INTRODUCTION

The pentenary absorber material CZTSSe gained attention in recent years as a possible indium- and gallium-free substitute for Cu(In,Ga)Se2 (CIGS) in photovoltaic applications. The conversion efficiency of a thin film device based on a hydrazine-based liquid process was reported to be 12.6%.\(^{1}\) By using the monograin technology it is possible to utilize this absorber material in a cost effective industrial roll-to-roll process.\(^{2}\) Efficiencies of up to 9.5%\(^{3}\) of CZTSSe monograin layer (MGL) devices with an approximate active area ratio (AAR) of about 80% were certified. The evaluation of the AAR was described in details in a previous paper.\(^{4}\) The conversion efficiency of the active CTZSSe material is in the range of 12% which is comparable to the record efficiencies measured for thin film devices. As demonstrated in the Supporting Information the record cell is of remarkable photocurrent homogeneity within ±3%.

Despite the beneficial properties such as a direct tunable bandgap, high absorption coefficient and low temperature coefficient,\(^{5-7}\) the efficiency of photovoltaic applications with CZTSSe as absorber is still considerably smaller than
the record efficiency of CIGS, which was reported to be 22.6%. Several possible reasons for a reduction of device performance parameters such as open circuit voltage ($V_{oc}$) and short circuit current density ($j_{sc}$) of CZTSSe compared to CIGS thin film photovoltaic devices were reported in the literature and summarized by Aninat et al. To tackle performance reducing effects in CZTSSe MGL devices we combined several opto-electrical analyzing methods such as light beam induced current (LBIC) mapping, scanning electron microscopy (SEM), photoluminescence (PL), electroluminescence (EL), and transmission measurements.

First results of LBIC analysis on the here investigated devices have been published in a recent paper, in which a statistical analysis was developed allowing to analyse the active and inactive areas. Additionally an inhomogeneous current density distribution had been observed. To evaluate the reason for these inhomogeneities and performance reducing effects we extended the investigation by including additional analysis methods. Using these techniques several suspected parameters such as locally different reflection or transmission of the layers on top of CZTSSe as well as resistance differences can be eliminated as a cause for major performance differences in MGL devices. Instead variations in the $p$-$n$-heterojunction barrier height can be identified as causing these variations.

### EXPERIMENTAL

CZTSSe monograins are synthesized from copper, zinc sulfide, zinc selenide, tin, and sulfur precursors in potassium iodine (KI) as flux material as described in detail in previous papers. After the synthesis of the CZTSSe monocrystals a washing procedure with water removes the KI, after which the powder is dried and sieved to obtain powders of desired grain sizes. This is followed by a heat treatment step at 740°C and the deposition of cadmium sulfide (CdS) by chemical bath deposition employing cadmium acetate as cadmium source and thiourea as sulfur source in an ammonia solution. A more detailed description of the synthesis and post treatment processes of CZTSSe monograins can be found elsewhere. By partial embedding monograins in a thin layer of polymer a so called MGL is formed. The front contact is established by sputtering a transparent conductive oxide (TCO) layer (intrinsic and aluminum doped zinc oxide). The conductivity of the TCO is enhanced by applying a thin layer of silver nanowires and a current collector made by silver paste allows the establishment of a reliable contact for electrical measurements. By gluing the MGL with transparent polymer on soda lime glass the front side is sealed. For establishing back contacts the samples are dipped into concentrated sulfuric acid to etch the surface of the embedding polymer on the backside which makes the monograins in the MGL easily accessible, followed by an abrasion process by sand paper to open the monograins. By pasting graphite onto the abraded backside Ohmic back contacts are established. SEM images of single grains after applying a graphite layer embedded in polymer and a cross-section of a finished device can be found elsewhere.

The LBIC, EL-spectra and PL-spectra investigations are conducted by means of a Horiba Jobin Yvon Labram HR800 instrument, Horiba Ltd, Kyoto, Japan. As excitation source a red (633 nm) laser is used for the LBIC measurements and a green (532 nm) laser for the PL measurements respectively. The intensity of the excitation laser is adjusted by neutral gray filters, which reduces the light intensity to around 0.013 and 0.08 μW for the LBIC and to 2.8 mW for the PL measurements. The illuminated area is evaluated to be around 20 μm$^2$. The LBIC current is measured by means of a lock-in amplifier and a scanning rate of around 10 measurement points per second is used. The exposure time during EL and PL measurements is 30 and 3 seconds respectively. The wavelength dependent transmission analysis of a monograin monolayer and the corresponding polymer layer is conducted by a Newport Oriel 300W Xenon lamp with a Cornerstone 260 Monochromator, silicon detector and a Merlin radiometer system, all from Newport Corporation, Stratford, CT. A Nikon SMZ 260 Monochromator, silicon detector and a Merlin radiometer system, all from Newport Corporation, Tokyo, Japan, is used for transmission imaging. EL imaging is conducted by means of an Andor iKon M camera, Oxford Instruments plc, Abingdon, UK.

### RESULTS AND DISCUSSION

#### 3.1 Performance related differences between CZTSSe MGL devices

The electrical performance parameters derived from $j/V$-measurements at standard test conditions of low efficiency (2%-6%) MGL samples as already investigated in Ref. [4]
show considerably different values. This is most prominent seen in the short circuit current density, but also variations in open circuit voltages and fill factors are clearly noticeable (Figure 1). Attributed to the high differences in $j_{sc}$ and the semitransparency of the MGLs, initially a difference in the active area as well as optical effects have been suspected as the major cause for the high variability of the parameters of the samples. The semitransparency of the MGLs can be seen in Figure 2, where the transmission of an empty polymer layer before the application of CZTSSe grains as well as an MGL sample is displayed. While the transmission of the polymer is independent of the wavelength and reduced to around 95% by reflection and absorption, the MGL sample shows a transmission of around 13%-14% in the short wavelength range up to the optical bandgap. This optical bandgap is, as extracted by using the tilted dashed line, at around 880 nm (1.41 eV), which corresponds to the peak positions of the PL spectra shown below. The active area of the MGL samples is further reduced by electrically fully or partially inactive grains. By superposition of SEM and LBIC images (Figure 3B) and transmission and LBIC images (Figure 3C) respectively, such inactive CZTSSe areas are identified. Grains without back contact due to insufficient abrasion of the backside of the sample are visible in the transmission image as well as in the SEM image, however, they do not show an LBIC response. An example for such a grain is given in Figure 3 indicated by the solid circle. However, a grain can also be just partially inactive when the corresponding area is covered by electrically insulating but optically transparent polymer, which prevents an electric front contact on this area. This part of a grain is seen in the transmission image, but it is not visible in the LBIC and SEM images. Such an inactive part of a grain is (as an example) indicated by the dashed circle in Figure 3. Such inactive absorber areas explain the difference between the optical transmission and the active area measured by LBIC, however, as it was shown previously, the electrical active area presented as the AAR does not explain the high difference in electrical performance parameters. Partially lower and inhomogeneous current values from the LBIC evaluation can be seen best in the homogeneity plot (current density distribution) of Figure 4, where sample 1 shows a high number of measurement points at a relatively narrow current range with high current values, while the majority of the measurement points of sample 2a and sample 2b are distributed in a wider current range with lower current values. The full width at half maximum in homogeneity plots for samples 1, 2a, and 2b can be extracted to be 0.46, 0.65, and 0.62 nA which represents a standard deviation of 6%, 20%, and 25% respectively. These homogeneity differences and their origin are investigated in more detail hereafter.

3.2 | Opto-electrical homogeneity investigations

Measurements of the same area of sample 2b by LBIC and EL imaging show that the vast majority of grains show an inverse correlation between the response intensities of these two analyzing methods, where grains with high LBIC response show low EL response and vice versa. In Figure 5 this correlation is seen, with two grains selected and

![Figure 2](image2.png)

**FIGURE 2** Transmission measurements of a monograin layer (MGL) sample and of an empty polymer layer. The tilted dashed vertical line indicates the bandgap.

![Figure 3](image3.png)

**FIGURE 3** Light beam induced current (LBIC) (A), superposition of LBIC and SEM image (B), and LBIC and transmission image (C) of an excerpt of sample 2b. The solid circle indicates an inactive grain without back contact, the dashed circle a part of a grain which is inactive due to missing front contact.
indicated by dashed circles as examples. These two grains were furthermore investigated by EL and PL spectra measurements (Figure 6). The rather broad and partially dissymmetrical peaks indicate the presence of different emission energies. Furthermore, the EL spectra show a clear shift of the peaks to lower energies compared to the PL spectra. It was reported already that disordering of CZTS Kesterites can lead to different emission energies and a peak shift of the PL spectrum toward lower energies.\textsuperscript{11,12} However, both investigated grains show similar peak positions of the PL spectra and the EL spectra, respectively, can be attributed to these different intensities. For PL measurements such intensity-dependent peak shifts were already reported before.\textsuperscript{12,13} The peak height of the EL spectra of grains A and B correspond well with the EL response intensity of the EL image as expected, and they also show a similar trend as the peak height of the PL spectra.

Some grains show distinctive patterns in both imaging methods (Figure 7). In Figure 7A a SEM image shows a grain with different oriented planes. These planes can also be identified by EL imaging (Figure 7B) and LBIC imaging (Figure 7C,D). Despite that the EL and LBIC images of the grain show a similar pattern, the response intensity is inversely correlated as it was already observed previously in Figure 5. It has to be noted that the LBIC measurements in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Homogeneity plot (current density distribution) of the light beam induced current response of samples 1, 2a, and 2b. The filled markers correspond to measurement points on the active area of the grains, while empty markers correspond to measurement points of the inactive area with the current being generated in the surrounding grains by reflected light.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Light beam induced current (LBIC) (A) and electroluminescence (EL) (B) image of sample 2b. Photoluminescence and EL spectra of specific grains indicated by dashed circles are seen in Figure 6.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Photoluminescence (PL) and electroluminescence (EL) spectra measurements of grains of sample 2b indicated by dashed circles in Figure 5.}
\end{figure}
Figure 7 were conducted with higher excitation laser intensity than in Figure 5. The different laser intensities can be found in the experimental part. Accordingly the absolute current signals in these figures are different.

Since different light reflection at differently oriented crystal planes was suspected as one reason for spatial current and luminescence variations, the angle of incidence on three planes with different orientations toward the light beam was changed. Tilting the sample during LBIC measurements by around 18° and thus changing the incident angle of the excitation beam (Figure 7D) did not result in a major change of the LBIC results compared to the LBIC image with the laser beam perpendicular to the sample (Figure 7C), which ensures that there is no major influence of the angle of incidence on the measurement results. The measurement response differences are not due to possible occurring reflection differences from the correlated planes.

Electroluminescence and PL spectra measurements (Figure 8) on three different planes of the grain as indicated by the dashed circles in Figure 7A show the same correlation between EL and PL spectra as in Figure 6, where the measurements were conducted on different grains. Thus, we conclude that the mechanism responsible for the differences in LBIC, EL, and PL response is the same, whether it appears on single grains or on different areas of grains.

Locally different resistances, either from the semiconductor material or the electrical contacts on the front and
backside can lead to a change of LBIC, EL and PL results. A local high resistance would limit the charge carrier extraction, hence a lower LBIC and higher PL response can be expected, which is in accordance with the observed results. However, a higher resistance would also limit the current flow to this area during EL measurements with an according lower EL response. Also local optical variances, eg, due to differences in transmission of the sealing material or the contact materials on the front side of the device, could also lead to a reduction of the excitation and thereby the measured emission intensity, and therefore to a reduction in LBIC, PL, and EL response. However, the images clearly show that the LBIC response is for all grains or crystal planes clearly inversely correlated with the PL and EL response (low LBIC response in all cases correlates with high PL and EL response and vice versa). Therefore, local optical or electrical variances cannot be the main reason for the opposite responses of LBIC and EL or PL signals.

The results that the photocurrent image measured by LBIC corresponds inversely to the image of the EL and PL intensities can easily be understood assuming variations in the barrier height of the \( p-n \)-heterojunction. We propose that grains or areas of grains with high LBIC response but low EL and PL response have a good \( p-n \)-heterojunction and thus a high barrier. Here, the charge carriers generated by illumination are separated efficiently and in a wide depletion region leading to a high LBIC response. At the same time the effective charge carrier separation leads to a decreased radiative recombination in PL measurements and thus in a lower PL response. If, on the other hand, grains or areas of grains have a considerably smaller barrier, charge carriers during LBIC and PL measurements are insufficiently separated, which leads to a lower carrier extraction during LBIC measurements and thus lower LBIC response and a high radiative recombination at the illuminated area of the PL measurement resulting in a high PL response. However, when conducting EL imaging and spectra measurements, the same voltage is applied to all electrically connected grains. The current flow over the \( p-n \)-junction barrier is controlled by the barrier height. A higher current flows over the lower barriers and consequently a higher EL response is seen for low barrier heights and lower current and EL response for higher barrier heights respectively. This mechanism explains the inhomogeneous photocurrent, PL and EL response, with the EL and PL intensities being inversely correlated to the LBIC response intensities. We therefore conclude that this variation in the barrier heights of different samples is the main factor for the differences in the observed current/voltage behavior.

Different overall barrier heights can also be seen when integrating the EL spectra measured for increasing applied voltages on different grains, as analyzed in Figure 9. The EL response for grain A in Figures 5 and 6 (high LBIC, low EL and PL response and therefore relatively high barrier) is increasing only slowly and nonlinear with increasing voltage, while the EL response for grain B in Figures 5 and 6 (low LBIC, high EL and PL response, low barrier) increases much faster and nearly linear with increasing voltage. Whereas the former is controlled by a (small) current across a barrier, while the higher current leading to luminescence at lower barriers is already controlled by an (Ohmic) resistance in the device. This supports the proposed mechanism above.

4 | CONCLUSIONS

Different opto-electrical investigation techniques such as LBIC, optical transmission, SEM, \( j/V \), EL imaging, EL and PL spectra measurements are used to characterize spatial variations in the solar cells made from monograin powder devices. Areas of relative to other areas high photocurrent show relatively low photo- and electro-luminescence. This is especially pronounced for cells with relatively low (here 2%-6%) solar efficiency. A detailed statistical analysis of the images reveals a variation of between ±6% and 25% of the
average current density. Areas with a high LBIC response and a low EL and PL response can be attributed to forming a high junction barrier, while areas with low LBIC response and high EL and PL response are those with a relatively low barrier junction. It is evident that the combination of complimentary investigation methods as it was presented in this paper is crucial for a correct understanding and interpretation of measurement results done on this material. For comparison a “good” CZTSSe solar cell with a cell efficiency of 9.5% and a material (or active-area) efficiency of about 12% shows a current variation of only ±3%.

Corresponding investigations should also be performed on thin-film and wafer-based solar cells and allow to extract reliable data for the homogeneity (given in % of the average photocurrent) as well as a deeper understanding of the reason for performance variations.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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