Defect activation and annihilation in CIGS solar cells: an operando x-ray microscopy study

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Abstract
The efficiency of thin-film solar cells with a Cu(In_{1-x}Ga_x)Se_2 absorber is limited by nanoscopic inhomogeneities and defects. Traditional characterization methods are challenged by the multi-scale evaluation of the performance at defects that are buried in the device structures. Multi-modal x-ray microscopy offers a unique tool-set to probe the performance in fully assembled solar cells, and to correlate the performance with composition down to the micro- and nanoscale. We applied this approach to the mapping of temperature-dependent recombination for Cu(In_{1-x}Ga_x)Se_2 solar cells with different absorber grain sizes, evaluating the same areas from room temperature to 100 °C. It was found that poor performing areas in the large-grain sample are correlated with a Cu-deficient phase, whereas defects in the small-grain sample are not correlated with the distribution of Cu. In both samples, classes of recombination sites were identified, where defects were activated or annihilated by temperature. More generally, the methodology of combined operando and in situ x-ray microscopy was established at the physical limit of spatial resolution given by the device itself. As proof-of-principle, the measurement of nanoscopic current generation in a solar cell is demonstrated with applied bias voltage and bias light.

1. Introduction
In the last several years, the photovoltaic industry has grown dramatically, and large factories have achieved economies of scale capable of producing modules with power conversion efficiencies in the range of 17%–24.4%. These devices are based on silicon (Si), cadmium telluride (CdTe), and copper indium gallium diselenide (Cu(In_{1-x}Ga_x)Se_2, CIGS), all reaching costs lower than $0.5/W [1, 2].

CIGS-based solar cells have emerged as one of the most promising candidates for high-efficiency low-cost thin-film solar cells, and R&D efficiencies as high as η = 23.35% have been reported [3]. The compatibility with roll-to-roll manufacturing, flexibility, and lightweight characteristic make CIGS technology extremely attractive for the integration of solar cells on uneven structural surfaces, car roofs, RVs, and portable electronic components. Some authors have even suggested CIGS application in space, based not only on the weight savings that can significantly reduce launching costs, but also on the stability under and recovery from electron and proton irradiation [4, 5].

The intrinsic low production cost, low weight, and flexibility of CIGS modules make them an attractive candidate for tandem applications, where a cell with a wider bandgap is stacked on top to absorb the higher energy photons and generate more power [6, 7]. Increasing the module efficiency is especially important because module installation costs now dominate the manufacturing costs. Higher efficiency means that fewer panels...
need to be installed to meet predetermined power requirements, which in turn reduces the overall cost of the installation.

While the CIGS solar cell record sits in the >23% range, the commercial-size module record for CIGS has just recently reached 17.52% on glass substrates and 17.44% on a flexible substrate [8–10]. These values, while promising, are still several percentage points lower than the PV industry mammoth—silicon [1]. It is generally accepted that inhomogeneities at the nano- and micrometer scale, which riddle CIGS absorbers, dominate the overall cell and module performance [11]. Several authors have reported that bandgap variations due to inhomogeneous concentrations of In and Ga combined with the carrier distribution that compensates unevenly distributed donor and acceptor sites, create a spatial variation of charge density. This locally shifts the energy bands, limiting the voltage [11–14] and the device efficiency due to increased charge-carrier recombination [15, 16].

A better understanding of the origin of defects in this absorber, their activation and annihilation, as well as their sensitivity to operating and processing conditions is needed to gain insight into the underlying performance drivers. The challenge, however, has always been to bridge the gap between nano-scale effects in structure and composition with the macro-scale device performance. Multi-modal x-ray microscopy offers a unique suite of characterization methods to probe multiple material properties and simultaneously gather solar cell device information, enabling their direct point-by-point correlation [17, 18].

The methods include x-ray beam induced current (XBIC) [17, 19–21] and voltage (XBIV) [22] to probe the electrical performance, x-ray fluorescence (XRF) to probe the composition [23, 24], x-ray excited optical luminescence (XEOL) to probe the optical performance [25, 26], ptychography to probe the structure [27] including voids at CIGS grain boundaries [28], and x-ray diffraction to probe the lattice constant [29–31]. The applications of these methods in the field of photovoltaics are discussed in various review articles including [17, 32]. In most cases, XRF and XBIC have been used to correlate the absorber composition with performance at the micro- and nanoscale [14, 20, 33–42]. Only recently, XBIC and XRF have been combined with nanodiffraction [29–31], and it has been found that the atomic distances decrease towards grain boundaries in CdTe [31], and that they increase towards grain boundaries in CIGS [29]. The latter study had been performed on CIGS solar cells that were co-deposited with the samples that we denote ‘large grain CIGS’ in this study.

Here, we investigated for the first time the nanoscopic performance of industrial CIGS solar cells using in situ and operando x-ray microscopy. In the following, we describe how we tracked the performance of individual defects upon heating from room temperature to above the maximum operating temperature, and subsequent cooling. Two measurement modes, XBIV and XRF, allowed us to simultaneously assess the electrical performance and elemental distribution with sub-grain-size resolution. This combination enabled the clear identification of areas with high recombination: while low x-ray beam induced voltage can generally be caused by thin absorbers or bandgap variations [22], locally low voltage can be ascribed to enhanced recombination at electronic defects in the absence of large elemental variations.

The samples studied include two types of CIGS solar cells that were synthesized at different temperatures to yield different grain sizes: the sample denoted here as ‘Large grain CIGS’ (LG) was grown at a higher temperature relative to the sample denoted ‘Small grain CIGS’ (SG) that was grown at a lower temperature. While the growth temperature yielding the maximum open-circuit voltage ($V_{oc}$) lies between the growth temperatures of the LG and the SG sample, these samples were chosen as they were expected to be limited by different defects. Small-grain CIGS contains more recombination-active grain boundary interfaces and bandgap variations, which reduce the $V_{oc}$. In large-grain CIGS, on the other hand, the $V_{oc}$ is suspected to be reduced by the appearance of detrimental secondary phases [43] at the back electrode that compensate the advantageous effects of fewer grain boundaries with larger grains.

### 2. Experimental

The typical CIGS grain size was 1.6 $\mu$m and 0.8 $\mu$m for the LG and SG samples, respectively, as determined by electron back-scattered diffraction imaging and in agreement with x-ray nanodiffraction measurements [29]. The solar cells were grown by MiaSolé using growth processes detailed in [44, 45]. The 1.7–1.8 $\mu$m thick absorber layer of CIGS is grown in an industrial roll-to-roll process on a stainless steel substrate coated with 700 nm of Na-doped Mo that serves as the back electrode. The front contact consists of 50 nm CdS and 200 nm ZnO as shown in figure 1.

For the temperature control during this experiment, a heating stage [46] developed for the in situ growth of CIGS [47, 48] has been adapted for electrical XBIC & XBIV measurements in combination with XRF measurements. The experiments were conducted in N$_2$ atmosphere. The sample temperature was controlled to within ±0.1 °C of the nominal temperature via four thermocouples in the heating stage that were calibrated.
using a pyrometer. After changing the nominal temperature, 20 min were taken for stabilization and homogenization of the temperature distribution.

The scanning x-ray microscopy measurements were performed at the beamline 2-ID-D [49] of the advanced photon source (APS) at Argonne National Laboratory (ANL). Figure 1 shows schematically the key components of the experimental setup. The energy of the incident x-ray photons was set to 10.5 keV, just above the Ga K edge for maximum sensitivity to the absorber elements Ga and Cu. Note that at this incident energy the sensitivity to In is fairly reduced and there is negligible sensitivity to Se, Na or K. The x-ray beam was modulated at a frequency of 318 Hz by an optical chopper upstream of the focusing optics and detectors [21]. The chopper consists of 300 μm spring steel that enables a modulation ratio of > 10^12 between x-ray ON/OFF periods. Being located > 20 cm upstream of the beam/sample interaction point, the chopper did not lead to any XRF signal beyond the background of the experimental setup.

After the chopper, the modulated x-ray beam passed an ion chamber for beam-intensity reference and was focused by a zone plate with central beam stop onto the sample. The numerical aperture of the optics was 1.2 mrad, and the probe size on the order of 140 nm. At the microprobe instrument of beamline 2-ID-D, the diffraction-limited resolution of about 50 nm cannot be achieved due to (a) beam incoherence and (b) vibrations between the x-ray optics and the sample.

Between the zone plate and the sample front contact, an order sorting aperture (OSA) removed higher orders, and a polyimide foil separated the heating stage environment from the experimental hutch. The sample surface was perpendicular to the incident x-ray beam, and the excident fluorescence x-ray photons were caught by an energy-dispersive single-element Si detector under a central angle of 43° to the incident beam. For the 2D measurements, the heating stage including the sample was scanned across the probe beam. Optimized for high-speed measurements with limited beam damage and high throughput, we used the continuous, or fly-scan, mode [50] for fast XBIV measurements; the horizontal motion was the continuous one (inner loop), the vertical motion was not continuous (outer loop). The dwell time was 100 ms with a step size of 200 nm × 200 nm. Only for the overview map of the SG sample (right panel of figure 2), a dwell time of 10 ms was used. For the overview map of the LG sample (left panel of figure 2), a step size of 1 μm × 1 μm was used.

To collect high-sensitivity XRF measurements combined with an XBIC measurement such as in the case of figure 9, we used the step–scan mode with 1 s dwell time and 200 nm × 200 nm step size. From the XRF spectra of the sample and thin-film references, the elemental distributions of Cu and Ga were determined using the analysis software MAPS [23, 51, 52]. The XRF data were corrected for self-absorption effects, as discussed in [24], with a sensitivity analysis included as well. Note that misalignment during the sample change from the LG to the SG sample caused ~2 × lower XRF counts in the SG sample, which appears as lower concentrations in figure 4 (part of the XRF detector was shielded by the heating stage). In addition, the XRF reference was measured under slightly different conditions, which causes an underestimation of the true Cu and Ga area densities that should, in fact, be similar for the LG and SG samples. The experimental uncertainty in the absolute quantification of area densities by XRF is not uncommon, despite the detection limit for Cu and Ga being on the order of 10^-6 (relative atomic concentration) under the given experimental conditions. Apart from the misalignment, errors in the absolute quantification arise from limited applicability of the thin-film limit, incomplete self-absorption correction, and errors of the concentrations in the reference. Note, however, that these systematic errors only

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**Figure 1.** Experimental setup for the simultaneous measurement of the electrical solar cell performance via lock-in amplified x-ray beam induced current or voltage and of the composition via x-ray fluorescence (XRF) under in situ and operando conditions at a synchrotron beamline.
affect the absolute concentration level, not the relative changes within maps, from which all conclusions will be drawn.

The temperature-dependent XBIV scans were performed over \(20 \, \mu m \times 20 \, \mu m\), hence measuring \(100 \, px \times 100 \, px\). Due to imperfect compensation of the thermal drift, we used image registration [53] to align the maps at different temperatures. For comparability of the maps, we cropped the maps to show only the areas that were measured at all temperatures in the case of the LG sample. In the case of the SG sample, stick-slip motion of the sample below \(40 \, ^\circ C\) and above \(80 \, ^\circ C\) did not allow for the measurement of the same area throughout the entire temperature range. Therefore, the comparable temperature range of the SG sample is limited to \(40 \, ^\circ C–80 \, ^\circ C\).

For the highest signal-to-noise ratio of the XBIC and XBIV measurements, we utilized lock-in amplification as introduced in detail earlier [21, 22, 28, 39]. The front contact being exposed to the incident x-rays was grounded to suppress contributions of replacement currents for ejected electrons to the measured XBIV & XBIC signal, which should include only the signal from the absorber layer [17]. For the XBIV measurements, the solar cell was operated under open-circuit conditions, and the signal was directly sent to the voltage input of the MFLI lock-in amplifier from Zurich Instruments, where a demodulator and a low-pass filter (10 Hz cut-off frequency (~3 dB BW), 48 dB/oct slope) extracted the signal above the noise level. For the XBIC measurement, the solar cell was operated with 100 mV forward bias voltage applied by a current pre-amplifier (SR570 from Stanford Research Systems), whose output was sent to the lock-in amplifier with identical demodulator and low-pass filter settings as for the XBIV measurements.

3. Results

3.1. Microscopic defects
Prior to the investigation of the temperature dependence of recombination at nanoscopic defects, we evaluated the pristine state of the solar cells at a larger scale. Figure 2 shows the resulting XBIV measurements, representing typical areas of the LG and SG sample, several \(100 \, \mu m\) away from the cell edges to avoid border effects. Throughout the manuscript, color scales show always the entire data range except for the differential voltage maps in figure 3, where the scale is the same for all maps for comparison.

When comparing the overview maps of the two samples, we note first the different voltage scale. The SG sample outperforms the LG sample, and relative variations in the SG sample are smaller. Based on the fact that the poorest areas limit the overall device performance, this suggests that the LG sample is limited by the large defect areas, where the voltage drops to <20% of the median.

6. The XBIV signal can be thought of as the measurement of the \(V_{oc}\) with highly localized electron-hole pair generation.

7. In most cases, the XBIC signal is a measurement of the short-circuit current \(I_{sc}\) with highly localized electron-hole pair generation, but any point of the current-density curve \(I(V) = XBIC(V)\) can be evaluated by applying a bias voltage as we demonstrate in figure 9.
Second, we note that the structure of high and low performing areas is different: in the LG sample, we can distinguish large islands, many \( \mu \text{m}^2 \) in area, with dramatically poorer performance compared to the large areas of relatively homogeneous high performance. In contrast, the SG sample does not show large under-performing islands, but the performance variations are spatially at a smaller scale.

The temperature dependence of the large poor-performing areas in the LG sample has been studied previously [39]. The reason for the poor performance of these defects is still under investigation, but no correlation was found with the area density of Zn, Ga, and Cu, which excludes pinholes in the absorber or poor ZnO coverage as reasons. Most likely, the low performance of these areas is related to junction effects, but the limited sensitivity to the Cd or S distribution prevented the ability to test correlations of the electrical performance with the CdS thickness.

3.2. Nanoscopic defects

In this study, we focus on the nanoscopic performance of electronic defects. For this purpose, we have performed high-resolution measurements of selected areas from figure 2 that are marked with white rectangles. The areas have been selected because they are not dominated by the larger defects discussed above.

Starting at room temperature, the solar cell temperature was increased in steps of 20 °C up to 100 °C, and the XBIV signal was measured in precisely the same area. The middle part of figure 3 shows the resulting
For direct comparison of the spatially resolved voltage variation that is induced by each temperature step, the XBIV measurements $V_1(x, y)$ and $V_2(x, y)$ at coordinates $(x, y)$ were normalized to the median value at each temperature, and the voltage difference of subsequent temperature steps 1 and 2 was calculated as

$$\Delta V(x, y) = \frac{\text{median}[V_2(x, y)] - \text{median}[V_1(x, y)]}{\text{median}[V_1(x, y)]}.$$  

(1)

$\Delta V > 1$ indicates a relative voltage increase compared to the median voltage, which is indicated in green, and $\Delta V < 1$ indicates a relative voltage decrease, which is indicated in red.

This normalization is required for a direct nanoscopic comparison, as the spatial variations would otherwise be dominated by the overall trends that are expected with increasing temperature. Specifically: the voltage drops as the temperature increases due to an increase in recombination and bandgap narrowing [54, 55]; and the annealing of CIGS solar cells leads to a substantial voltage increase [56]. Here, we observe the former effect as a consistent voltage decrease from 16 °C to 100 °C in the LG sample, and from 40 °C to 80 °C in the SG sample. The latter trend manifests clearly in the LG sample as a five-fold voltage increase from the initial measurement at 16 °C and the final LG measurement after the full heating cycle and cool down at 18 °C. Note that these effects dominate over any beam damage; only between 16 °C and 40 °C, we observed significant beam damage (see figure 2(f) of [39]; the LG area investigated here is at coordinates $(x, y) \approx (25 \mu m, 25 \mu m)$). Above 40 °C, the scanned area showed barely any performance difference compared to the non-damaged areas, and no difference can be observed in the annealed state after cooling down (see figures 5(c)–(d) in [39]). In the following, we discuss characteristic signatures of temperature dependence highlighted by white shapes in figure 3.

In the LG sample, A1 denotes the defect area with both lowest performance and largest footprint. Defect areas A2 and A3 are smaller and their impact is not as strong, but they share with A1 the key signature: they all improve significantly from 40 °C to 100 °C relative to neighboring areas. Partially, this effect is reversible. Upon cooling from 100 °C to 18 °C, the relative performance of areas A1–A3 decreases; however, the absolute voltage remains significantly higher than in the pristine state ($\sim 12$ versus $\sim 2.5 \mu V$), which indicates an irreversible annealing effect.

Figure 4 shows the area density of the absorber elements Cu and Ga measured at 60 °C. At other temperatures, XRF measurements were taken with lower sensitivity, but no temperature-induced changes in the Cu and Ga distribution were observed. In all three areas A1–A3, the low performance is accompanied with a substantially lower Cu concentration. This pattern is true for many other spots of low performance. At the same time, the difference of the Cu and Ga densities between LG and SG CIGS is caused by systematic errors in the absolute quantification from the XRF measurements as detailed in section 2. This does not affect the relative density variations within the maps, from which all conclusions will be drawn. The true area densities of Cu and Ga are similar for the LG and SG samples.

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Note that the difference of the Cu and Ga densities between LG and SG CIGS is caused by systematic errors in the absolute quantification from the XRF measurements as detailed in section 2. This does not affect the relative density variations within the maps, from which all conclusions will be drawn. The true area densities of Cu and Ga are similar for the LG and SG samples.
time, the Ga distribution does not follow the same trend in general\(^9\). The fact that only the Cu concentration changes suggests that voids or pinholes in the absorber layer are not the cause for the performance decrease (which would show up as a reduced concentration of all absorber elements). Rather, a deficiency of Cu relative to Ga (and eventually In and Se, to which these measurements are not sensitive) appears to be responsible for the locally low voltage.

The statistical correlation of the nanoscopic electrical performance with the absorber element distribution across the entire map further corroborates this interpretation. Figure 5 shows a clear positive correlation between the voltage and the Cu concentration (relative standard deviation of the slope: only 2.7\%), whereas no correlation is observed between the voltage and the Ga concentration (relative standard deviation of the slope: 42\%). These results of locally poor performance at areas of low Cu area density are in line with the observation of amorphous secondary phases in the CIGS absorber that were observed by electron microscopy and found to be Cu-poor and Na-rich [43]. Figures 3–5 provide direct evidence for the detrimental electrical impact of these phases.

Area B denotes a unique defect characteristic that has not been observed elsewhere. During the first temperature increase to 40 °C, this defect is created and manifests as the strongest relative voltage decrease. Upon a subsequent temperature increase, this defect is nearly completely annealed out. This area neither stands out in the elemental distribution of the absorber layer, nor of Zn (not shown here), which excludes pinholes or voids in the absorber layer or top electrode as cause. Furthermore, we can exclude local beam damage as cause for this electronic defect, as this area has not absorbed a higher dose than any other area of these high-resolution maps. Thus, the reason for the creation and annihilation of this defect remains unclear. We may speculate that crystallographic or chemical rearrangement beyond the sensitivity of these measurements could have caused the defect in area B.

In the SG sample, there are more areas with high spatial performance gradients than in the LG sample. At 40 °C, we can distinguish between poor and high performing areas showing up in blue and orange, respectively. Note that the distribution of the poor performing areas does not match the grain boundary distribution, which is at a smaller scale (compare 0.8 \(\mu\)m typical grain size versus well-performing areas sized several \(\mu\)m\(^2\)). Hence, the partial decrease of Ga at A1 and A2 can be explained by topological variations. Note that other areas show significantly lower Ga concentration without corresponding voltage drop.

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\(^9\) The partial decrease of Ga at A1 and A2 can be explained by topological variations. Note that other areas show significantly lower Ga concentration without corresponding voltage drop.
grain boundaries are not generally under-performing, but defective areas may still be among the grain boundaries.

Within the defective areas, C1 and C2 stand out. There, the performance subsequently increases with temperature until the defects are annihilated to a large extent at $80^\circ$C. As a consequence of this defect annihilation, areas C1 and C2 outperform other areas at $80^\circ$C that showed similar or even better performance at $40^\circ$C.

Area D shows the opposite behavior. Being at $40^\circ$C one of the best-performing areas, this area suffered the strongest voltage drop as a result of the temperature increase. Neither the performance changes of areas C nor D in the SG sample can be explained by compositional particularities, which would show up as features in the area density maps in figure 4 or in the statistical analysis in figure 5. Therefore, we can exclude topological defects such as pinholes or voids as cause. We emphasize that the amount to which the performance changes and electronic defects are activated and annihilated at the nanoscale, even at moderate operation temperatures, is remarkable.

4. Discussion

4.1. Statistical analysis

For a quantitative analysis of the temperature-dependent performance variations, all pixels of the maps in figure 3 are added up in histogram-like violin plots in figure 6.

First, we note the above-mentioned trends of decreasing voltage at higher temperatures, and a voltage boost after annealing. However, the slope of the voltage decrease—a convolution of the negative temperature coefficient and the positive annealing effect—is noteworthy: while the LG sample starts at lower voltage than the SG sample in their pristine states, the temperature-induced voltage decrease is less pronounced such that the median performance is comparable at $60^\circ$C, and the LG sample outperforms the SG sample at higher temperatures. As the temperature coefficient is not expected to depend dramatically on the grain size, this suggests that the annealing effect is more pronounced in the LG sample.

A closer look at the high- and low-performing tails provides further insights: in the LG sample, the voltage of the low-performing areas remains fairly constant throughout the entire temperature range, which means that temperature-coefficient and annealing compensate each other there. As a result, the distribution gets narrower towards higher temperatures. This corroborates the argument that low-performance areas profit more from the annealing than the already-good areas. In the SG sample, this effect is far less pronounced. We may speculate
Figure 7 shows the histograms of the normalized x-ray beam induced voltage. They support the key observations of figure 6: upon heating, the distributions get narrower, even though the signal decreases in absolute values (note that the normalized distribution would get wider for constant voltage spread and decreasing signal); this trend is more pronounced in the LG sample. After cooling down, the narrow distribution is maintained to large extent. Most importantly, the low-voltage tail is entirely cut as a result of the annealing: the area with minimum performance generates more than twice the voltage of the area with maximum performance before annealing (see figure 6). The histograms clearly show that not only the narrowing effect is stronger for the LG sample, but the voltage distribution is significantly narrower already in the pristine state. The wider XBIV distribution of the SG sample is indicative of the high degree of local inhomogeneity that is directly related to the small grain size and per se reduces the efficiency [11].

4.2. Spatial resolution

Generally, the spatial resolution of XBIC and XBIV measurements can be limited by any of the four following parameters: (A) step size of the scan; (B) x-ray probe size in the sample; (C) beam-sample interaction radius including the effects of secondary electrons and photons; (D) charge-collection length (approximated by the diffusion length of the minority charge carriers) in the absorber layer.

The beam-sample interaction radius is defined as the radius of a cylinder in the absorber layer, within which 68% (1-sigma) of the total dose in the absorber layer is deposited after considering all secondary photon-electron interactions such as scattering or secondary fluorescence. For this purpose, the dose density in the layer stack has been simulated using a modified version of the Monte-Carlo code Penelope [57]. Then, the interaction radius has been determined from the three-dimensional dose density using the same procedure as for perovskite solar cells in [32]. For the CIGS samples and measurement geometry of this study, the simulations yielded an interaction radius of 160 nm.

Precise values of the minority-carrier diffusion length are not known for the studied devices. However, we can estimate from the performance that the diffusion length should be on the order of the absorber thickness under standard measurement conditions, i.e. 1 to 2 μm at 25 °C. Hence, the diffusion length limits the measurement resolution in these measurements, being significantly larger than the step size, probe size, and interaction radius.

In the temperature series of figure 3, all scan parameters were constant. Most importantly, the step size was constant (200 nm), and the temperature-dependence of the probe size (140 nm) and the interaction radius (160 nm) is negligible, as the involved x-ray energies are more than five orders of magnitude higher than the thermal energy. In contrast, the diffusion length in CIGS decreases substantially at higher temperatures due to
the increased recombination rate, and becomes comparable to the step size. This leads to a temperature-
dependence of the spatial resolution of XBIC and XBIV measurements.

Experimentally, the impact of temperature on the spatial resolution is visible in the XBIV maps in figure 3. The careful reader may have noticed that the maps seem to get sharper with increasing temperature, with the measurement taken at 100 °C being the sharpest. Most clearly, the effect of reduced diffusion length and enhanced resolution at higher temperature can be observed at the following instances of the LG sample:

(i) high performing areas such as left of A2 and between A2 and A3 appear to be smeared out at low temperatures, but show substructures at high temperatures;
(ii) the contrast increases with temperature in areas with small-range performance variations such as between A2 and B;
(iii) recombination-active areas such as A1 appear larger at low temperatures and get locally more constrained as the diffusion length becomes smaller at higher temperatures.

For the quantification of the apparent ‘sharpness’ variation, we have performed a line-wise fast fourier transform (FFT) of the XBIV signal from the uncropped maps shown in figure 3 after their stretching to their respective min-max values. Figure 8 shows the result of the FFT, averaged over all lines in the maps. The key outcome of this FFT analysis is the amplitude increase with temperature at high spatial frequencies, which is a measure of the pixel-to-pixel variation and as such of the spatial resolution of the measurement.

This analysis provides experimental evidence for the spatial resolution of XBIC, XBIV, and XEOL not necessarily being limited by the probe size, and demonstrates that fundamentally higher spatial resolution can be achieved in devices with shorter diffusion length.

4.3. Outlook

The left panel of figure 9 shows the XBIC signal of the same area of the SG sample as in figure 3. The right panel shows the correlation of the XBIC and the XBIV signal as a 2D histogram and a fit of the corresponding scatter plot. Note that the standard deviation of the slope is only 2.5%. Following the argumentation of [22, 29], this indicates that the XBIC and XBIV variations are caused by recombination (or absorber thickness variations, which we can exclude here by the XRF measurements), and excludes bandgap variations as cause. Therefore, the recombination-sensitive XBIC and XBIV signal may be interpreted in this study as a measure of the charge-collection efficiency.

For the map in figure 9, we have evaluated the XBIC signal under conditions that involve all elements of outdoor operation conditions, combining a typical operating temperature (60 °C) with the application of forward bias voltage (100 mV) and bias light (on the order of 0.1 W m⁻²). Under actual outdoor operating conditions

10 In both figure 3 and figure 8, the effect of increasing sharpness at elevated temperatures seems to be more pronounced in the LG sample than in the SG sample. While we cannot exclude that this is caused by the smaller temperature range covered in the SG sample, the different grain size offers an alternative explanation that is compatible with the experimental data: due to the higher recombination rate at defect-decorated grain boundaries compared to the grain cores, the diffusion length in the SG sample may be smaller than in the LG sample, which would increase the spatial resolution of XBIV and XBIC in the SG sample already at lower temperatures.

11 A FFT of the 2D XBIV maps was performed (not shown), in addition to the 1D analysis shown here. However, the 2D FFT is too sensitive to slight offsets in vertical direction from motor irreproducibilities that mask other effects. By analyzing only the horizontal components, this measurement artifact is mitigated. The stretching is necessary, as the relative pixel-to-pixel variation decreases with increasing temperature due to the narrower distribution. This would lead to a reduction of the entire FFT curve, making it insensitive to the high-frequency change. For higher statistics, the FFT analysis was performed on the uncropped data.
conditions, the forward voltage and the light intensity are higher; for instance, at maximum power point (MPP),
the voltage is on the order of 500 mV, and bias light should add up to 1000 W m$^{-2}$ with the spectrum AM1.5g.
Therefore, the direct current in the solar cells is under outdoor conditions substantially higher than under the
conditions of figure 9, such that the small modulated XBIC signal on top of it would vanish in the noise.

This combined in situ and operando experiment shows exemplarily the flux limitation at state-of-the-art
synchrotron beamlines today. However, several 4th generation synchrotrons that are based on a multi-bend
achromat lattice will be seeing light within the next few years [58–61]. Compared to 3rd generation
synchrotrons, the brilliance will be boosted by ~2 orders of magnitude, which directly translates into increased
focused photon flux at nanoprobe endstations. This will enable entirely new experiments at time and length
scales that have not been accessible so far. For example, such studies can cover larger areas and larger amounts of
samples in the future, and the nanoscopic charge-collection efficiency can be evaluated by XBIC under actual
operating conditions. Beyond that, the mapping of full current–voltage curves under different conditions is
within reach, which will yield parameters such as the saturation current density ($J_0$) or the ideality factor ($n$) at
unparalleled spatial resolution.

5. Conclusions

Based on multi-modal scanning x-ray microscopy, we have studied the performance variations in two types of
CIGS solar cells with different grain sizes upon annealing. For both types, we have observed a lower performance
at higher temperatures, which is in agreement with the generally expected higher recombination activity. Also,
the observed performance increase induced by the first annealing after synthesis is widely known.

For the first time, however, we have directly observed the creation and annihilation of defects in industrial
CIGS solar cells at the intrinsic resolution limit of the diffusion length. Hereby, we have identified a type of
highly recombination-active electronic defect that is related to low Cu concentration. Both on the level of
individual defects as well as by statistical means, poor performance has been shown to be correlated with low Cu
concentration. Note that we have not found any correlation between the nanoscopic performance and the Ga
concentration despite the greater sensitivity of these measurements to Ga, which excludes topological variation
or voids as the cause. Rather, this suggests a Cu-poor phase being responsible for the recombination activity in
large-grain CIGS grown at elevated temperature.

By demonstrating the combination of operando with in situ measurements of the XBIC signal with applied
bias voltage and bias light at outdoor operating temperatures, we have laid out a path towards nanoscopic
performance mapping under actual operating conditions. Such measurements will be enabled by nanoprobe
endstations at 4th generation synchrotrons.

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