Grain Engineering: How Nanoscale Inhomogeneities Can Control Charge Collection in Solar Cells

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Abstract

Statistical and correlative analysis are increasingly important in the design and study of new materials, from semiconductors to metals. Non-destructive measurement techniques, with high spatial resolution, capable of correlating composition and/or structure with device properties, are few and far between. For the case of polycrystalline and inhomogeneous materials, the added challenge is that nanoscale resolution is in general not compatible with the large sampling areas necessary to have a statistical representation of the specimen under study. For the study of grain cores and grain boundaries in polycrystalline solar absorbers this is of particular importance since their dissimilar behavior and variability throughout the samples makes it difficult to draw conclusions and ultimately optimize the material. In this study, we present a nanoscale in-operando approach based on the multimodal utilization of synchrotron nano x-ray fluorescence and x-ray beam induced current collected for grain core and grain boundary areas and correlated pixel-by-pixel in fully operational $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ solar cells. We observe that low gallium cells have grain boundaries that over perform compared to the grain cores and high gallium cells have boundaries that under perform. These results demonstrate how nanoscale correlative X-ray microscopy can guide research pathways towards grain engineering low cost, high efficiency solar cells.

Keywords: CIGS, Grain Boundaries, Solar Cells, Synchrotron, XRF, XBIC

1. Introduction

What makes polycrystalline (PC) absorbers interesting for large scale deployment solar modules? Growth processes for PC solar cells, are generally faster, cheaper, and less energy intensive, leading to a reduced energy payback time for the final module.[1] The interest in PC solar cells is observed very clearly in the photovoltaic market, where 76% Of the ~ 57 GWp of modules manufactured globally in 2015, came from polycrystalline silicon and thin film solar cells.[2] Lower cost is also driving research of PC growth methods for III-V materials, which are typically grown as single crystals.[3]

While the cost is lower, PC materials have unique challenges when it comes to optimization and tuning of the desired properties. Due to the large variability in chemical, structural and electrical properties of both grain cores and grain boundaries, the path to optimization is not always clear. Measurement techniques having the resolution and sensitivity needed to quantify this variability have an inherent trade off between spatial resolution and area under study. Moreover, the specimens under study are very small fractions of a device and operando measurements of the devices are not possible. We propose to use synchrotron based x-ray microscopy and a suite of techniques based on the collection of electrical response from the x-ray excited area that can help circumvent this limitation. X-ray based tech-

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niques are non-destructive and have a large penetration depth of several micrometers, which allows for the measurement of completed solar cell devices. Details on current state of the art nanoscale x-ray imaging and the x-ray beam induced current technique can be found elsewhere.[4, 5, 6, 7, 8, 9] Synchrotron measurements provides a benefit over electron microscopy based techniques which are limited in penetration depth to a few hundred nanometers and can require extensive sample preparation in the case of transmission electron microscopy. Additionally due to the small penetration depth, electron beam induced current is much more sensitive to junction quality, surfaces, and interfaces rather than bulk properties.[10]

Grain boundaries are typically regions of high recombination, due an increased defect density, including dangling bonds, point defects, dislocations, and impurities. These effects can be mitigated, for example, by the addition of Na in $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ (CIGS).[11] Internal gettering has improved some grain boundaries in polycrystalline silicon by reducing the dislocation density, and clustering small metal precipitates across a large area into larger precipitates in isolated regions.[12] However, the potential of grain boundaries in solar cells is underestimated by only mitigating their negative impact. In fact, grain boundaries can even outperform crystalline regions, and the overall solar cell performance can be dramatically improved by clever engineering of high-performance grain boundaries.

In this work we will present our operando approach using polycrystalline $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ (CIGS) thin films as the specimen of study. The performance of these films is well known to be driven by electrical and compositional inhomogeneities. [13, 14, 15] Furthermore, the plethora of reports arguing dissimilar trends makes the case for the need of a statistical approach, which is one of the main points of our study. Studies of copper variations at grain boundaries in $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ have reported copper concentration at grain boundaries to increase [16, 17], decrease [18, 19], and remain constant[20, 21], relative to the grain core. While the observations of copper concentration at grain boundaries vary between reports, it is typically argued that grain boundaries are not detrimental to local current collection. [22, 23, 24]

In this work we couple the use of nano x-ray fluorescence (XRF) with nano x-ray beam induced

Figure 1: Overview of beamline setup and measurement capabilities for XRF and XBIC, capable of collecting composition and charge carrier collection efficiency simultaneously with high spatial resolution.

current (XBIC), spatially resolved and measured simultaneously, to study the correlation between compositional inhomogeneities and electrical properties with nanoscale resolution. A schematic of the experimental set up is shown in Figure 1. Given that the XBIC and XRF signals are excited by the same nanoprobe x-ray beam, we are able to report for the first time a spot-to-spot correlation between electronic and compositional properties. In the following sections, we demonstrate the powerful nature of these correlative measurements while we apply it to two completed $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ devices with low and high average gallium contents - bandgap tracks linearly with Ga content in $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ devices. Higher gallium content films are of interest for tandem devices, however films with higher GGI values of >0.4 tend to have a lower efficiency which has been attributed to a nonlinear increase in open-circuit voltage with increasing bandgap.[25] The statistical meaningfulness of this technique allows to explain the large variations reported in literature and even more important show a clear trend of the differences between GB and GC, opening the door to future optimizations.

Figure 2: (A) XRF image of the sum of the Cu and Ga channels. Indium was not used to reduce the noise in the image. The dashed black lines over the image are the result of the watershed image processing technique. (B) A backscattered electron image of the same location measured by XRF. A watershed is overlaid on each of the images confirming its identification of grains and grain boundaries (C,D) The isolation of grain boundaries and grain interiors as related to the watershed image.

2. Methods

CIGS devices with average $[\text{Ga}]/[\text{Ga}+\text{In}]$ (GGI) values of 0.3 and 0.6 were grown at the National Renewable Energy Laboratory, using a 3-stage co-evaporation.[26] The device structure is comparable to that shown in Figure 1, with a 200 nm ZnO layer, 50 nm CdS, 1.8 μm CIGS, 700 nm Mo, grown on a 1.6 mm soda lime glass substrate. Because typical CIGS grain sizes are 1-2 μm , CIGS layers were grown slightly thinner than the typical 2-3 μm to ensure a single layer of columnar grains. Final device solar energy conversion efficiencies were 18% and 14% for GGI = 0.3 and GGI = 0.6 respectively.

Samples were measured at the hard x-ray nanoprobe beam line at the Advanced Photon Source.[27] The angle between the beam and detector was fixed at 90° and the sample was tilted to 75° from the sample surface to the incident beam. We chose a beam energy of 10.5 keV, just above the Ga absorption K-edge, for the highest cation sensitivity; Se, requiring higher beam energy, was not measured but is of limited interest for this study. Preliminary studies have shown that its concentration varies little and has less impact on the solar cell performance than the cations. Zone plates with

180 μm diameter and 50 nm outer zone width were used giving a 60 nm beam full width at half maximum (FWHM) and a depth of focus of 52 μm .

The collected XRF spectra were fitted using the MAPS software developed at APS [28, 29] and quantified using a thin film standard of known composition produced by AXO Dresden. We corrected the data for surface roughness, losses due to beam and fluorescence attenuation, and depth dependent compositional variations due to gallium grading following the steps described elsewhere.[30] XBIC data were converted to x-ray collection efficiency (XCE) by dividing the total number of carriers collected by the total number of carriers generated. The carrier generation was estimated based on the incident photon flux, the percent of photons absorbed in the material, and the ionization energy of the material. Due to uncertainty in the estimation of the incident photon flux, the maximum of the data set was scaled to 100 % XCE for ease of comparison.

Grain boundary regions were isolated from grain core regions using a watershed analysis.[31] Grain cores were regions identified as 400 nm away from a grain boundary, to account for the tilt of the sample during the measurement. Figure 2A shows an XRF map of the CIGS layer and a corresponding SEM Backscattered electron image of the same region (Figure 2B). The watershed analysis was conducted using the XRF map and then overlaid on the SEM image. Since XRF is not a structural measurement, an alternative method is needed to validate the watershed. The good agreement between the two images confirms that grain boundaries were properly identified.[32] Figure 2C and D show the resulting image after separation of grain boundary and grain core regions respectively.

3. Results

Figure 3 shows the Copper, Gallium and Indium XRF channels of a CIGS device side by side to the x-ray collection efficiency map (from XBIC) and the calculated GGI and $[\text{Cu}]/[\text{Ga}+\text{In}]$ (CGI) ratios. The black lines in the figure delineate the position of the grain boundaries, defining in this case three different grains with very different composition and electrical behavior. It can be seen that the top left grain core has a higher gallium and copper concentration compared to the neighboring grains, as well as a higher GGI and CGI. Throughout the map indium anti-correlates with copper and gallium, something

Figure 3: Typical XRF/XBIC maps of the Cu, Ga, In channels and the elemental ratios GGI and CGI. Atomic percent, refers to the cation (Cu,Ga,In) percentage as Se was not detected. Each map is $2 \times 2 \mu\text{m}^2$ with 50 nm step size.

we observed in multiple scans. The indium and gallium anti-correlation is expected since they are substitutional in the CIGS matrix. Even though this technique does not provide atomic resolution the indium-copper anti-correlation could point to the generation of Cu_{In}'' acceptor or $\text{In}_{\text{Cu}}\cdot$ donor anti-site defects. It can be seen that regions with higher Cu and Ga (lower In) content have higher XCE than regions with lower Cu and Ga concentration. Composition does not seem to be the only source of variations in XCE as can be noted from the bright triangular-shaped region in the current collection map that does seem to have a counterpart in the composition maps. In this map Ga rich and In poor boundaries are able to be detected. Similar maps to 3 were collected in multiple spots on both low and high gallium CIGS samples. Over 1000 data points were acquired for grain cores and grain boundaries in these samples and most of the data treatment described hereafter is highly statistical in nature.

Figure 4 shows the distribution of the composition and charge carrier collection efficiency measured at grains and grain boundaries for both low and high GGI absorber layers. For low GGI (Figure 4 A-F), there is a noticeable change in the composition between the grain boundaries and grain cores. The compositions measured follow a normal distribution, with similar standard deviations at GBs and GCs, and shifts observed in the mean. The average copper content across all boundaries is observed to be 0.5 ± 0.05 at.% higher than the grain cores. An increase in gallium (0.65 ± 0.03 at.%) and decrease in indium (-1.1 ± 0.08 at.%) was observed as well at boundaries with respect to cores. Similar trends were observed for the CGI and GGI elemental ratios. The average CGI increased from grain cores to grain boundaries by 1.5 ± 0.2 % and GGI increased by 1.4 ± 0.08 %. The uncertainty was calculated as the standard error with 95% confidence. These values are smaller than other composition variations reported due to the relatively large beam spot size compared to grain boundary area. Further information on the impact of beam spot size can be found in the supplemental information, Figure S1. The XCE also shows a 1.6 ± 0.3 % increase from grain cores to grain boundaries indicating improved charge transport at grain boundaries.

For high GGI (Figure 4 G-L) absorber layers, the change in composition between GC and GB is smaller than the change observed for low GGI. A negligible change in copper concentration from GC

Figure 4: (A-L) Shows the distribution of Copper, Gallium, Indium, CGI, GGI concentration, and XCE for 30% and 60% Gallium Samples between grains and grain boundaries. The histograms show the distribution of composition measured at each region and the solid line is a fit to a normal distribution. The data point next to the distribution represents the mean $\pm$ the standard error with 95 % confidence. The non-normal distributions seen in the collection efficiency are acknowledged by a dashed curve rather than solid line.

to GB (0.19 ± 0.04 at. %) was observed, near the detection limits for this measurement. A slight increase in CGI 0.69 ± 0.13 at. % approximately half that of the low GGI film. A larger change was observed for gallium (0.55 ± 0.03) and indium (-0.7 ± 0.06) as well as a positive change in GGI (1.2 ± 0.1 at. %). The largest change for this sample was observed in the XCE with a decrease of 8.0 ± 0.3 % from GC to GB. The non-Gaussian distribution of the grain core XCE should be noted. This is likely due to the large variation observed in collection between large and small grains. Because the data is represented on a pixel by pixel basis the larger grains with a higher XCE are weighed more heavily. A table listing the values depicted in Figure 4, can be found in the supplemental information Table S1.

We plotted the copper, gallium and indium concentrations and elemental ratios against the measured XCE, on a pixel by pixel basis, for all grain cores and grain boundaries. The data was fit to a line and the slopes were extracted, representing the change in atomic percentage with respect to the change in collection efficiency. Large values for slope indicate that for a large change in composition a smaller change in collection efficiency is observed. Similarly, smaller slopes indicate a higher dependence of collection efficiency on composition. However due to the wide distribution of composition values, there is a minimum threshold above which a correlation can be detected. This threshold was determined as the standard deviation of the composition divided by the maximum change in collection efficiency.

An example of this is shown in the subset of Figure 5. An analysis of the residuals of the fit can be found in the supplemental information Figure S2. The results are shown in Figure 5 with the height of the bar correlating to the magnitude of the slope extracted from the scatter plot and the uncertainty is represented as the standard error of the slope with 95 % confidence. Slopes that fall below the minimum threshold are shown without color.

For low GGI absorbers, we observe that Cu and Ga correlate positively with collection efficiency and In correlates negatively. XCE seems to be more dependent on gallium concentration, compared to copper and indium, due to the smaller slope. Both CGI and GGI correlate positively with collection efficiency, indicating that increasing the GGI and CGI at both grain boundaries and grain cores in low GGI CIGS will lead to improved charge

Figure 5: Shows the values of slope, correlating composition and elemental ratios charge collection, at different regions, for both low and high GGI CIGS. High slopes indicate a small change in XCE for large composition variations. A low slope indicates small change in composition has a large impact on collection efficiency. The error bars represent the standard error associated with the slope with 95 % confidence. Bars shown without color fall below the detection limit for this analysis. The inset shows a scatter plot of each pixel in a Cu and In XRF map plotted against XCE.

carrier collection. The XCE is more sensitive to changes in CGI and GGI at grain boundaries than the grain cores, indicating a potential area for improvement.

Collection efficiency at grain boundaries in the high gallium absorber exhibit is largely independent of composition, or below the detection limits of this analysis. The grain cores show a unique behavior with CGI showing a strong positive correlation with XCE, and largely independent of indium and gallium concentration. This suggests that, although the change in copper concentration between grain boundaries and grain cores is small, increasing the CGI at grain cores will lead to increased carrier collection.

4. Discussion

We have shown that sub-nanometer spatial resolution is not required to detect composition variations at grain boundaries in CIGS, as previously reported.[16] However high sensitivity is required to detect the compositional variations. The high flux of synchrotron light sources, combined with meaningful statistics from measuring multiple spots, yields improved sensitivity to elemental variations. For a single measurement of one pixel we are sensitive to ~ 1 at. % variation in composition. However when comparing data for over 1000 pixels (at 10.4 keV) our sensitivity approaches ± 0.13 % for Cu, ± 0.19 % for Ga, ± 0.24 % for In, ± 0.18 % for CGI, and ± 0.23 % for GGI, which is below the

range of values reported in this work for low gallium absorbers. Our analysis of the variation in the overall copper content in high gallium absorbers could be limited by this sensitivity. By having high statistics, we are able to detect composition variations much smaller than the FWHM of the beam. As mentioned previously the large size of the beam relative to length scale of composition variations around grain boundaries, is the reason the values reported here are smaller than those reported in other works.

Our results show a similar Cu and In anti-correlation as reported by [17, 16] and clarifies the average behavior of low and high gallium absorbers across multiple boundaries and show that it is not just Cu and In that segregate at boundaries but the CGI and GGI as well. Given the exhibited Cu and In anti-correlation and the increase in GGI at the boundaries., one could imagine that there is an increase of Cu-In antisites at grain boundaries similar to that suggested by others.[19, 16]

Copper, while shown to be highly mobile in CIS appears to be less mobile in higher gallium CIGS because of the much smaller variation in concentration at grains and grain boundaries, within the detection limits of the measurement.[33] This could be due to the increased stability of the chalcopyrite phase with increasing gallium content.[34]

The increased gallium content observed at the grain boundaries for both low and high GGI films could explained by the preferential coordination numbers of In and Ga. It has been shown in chalcogenide glasses that indium prefers to have a fixed

coordinated with oxygen while gallium can assume a range of coordinations.[35, 36] This could explain why gallium tends to segregate towards grain boundaries during growth, where the coordination environment is varied. This allows for indium to sit in the indium higher coordinated grain core.

Additionally, the variations in the predicted bandgap based on GGI from XRF data are ~ 20 meV which aligns well with PL data measured on the same samples and previously reported values.[37] The good agreement between composition and PL shown in Figure S3 and Figure S4, allows us to correlate composition variations with bandgap fluctuations. The likely cause for the increased collection at grain boundaries in low gallium CIGS is the composition induced electron barrier from an increased GGI and the potential well for holes created by an increased CGI. The decrease in collection at grain boundaries in high gallium absorbers is likely due to the barrier created for electrons by an increased GGI and the 50% smaller hole potential well. The GC collection efficiency for low GGI absorbers could be improved by decreasing this offset,(ie: increasing the CGI and GGI). This behavior would also explain why the performance of low gallium CIGS is largely independent of grain size.

To improve the collection efficiency of high Gallium CIGS, increasing the CGI at grain cores could promote collection there. Because the collection at grain boundaries is largely independent of composition, the grain cores are regions that should be focused on. Additionally, increasing the average grain size could boost collection efficiency as well to limit the impact of grain boundaries. Due to the apparent lower Cu mobility in high gallium CIGS, adapting growth conditions to enhance copper segregation could be beneficial. Extending the second (copper poor) stage of the co-evaporation process with a long hold at a fixed temperature or decreasing the temperature to enter the mixed phase regime, could improve elemental segregation as well. These processing steps could result in better passivated grain boundaries and increase collection efficiency. Having a higher copper concentration at the grain cores than the grain boundaries would repel holes, electrically passivating the boundaries and improving current collection in the grain cores.

Lastly, the decreased XCE determined at grain boundaries for high gallium CIGS could be the source for reduced V_{oc} in these devices. Because V_{oc} and recombination are highly correlated, a re-

duced XCE caused by higher recombination can be correlated to a decrease in voltage as well. It is important to emphasize however, that XCE is a current measurement.

5. Conclusions

By modifying the growth conditions of high gallium CIGS absorbers, and promoting the beneficial effects of composition inhomogeneities observed in this work, the efficiency deficit of these materials can be reduced, enhancing the potential for higher efficiency single junction cells and tandem devices. We also emphasize that the same approach utilized here can be applied to other material systems to better understand the role of grain boundaries. An important driver for this is, to improve energy conversion efficiency while maintaining low cost. Utilizing highly statistical analyses and correlative measurement techniques are critical on this front. Accounting for variability in grain boundary properties will be a key component of our ability to engineer grain boundaries to improve device performance.

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