Phys. 1987;61(9):4662–4669.
43. Eisinger IL, Granata JE, Sites JR, Hsu J, Kessler J. Blue-photon modification of nonstandard diode barrier in CuInSe2 solar cells. Sol. Energy Mater. Sol. Cells. 1998;53(3-4):367-377.
44. Kedem N, Brenner TM, Kulbak M, et al. Light-induced increase of Electron diffusion length in a p–n junction type CH3NH3PbBr3 Perovskite solar cell. J Phys Chem Lett. 2015;6(13):2469-2476.
We estimated the influence of various doping densities $N_D$ and interface charge $N_{IF}$ values on the fluctuations $\Delta N_{IF}$ (Table 10) and $\Delta N_D$ (Table 11) as well as on the corresponding average amplitude of fluctuations $\sigma$. The calculations were based on the method described in the Section 3.1 assuming two cases and $\Delta w_{SCR} = 200$ nm. Table 10 represents the Case I where $\Delta N_D = 0$, whereas Table 11 depicts the Case II where $\Delta N_{IF} = 0$.

**TABLE 10** Dependence of fluctuations in $N_{IF}$ ($\Delta N_{IF}$) and corresponding $\sigma$ on various $N_D$ and $N_{IF}$ values (Case I)

| $N_D$       | $N_{IF} = 10^{10}$ cm$^{-2}$ | $N_{IF} = 5 \times 10^{10}$ cm$^{-2}$ | $N_{IF} = 10^{11}$ cm$^{-2}$ |
|-------------|-----------------------------|----------------------------------------|-----------------------------|
|             | $\Delta N_{IF}$ (cm$^{-2}$) | $\sigma$ (meV)                        | $\Delta N_{IF}$ (cm$^{-2}$) | $\sigma$ (meV) | $\Delta N_{IF}$ (cm$^{-2}$) | $\sigma$ (meV) |
| $10^{17}$ cm$^{-3}$ | $1.9 \times 10^{10}$ | 28                                      | $2.1 \times 10^{10}$ | 9             | $2.4 \times 10^{10}$ | 6             |
| $5 \times 10^{17}$ cm$^{-3}$ | $8.1 \times 10^{10}$ | 57                                      | $8.9 \times 10^{10}$ | 27            | $10.1 \times 10^{10}$ | 18            |
| $10^{18}$ cm$^{-3}$ | $15.8 \times 10^{10}$ | 73                                      | $17.2 \times 10^{10}$ | 39            | $19.6 \times 10^{10}$ | 28            |

**TABLE 11** Dependence of fluctuations in $N_D$ ($\Delta N_D$) and corresponding $\sigma$ on various $N_D$ and $N_{IF}$ values (Case II)

| $N_D$       | $N_{IF} = 10^{10}$ cm$^{-2}$ | $N_{IF} = 5 \times 10^{10}$ cm$^{-2}$ | $N_{IF} = 10^{11}$ cm$^{-2}$ |
|-------------|-----------------------------|----------------------------------------|-----------------------------|
|             | $\Delta N_D$ (cm$^{-3}$)    | $\sigma$ (meV)                        | $\Delta N_D$ (cm$^{-3}$)    | $\sigma$ (meV) | $\Delta N_D$ (cm$^{-3}$)    | $\sigma$ (meV) |
| $10^{17}$ cm$^{-3}$ | $9.7 \times 10^{15}$ | 3                                      | $1.2 \times 10^{16}$ | 3             | $1.4 \times 10^{16}$ | 3             |
| $5 \times 10^{17}$ cm$^{-3}$ | $1.8 \times 10^{17}$ | 8                                      | $2.2 \times 10^{17}$ | 10            | $2.8 \times 10^{17}$ | 12            |
| $10^{18}$ cm$^{-3}$ | $7.1 \times 10^{17}$ | 14                                     | $8.5 \times 10^{17}$ | 16            | $1.1 \times 10^{17}$ | 20            |