X-ray vision of Cu(In,Ga)Se$_2$: from the Ga/In ratio to solar-cell performance

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Abstract

Cost efficiency and defect passivation are the two major challenges that thin-film solar cells have to overcome for economic competitiveness. For Cu(In,Ga)Se$_2$ solar cells, the first is addressed by an increase of the Ga/In ratio, which widens the bandgap favorably for tandem applications and reduces the requirement of costly, rare In. The second is addressed by heavy alkali post-deposition treatments. However, the maximum device efficiency is typically achieved with a comparably low Ga/In ratio, which is in contrast to the economic interest of a higher Ga/In ratio and makes it paramount to identify, understand and mitigate the sources of local underperformance in Ga-rich cells. In this work, we investigate a series of Cu(In,Ga)Se$_2$ cells with varying Ga/In concentration in the absorber, using multi-modal scanning x-ray microscopy. In particular, we analyze differences in chemical composition and electrical performance on the nanoscale, with a focus on the effect of Rb. We find that In-rich cells show, along with a greater overall performance, a more homogeneous distribution of the nanoscale performance compared to the Ga-rich cells. Our analysis on Rb suggests that this effect is due to a more effective passivation of structural defects in the absorbers, i.e. voids and grain boundaries. These results shine light on the causes of the superiority of Ga-poor/In-rich absorbers and substantiate the trend to higher defect density for Ga-rich absorbers.

1. Introduction

As humanity is racing towards a climate and energy crisis, renewable and clean energy sources are key to a sustainable future [1]. Thin-film solar cells offer an interesting perspective due to their low energy pay-back time [2] and material requirements compared to Si solar cells [3]. Furthermore, their compositional nature allows the bandgap to be tuned, which is of particular interest for tandem applications [4–6]. However, current state-of-the-art thin-film solar cells still contain scarce elements, namely In in Cu(In,Ga)Se$_2$ solar cells. Thus, the manufacturing of thin-film solar cells from more abundant elements is an aspiration. In case of Cu(In,Ga)Se$_2$ solar cells, a record efficiency was found with a $X_{GGI} = [\text{Ga}]/([\text{In}]+[\text{Ga}])$ ratio (denoted as ‘GGI’) of 0.3 [7], corresponding to a bandgap of 1.08 eV [7]. This bandgap matches one of the two efficiency maxima of the detailed-balance limit [8] for single-junction solar cells with AM1.5G spectrum, but solar cells with an absorber bandgap matching the second, wide-bandgap, efficiency maximum at 1.34 eV would be desirable with $X_{GGI} = 0.5$ [9]. For tandem applications with a Si bottom cell, an even wider bandgap above
1.4 eV would be ideal. Hence, solar cells with lower In concentrations would be desirable, but the efficiency of Cu(In,Ga)Se₂ solar cells with GGI values above 0.3 declines [10].

Lateral inhomogeneities pose another challenge that thin-film solar cells have to overcome to become competitive on the photovoltaics market [11–13]. Bandgap fluctuations induced by inhomogeneities and defects affect the efficiency of the whole cell. Therefore, it is paramount to identify, understand and mitigate the sources of local underperformance [11, 14, 15].

The effects of adding alkali elements such as Na, K and Rb in a post-deposition treatment to mitigate defects has been extensively studied before [16–22], and a segregation of the alkali elements to grain boundaries has been consistently observed. The diffusion mechanism for alkali metals is assumed to be dominated by Cu vacancies (V\text{Cu}) at grain boundaries, and only small alkali metals can move via interstitial positions into grains [23, 24]. This leads to the formation of Rb\text{Cu} sites at grain boundaries, while Na diffuses into grains via interstitial positions, effectively increasing the doping of the material [16, 25].

Inhomogeneities at the sub-micrometer scale include chemical defects and voids; they pose a particular characterization challenge and require imaging techniques on the nanoscale to study them [13]. Synchrotron-based scanning x-ray microscopy offers ideal tools for that purpose and has been used extensively in the last years [18, 26–33]. Hard x-rays allow to penetrate fully functional solar-cell stacks, and the multitude of available measurement modalities [31, 33, 34] can give complementary information. The combination of x-ray beam induced current (XBIC) and x-ray florescence (XRF) measurements has been established as sensitive approach to probe the spatially resolved electrical performance together with the composition [27, 30, 31, 35].

In a previous study by West et al [12], two cells were measured with \(X_{GGI} = 0.3\) and \(X_{GGI} = 0.6\), respectively. It was highlighted that the latter cell has a steeper local GGI gradient from grain core to grain boundary. To elucidate the underlying cause of the efficiency loss upon GGI increase, we simultaneously assessed XBIC and XRF of four solar cells with different nominal depth-averaged GGI (\(X_{GGI}\)) values between 0.39 and 0.49. Beyond macroscopic comparison, we used point-by-point correlation to link performance and composition for each cell individually. We studied co-evaporated Cu(In,Ga)Se₂ cells which had undergone Rb post-deposition treatment, as the world record efficiency of 22.6% for co-evaporated Cu(In,Ga)Se₂ cells was achieved with this system [36]. Therefore, we evaluated especially the behavior of Rb at identified voids and the impact on the charge-collection efficiency relative to the surrounding absorber matrix. For an inter-cell comparison, we performed a meta-analysis. This is a statistical tool commonly used in medicinal studies to congregate smaller studies into a bigger sample pool [37]; here, the individual voids are treated as sub-studies.

2. Experimental setup

2.1. Samples

The Cu(In,Ga)Se₂ solar cells were synthesized on glass substrates with an SiO₂ diffusion barrier below the 500 nm Mo back contact deposited by sputtering as described in [38]. The bandgap-graded Cu(In,Ga)Se₂ absorber layers were deposited using a multistage co-evaporation process below 450 °C substrate temperature, and were subjected to an in-situ NaF & RbF post-deposition treatment in Se ambient.

The CdS buffer layer (45 nm) was deposited in a chemical bath, followed by sputter deposition of ZnO (250 nm) as transparent conductive oxide, and a MgF₂ layer (105 nm) as anti-reflective coating. An electron-beam evaporated Ni–Al grid was used to contact the cells.

They were manually isolated by peeling off surrounding Cu(In,Ga)Se₂ material. The Ni–Al grids were electrically connected to a dedicated printed-circuit board using thin Cu wires and manually applied silver paint (far from the investigated region of interest). Figure 1 shows a scheme of the samples and the experimental setup. The wiring for XBIC measurements followed the description in [27] with the front contact grounded to avoid contributions of the replacement current for ejected electrons to the XBIC signal. The sample preparation was noted before in [39].

The solar cells were prepared with four different \(X_{GGI}^{\text{Nom}}\) values that are used for referencing the cells in this work. They are listed in table 1 along with the bandgap \(E_g\) from external-quantum-efficiency measurements, the absorber-layer thickness \(d_{\text{nom}}\) as well as the open-circuit voltage \(V_{\text{OC}}\), \(V_{\text{OC}}\) deficit \(E_g/q - V_{\text{OC}}\), short-circuit current density \(J_{\text{SC}}\), fill factor FF and the efficiency \(\eta\) from current–voltage measurements of co-processed sister cells using an AM1.5G spectrum with 1000 W m⁻² illumination intensity. For the respective current–voltage and external quantum-efficiency measurements, we refer to the supporting information (SI). These measurements highlight that high efficiency is associated with high In concentration (low \(X_{GGI}^{\text{Nom}}\)) and low \(V_{\text{OC}}\) deficit, which means that the voltage remains below expectations for cells with high \(X_{GGI}^{\text{Nom}}\) and is one of the key motivations for this study.
Figure 1. Scheme of the experimental setup for multi-modal measurements including XRF and XBIC of a Cu(In,Ga)Se$_2$ solar cell. The color gradient in Cu(In,Ga)Se$_2$ indicates a higher (darker) and lower (brighter) GGI value. The samples were scanned in the $y$–$z$ plane.

Table 1. Nominal properties and characteristic solar-cell parameters of the four solar cells from current–voltage and external quantum-efficiency measurements, including the nominal absorber-layer thickness $d_{\text{Nom}}$, bandgap $E_g$, open-circuit voltage $V_{\text{OC}}$, short-circuit current density $J_{\text{SC}}$, fill factor FF, and the efficiency $\eta$. The cells are referred to by their $X_{\text{GGI}}$ value, and the mean stoichiometric value of Ga $\bar{\nu}_{\text{Ga}}$ from synchrotron XRF measurements is shown for comparison.

| $X_{\text{GGI}}$ | $\bar{\nu}_{\text{Ga}}$ (.) | $d_{\text{Nom}}$ ($\mu$m) | $E_g$ (eV) | $V_{\text{OC}}$ (V) | $E_g/q - V_{\text{OC}}$ (V) | $J_{\text{SC}}$ (mA cm$^{-2}$) | FF (%) | $\eta$ (%) |
|------------------|------------------------|-------------------|-----------|----------------|-------------------------|-------------------|--------|---------|
| 0.39             | 0.35                   | 1.97              | 1.166     | 0.756          | 0.41                    | 32.4              | 0.76   | 18.7    |
| 0.42             | 0.36                   | 2.13              | 1.175     | 0.755          | 0.42                    | 30.8              | 0.74   | 17.2    |
| 0.46             | 0.41                   | 2.32              | 1.197     | 0.769          | 0.43                    | 31.2              | 0.74   | 17.6    |
| 0.49             | 0.42                   | 2.62              | 1.203     | 0.773          | 0.43                    | 29.7              | 0.73   | 16.8    |

2.2. Measurements

The x-ray microscopy measurements were performed by scanning the sample-surface plane ($y$–$z$) across the focused x-ray beam at the micro-probe endstation of the hard x-ray scanning microscopy beamline P06 [40] at PETRA III (Deutsches Elektronen-Synchrotron DESY) in Hamburg, Germany, as shown in figure 1. The photon energy was set to 15.25 keV and the coherent part of the x-ray beam was focused by Be compound refractive lenses (CRL) and a correcting phase plate [41] to 108 nm × 105 nm (horizontal × vertical, FWHM). The subsequent XBIC and XRF measurements were optimized for the electrical and compositional assessment. The scans were performed in continuous mode and covered an area of 10 $\mu$m × 10 $\mu$m with a set scanning speed of 5 $\mu$m s$^{-1}$ and 0.5 $\mu$m s$^{-1}$ for XBIC and XRF measurements, respectively, assessed every 50 nm.

For maximum signal-to-noise ratio, lock-in amplification was utilized as described in [30]. A chopper (MC200B, Thorlabs) modulated the incident x-ray beam at 8.015 kHz, and the XBIC signal was demodulated to the chopper frequency using a lock-in amplifier (UHFLI, Zurich Instruments) after the signal underwent amplification by 1 $\mu$A V$^{-1}$ through a current pre-amplifier (SR570, Stanford Research Systems). The low-pass filter cut-off frequency of the lock-in amplifier was set to 501.1 Hz (8th order). For the quantitative current evaluation, the XBIC signal was normalized to the incident x-ray photon flux and to the effective pixel dwell time.

X-ray fluorescence photons were detected by a silicon drift detector (SII Vortex EM, Hitachi) that was placed 2 cm from the sample under an angle of 8.25° to the sample surface. The XRF detector was read out by a pulse processor (Xspress3, Quantum Detectors). Fluorescence spectra were fitted using PyMca [42] (V. 5.3.3.) to obtain XRF count rates $\Phi_{\text{Element}}$ and stoichiometric fractions $\nu_{\text{Element}}$ (see SI of [33]) for every element, taking self-absorption, photon flux and dwell time into account. The resulting images from two subsequent scans optimized for XBIC and XRF signal were registered and aligned as described in [43] based on the distribution of Se.

3. Results

3.1. Performance

Table 1 shows that the overall efficiency of the investigated Cu(In,Ga)Se$_2$ solar cells decreases with a higher $X_{\text{GGI}}$. To go from a macroscopic to microscopic evaluation of the performance, its distribution over the scanned maps has therefore been measured with XBIC. X-rays with an energy of 15.25 keV have an extinction
Figure 2. Distribution of $I_{\text{XBIC}}$ for the four investigated Cu(In,Ga)Se$_2$ solar cells as 2D maps and violin plots. The dashed lines indicate the 25th, 50th and 75th percentile of the distribution. The blue dots highlight the lowest value for each cell. The white lines in the 2D maps are contours indicating the 33 percentiles of low performance. All maps share the same color scale.

length of around 100 $\mu$m in Cu(In,Ga)Se$_2$ absorber material [44]. Accordingly, only 9%–12% of the incident photons are absorbed in the Cu(In,Ga)Se$_2$ layer, and the XBIC signal can be assumed to be constituted from electron–hole pairs being homogeneously distributed along the x-ray path (flat generation profile).

To compare the different cells without manipulating their charge-collection efficiency distributions, we have normalized the measured $I_{\text{meas}}$ to the estimated absorptance $A$ based on their nominal thickness $d_{\text{Nom}}$ and utilizing the Lambert–Beer law, as well as to the different rate of charge-carrier generation related to the bandgap-dependence. We have set the median of the resulting normalized $I_{\text{XBIC}}^*$ distribution to 1 for the cell with $X_{\text{Nom}}^{GGL} = 0.39$ and scaled the other distributions according to the ratio of the respective normalization factors $C$, yielding the normalized and re-scaled $I_{\text{XBIC}}$. For further details on the normalization procedure, we refer to the SI. The $I_{\text{XBIC}}$ maps are shown in figure 2 along with the corresponding distributions.

In these nanoscale performance measurements, the macroscopically measured superiority of the cells with lower $X_{\text{Nom}}^{GGL}$ is reflected in higher $I_{\text{XBIC}}$ values and narrower distributions. Conversely, broad distributions, as the higher $X_{\text{Nom}}^{GGL}$ cells display, are typical for poor solar-cell performance [11, 32]. The trend of decreasing performance with increasing $X_{\text{Nom}}^{GGL}$ is particularly well visible for the points with lowest performance in each cell that are highlighted with a blue dot. As the underperforming areas limit the overall solar-cell efficiency, the contours of the lowest 33 percentile are indicated with white lines in the 2D maps.

We further note that the spatial granularity of $I_{\text{XBIC}}$ seems to decrease with increasing $X_{\text{Nom}}^{GGL}$ from isolated small areas of underperformance for low-GGI cells to large interconnected areas for high-GGI cells. To elucidate and quantify this trend, we have evaluated for each point the shortest distance $d_{\text{min}}$ to an area of the underperforming 33 percentiles. The resulting distance-maps and -distributions are shown as violin plots and inlays in figure 3. The trend towards locally concentrated, severely underperforming areas with increasing $X_{\text{Nom}}^{GGL}$ value appears here as a rising median distance and broader distribution as well as larger structures in the 2D maps.

These results offer an explanation for the macroscopically seen lower performance for higher $X_{\text{Nom}}^{GGL}$: while high $X_{\text{Nom}}^{GGL}$ values lead to fewer spots of accumulated defects, we hypothesize that these defect areas have a greater negative impact than the more broadly distributed defects in solar cells with a lower $X_{\text{Nom}}^{GGL}$. 
Figure 3. Shortest distance $d_{\text{min}}$ of each point to an area of the underperforming 33 percentiles of the $I_{\text{ABC}}$ signal shown as violin plots and 2D maps. The dashed lines indicate the 25th, 50th (with numerical value in blue) and 75th percentile of the distribution. All maps share the same color scale.

Figure 4. (a)–(d) XRF count rate of selenium $\Phi_{\text{Se}}$ (gray scale) and count rate of Rb $\Phi_{\text{Rb}}$ (red scale) overlaid. The anti-correlation of Rb and Se illustrates the segregation of Rb towards material-deficit areas such as grain boundaries, voids and crevices. All color scales cover the entire range of the individual maps.

3.2. Distribution of Rb
For the type of Cu(In,Ga)Se$_2$ solar cells studied here, voids and crevices tend to appear in the top part of the absorber layer [13], and we used XRF microscopy to localize these material-deficit areas. We chose the excitation energy for our experiment (15.25 keV) just above the absorption edge of Rb (15.2 keV) to be most sensitive to the Rb distribution and evaluate its passivation effect on defects [16–22]. In Cu(In,Ga)Se$_2$ solar cells, the abundance of Cu is sub-stoichiometric to dope the absorber, while Ga and In share a lattice point with intentional spatial grading. Consequently, Se is the most homogeneously distributed absorber-matrix element [45], which allows to consider the depth-integrating XRF Se count rate $\Phi_{\text{Se}}$ as an estimate of the absorber-layer thickness. Accordingly, low $\Phi_{\text{Se}}$ values are usually associated with grain boundaries [33] or other material deficits such as voids [33] that may—or may not—lead to local underperformance [13].

Figure 4 shows the XRF count rates $\Phi_{\text{Se}}$ (gray) and $\Phi_{\text{Rb}}$ (red) of Se and Rb for the four cells. These maps clearly unveil the anti-correlation of Rb and Se and the segregation of Rb to material-deficient areas (i.e. low Se signal) such as grain boundaries, voids and crevices.
are 18 13 is negative as expected from the Rb segregation towards material-deficit absorber areas (see figure 5). This indicates a higher variation of $\nu_{\text{GGI}}$ for selected inter-dependencies: the Se count rate $\Phi_{\text{Se}}$, Ga stoichiometric fraction $\nu_{\text{Ga}}$, and Rb stoichiometric fraction $\nu_{\text{Rb}}$ from XRF measurements; the x-ray beam induced current $I_{\text{XBIC}}$ and the charge-collection efficiency $\eta_{\text{XBIC}}$ derived from $I_{\text{XBIC}}$. The lines are linear fits serving as a guide to the eye to illustrate the trend over the solar-cell series. The green and red background colors indicate positive and negative correlation, respectively.

3.3. Correlation

The statistical correlation between performance, absorber thickness, Rb concentration and lateral Ga distribution is investigated by Pearson’s correlation coefficient $\rho$ and shown in figure 5; the correlation coefficients of further modalities can be found in the SI.

The strong positive correlation of $\Phi_{\text{Se}}$ and $I_{\text{XBIC}}$ (purple squares in figure 5) is explained by the sample topology dominating the beam/sample interaction volume, which affects the XBIC signal and the fluorescence signal strength in comparable manner. Interestingly, this correlation decreases with increasing $X_{\text{GGI}}^{\text{Nom}}$, which indicates that other effects than topology—likely defects—gain importance.

For a qualitative assessment of the local performance, we compensated $I_{\text{XBIC}}$ for the influence of the beam-sample interaction volume and calculated the charge-collection efficiency $\eta_{\text{XBIC}}$ as motivated in [27] and described in the SI. The topology-corrected $\eta_{\text{XBIC}}$ is slightly positively correlated with $\Phi_{\text{Se}}$ for all cells (orange squares in figure 5), which indicates that areas with material deficit suffer from higher charge-carrier recombination compared to bulk absorber material, which is in agreement with earlier findings [18].

The In count rate $\Phi_{\text{In}}$ is low and strongly influenced by self-absorption artifacts related to the low L-line fluorescence energy [47], which directly translates into uncertainties of $X_{\text{GGI}} = \frac{\Phi_{\text{In}}}{\Phi_{\text{Se}} + \Phi_{\text{In}}}$. Therefore, the spatially resolved $X_{\text{GGI}}$ is not considered here. Instead, we used the stoichiometric fraction of Ga, scaled to the stoichiometric fraction of Se, $\nu_{\text{Se}} = 2$, to represent the depth-averaged stoichiometric Ga distribution $\nu_{\text{Ga}}$ in the absorber matrix. Note that the absolute values of the laterally averaged $\nu_{\text{Ga}}$ values listed in table 1 are slightly lower than the nominal $X_{\text{GGI}}^{\text{Nom}}$ values, which is probably caused by the effective $X_{\text{GGI}}$ differing from $X_{\text{GGI}}^{\text{Nom}}$ and by different experimental setups being used to measure the laboratory-based $X_{\text{GGI}}^{\text{Nom}}$ and the synchrotron-based $\nu_{\text{Ga}}$ values. Both effects should, however, not affect the observed intra- and inter-cell variation of $\nu_{\text{Ga}}$.

Figure 5 unveils a strong anti-correlation of $\nu_{\text{Ga}}$ and the topology-representing Se count rate $\Phi_{\text{Se}}$. This indicates a higher $X_{\text{GGI}}$ in material-deficit areas compared to areas with a thick absorber layer and is in agreement with reports about increased $X_{\text{GGI}}$ at grain boundaries compared to grain cores [12, 13, 18, 48, 49]. The slight decrease in anti-correlation towards higher $X_{\text{GGI}}^{\text{Nom}}$ cells may be caused by statistical effects of increasing absorber thickness, which is consistent with a sharper normalized Se count-rate distribution (see SI).

The correlation between the Rb concentration $\nu_{\text{Rb}}$ and the charge-collection efficiency $\eta_{\text{XBIC}}$ shown in figure 5 is negative as expected from the Rb segregation towards material-deficit absorber areas (see figure 4). This indicates that the charge-collection efficiency is worse in Rb-rich areas: although Rb has been associated with defect-passivation [18, 21], the defects are apparently not fully mitigated by Rb. Additionally, we observed a slight increase in the anti-correlation for cells with a higher $X_{\text{GGI}}^{\text{Nom}}$. This is compatible with the hypothesis that more severe defects are present in the cells with higher $X_{\text{GGI}}^{\text{Nom}}$ cells and hints towards the selectivity of Rb segregation towards material-deficit areas.

3.4. Meta-analysis

From the anti-correlation between $\nu_{\text{Rb}}$ and $\eta_{\text{XBIC}}$ alone, the passivating effect of Rb cannot be corroborated. Therefore, we have segmented those areas with the 4% lowest $\Phi_{\text{Se}}$ counts and a minimum size of three scan
pixels (0.0075 $\mu$m$^{-2}$) and declared them as ‘voids’ for further discussion as compared to ‘bulk’ for the remaining 96%. Figures 6(a) and (d) show exemplarily the $\Phi_{Se}$ map of the solar cell with $X_{\text{GGI}} = 0.49$, split between the areas considered as voids and bulk, respectively. For each void, we analyzed the relative measurements of $\nu_{Rb}$ and $\eta_{XCE}$ within the void areas ($\nu_{\text{void}}, \eta_{\text{void}}$) and compared them to the respective average values from bulk areas ($\nu_{\text{bulk}}, \eta_{\text{bulk}}$).

To compare the four cells, we have conducted a meta-analysis following the concept of [37], and treated each void as a sub-study. This allowed us to extract the effect size

$$X_w = \frac{\sum_{i=1}^{k} w_i x_i}{\sum_{i=1}^{k} w_i}$$  \hspace{1cm} (1)$$

from the spatially averaged measurands $x_i$ of each void with a corresponding weight $w_i$ whose calculation is detailed in the SI. Intuitively, the effect size can be understood as a weighted average.

Figure 6(g) shows the effect sizes $X_w$ of $\nu_{Rb}/\nu_{\text{bulk}}$ and $\eta_{XCE}/\eta_{\text{bulk}}$ for all four cells. It evidences that the Rb concentration is significantly higher in the areas declared as voids compared to the bulk areas, while the charge-collection efficiency is inhibited.

We have established the increased presence of Rb at material-deficit areas before already and can now quantify this increase to be on the order of 10%. Note that there is no systematic trend of the Rb effect size visible. In contrast, the effect size of the charge-collection efficiency decreases with increasing $X_{\text{GGI}}$. For the cell with the lowest $X_{\text{GGI}}$, the effect size of the charge-collection efficiency is close to the equilibrium. This means that voids do not significantly underperform, most likely due to the efficient Rb passivation. Towards higher $X_{\text{GGI}}$, the charge-collection efficiency at voids decreases relative to the surrounding areas despite of comparable total Rb concentration (cf. figure 4) and Rb segregation towards voids. This observation further corroborates the hypothesis of higher $X_{\text{GGI}}$ leading to increased severity of nanoscale defects that cannot be entirely mitigated by Rb passivation and deteriorate the macroscopic solar-cell performance.

3.5. Discussion

The experimental evidence for negative correlation between performance and the GGI ratio is clear–both at the macro- and the microscale. However, we can only hypothesize about the underlying reasons. From literature it is known that Cu(In,Ga)Se$_2$ solar cells with $X_{\text{GGI}} > 0.5$ form a deep defect in the bandgap [50, 51], which merges with the conduction band for smaller GGI values. This state is associated with a Ga$_{\text{Cu}}$ defect [50–52]. While the cells in this study were deposited with nominal GGI ratios below the threshold of 0.5, we consider the presence of locally enhanced GGI ratios likely, and the probability of such high-GGI spots should increase with the overall GGI. Accordingly, we expect an enhanced density of deep Ga$_{\text{Cu}}$ defects for high-GGI solar cells, whereas shallow V$_{\text{Cu}}$ defects dominate for low-GGI cells. The ineffectiveness of Rb
to passivate Ga$_{2}$Cu$_{2}$ defects explains the observed diminished passivation efficiency of Rb in solar cells with high GGI. The experimental confirmation of this hypothesis would require 3D-measurements with great sensitivity to the local GGI, which is beyond the scope of this study.

4. Conclusion

The compositional in-plane inhomogeneities of four Cu(In,Ga)Se$_{2}$ solar cells with different GGI have been measured and correlated with their nanoscale performance. In all samples, we observed lateral inhomogeneities in thickness, Rb concentration, GGI and charge-collection efficiency. Areas with material defects corresponding to grain boundaries, crevices or voids exhibit Rb as well as Ga enrichment along with charge-collection efficiency impairment.

We found that cells with an In-rich absorber outperform cells with a Ga-rich absorber both at the macro- and microscale and could establish distinct defect patterns: for low GGI, defects were comparably homogeneously distributed with limited impact on performance; in contrast, cells with high GGI unveiled concentrated defect clusters with a significantly stronger detrimental impact on the charge-collection efficiency. Investigating further the decreasing charge-collection efficiency with increasing GGI with a meta-analysis, we could corroborate the hypothesis that the Rb passivation of electronically more detrimental nanoscale defects is insufficient for cells with high X$_{GGI}$. This is in accordance with the evolution of deep Ga$_{2}$Cu$_{2}$ defect states that become more severe for absorber compositions with high GGI.

Altogether, these measurements show a consistent picture linking the macroscopic solar-cell performance to nanoscopic features. Specifically, we could demonstrate that Cu(In,Ga)Se$_{2}$ solar cells with a Ga-rich absorber suffer from severe electronic-defect clusters that are related to inefficient passivation of areas with material deficits.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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