Intergrain variations of the chemical and electronic surface structure of polycrystalline Cu(In,Ga)Se₂ thin-film solar cell absorbers

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The μm -scale spatial distribution of the elements of polycrystalline Cu(In_{1-x}Ga_x)Se₂ absorber surfaces is examined using x-ray photoelectron emission microscopy. The chemical composition varies from grain to grain, and a direct, linear anticorrelation between the In 3d and Ga 2p photoemission line intensities is observed. The line intensities are interpreted in terms of a varying value of $x = \text{Ga}/(\text{In} + \text{Ga})$; the band gaps calculated from the inferred compositions of the grains are shown to be normally distributed with a standard deviation of 40 meV. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4751261>]

The expected decrease in production costs promised by emerging thin-film photovoltaic (PV) technologies—e.g., those based on chalcopyrite Cu(In_{1-x}Ga_x)Se₂ (CIGSe) absorbers—has led to great interest in developing such solar cells to supplement or supplant wafer-based PV technologies. On a laboratory scale, CIGSe devices already yield efficiencies ($\approx 20\%$ on $\sim 0.42 \text{ cm}^2$)^{1–3} similar to polycrystalline Si-wafer based cells.¹ A peculiarity of the CIGSe technology is that polycrystalline devices have significantly and reliably higher efficiencies than do single-crystalline equivalents. Numerous experimental and theoretical^{4,5} examinations of the nature and effects of polycrystallinity on the CIGSe device behavior have focused on explaining this unexpected contrast with other photovoltaic technologies. At the same time, the potential limiting factors imposed by polycrystallinity have been discussed in detail^{6–8} in order to gain a better understanding of efficiency-limiting factors and, hence, the theoretical maximum efficiency of polycrystalline CIGSe devices.

Although it has been shown that the grain boundaries can be made to have little or no negative effect on the performance of CIGSe solar cell devices,⁹ some predictions suggest that other aspects of polycrystallinity and alloying of the chalcopyrite absorber materials may lead to efficiencies below the Shockley-Queisser limit of ca. 33%.¹⁰ Differences in the electronic and optical properties of the absorbers on the scale of the grain sizes¹¹ and below^{12,13} have revealed numerous laterally resolved variations that may lead to decreased performance. Here we will focus specifically on variations in the band gap caused by an inhomogeneous composition. Composition-related changes in the band gap have two distinct origins:⁸ direct variation caused by differences in alloying (i.e., dependence of the band gap on

$x = \text{Ga}/(\text{In} + \text{Ga})$ ¹⁴), and indirect strain-induced differences that can arise from local lattice constant variations.^{8,15}

In this letter, we present a study of the spatially resolved chemical and electronic surface structure of high-efficiency polycrystalline CIGSe absorbers.² By mapping the elemental distribution at the surface on the scale of the CIGSe grain size, we are able to deduce the nature and effects of intergrain inhomogeneities of the chemical and, thus, electronic structure and their potential impact on device characterization and performance.

The investigated CIGSe samples were fabricated at NREL. They were prepared by three stage co-evaporation on soda-lime glass (SLG) substrates with sputtered Mo back contacts.² Solar cells made from the absorber layers studied here had measured efficiencies between 17% and 19%. Air exposure was limited prior to measurement, with the samples packed under inert atmosphere for transport to the HZB, stored under ultra-high vacuum (UHV) conditions prior to the experimental campaign at BESSY II, mounted to sample holders in a dry-N₂ glove box, and introduced into the UHV experimental endstation (described below) via a N₂-purged glove bag directly attached to the load lock.

X-ray photoelectron emission microscopy (X-PEEM) measurements were used to map the element distribution of the surface of the polycrystalline CIGSe thin films. The measurements were performed at the UE49-PGMA microfocus beamline at the BESSY II synchrotron facility in Berlin using the SPEEM endstation equipped with an Elmitec PEEM II instrument.¹⁶ The excitation energy of the UE49-PGMA can be continuously varied from 100 eV to 1800 eV. The spot size on the sample is $8 \times 20 \mu\text{m}^2$ (FWHM) at a 16° angle of incidence (measured from sample surface). The X-PEEM images have been recorded with an accelerator voltage

between sample and microscope lens of 10 keV and a field of view (FOV) of 10 μm . The images have been normalized to (i.e., divided by) a brightfield image measured directly before the actual measurements to account for the characteristics of the detector. In order to be able to correct for thermal drifts, a number of images (several 10 up to a few 100) were recorded with relatively short acquisition times (1–10 s/image). The final image was then computed by adding up the individual *drift-corrected* images. Only the center $4 \times 4 \mu\text{m}^2$ sections of the X-PEEM images are used for analysis in this case, in order to minimize the effects of varying illumination and excitation energy over the FOV, as well as distortions near the edges of the images that occur as a result of the drift (and cannot be easily or reliably corrected for).

Element specificity is achieved by tuning the excitation energy and analyzer energy to focus on a particular characteristic photoemission line. The excitation energy was changed such that the kinetic energy of each photoemission line being studied was roughly the same (ca. 120 eV), and so effects such as detector transmission variations and differing electron inelastic mean free paths can be neglected when quantifying the individual spectral contributions. The images presented here are difference images calculated by subtracting an image of the off-resonance photoemission (i.e., the background signal recorded at ca. 5 eV lower binding energy than the photoemission line of interest) from the on-resonance photoemission. As a result, the element-specific X-PEEM images below represent a plot of the differential count rate at each pixel—for ease of use, this will be generally referred to simply as “intensity” throughout the manuscript.

Figure 1 displays element-specific X-PEEM images of the most prominent photoemission lines (In 3d_{5/2}, Ga 2p_{3/2}, and the overlapping Se 3d_{3/2,5/2}) of the studied CIGSe absorber. Certain corresponding regions are dark in all images; this is a topographical effect due to “shadowing” of the x-rays in the grazing incidence geometry. The overall intensity and signal-to-noise ratio of the Ga 2p signal (Figure 1(b)) is significantly lower than the others due to the In-rich CIGSe surface^{2,17} and to the relatively low photoionization cross section of the Ga 2p line (for excitation 120 eV above the ionization threshold as in this experiment, the Ga 2p

cross section is ca. 4.3 times lower than the In 3d cross section and 8.5 times lower than that of the Se 3d line¹⁸). Similarly, the Cu-poor surface and relatively low Cu 2p photoionization cross section prevented us from obtaining a usable measurement of the Cu distribution on the sample surface. These limitations cannot be completely overcome by increased measurement times, especially when thermal drifts have to be considered and the ability to correct for them is limited by the quality of each individual image. Direct comparison of the count rates of the images (as displayed in the intensity scales) is not possible in this case, due to fluctuations in the x-ray intensity during and between measurements, and to the different beamline aperture sizes used in the measurements—smaller aperture sizes were in particular needed to avoid saturation of the strong Se 3d signal, which is why the maximum intensities of Figures 1(a) and 1(c) are comparable despite the higher photoionization cross section of the Se 3d line.

A pronounced spatial anticorrelation of the In 3d (Figure 1(a)) and Ga 2p (Figure 1(b)) photoemission intensity can, however, be observed in several areas of the respective X-PEEM images. This observation suggests a corresponding inhomogeneity in the chemical surface structure of these regions. As the chalcopyrite band gap is related to the Ga/(In+Ga) ratio of the CIGSe material,^{5,14} this is also an indication for an inhomogeneity of the surface electronic structure.

In order to quantify the observed intensity variations, 104 regions of interest (ROIs) covering the center of each image were identified and compared. The white lines overlaying the Se 3d image (Figure 1(c)) indicate the boundaries of these regions. Except for the very dark areas of the image, the intensity of the Se 3d X-PEEM image is quite uniform (regardless of image contrast settings) and representative mostly of the topography of the sample. The ROI boundaries were drawn such that each region represented (as best as possible) a single grain at the surface: they correspond to areas of relatively uniform intensity (in all maps) and do not cross any obvious intensity boundaries. As a result, different facets of the same grain may fall in different ROIs if there is a noticeable variation in illumination, and conversely multiple grains could be grouped into the same ROI if there are no

FIG. 1. Spatial distribution of (a) In 3d, (b) Ga 2p, and (c) Se 3d photoemission intensities on the surface of a Cu(In,Ga)Se₂ absorber measured using X-PEEM. The image size is roughly $4 \times 4 \mu\text{m}^2$. The intensity scales are in (differential) counts per second.

noticeable changes in intensity or boundaries between them. Neither occurrence would significantly affect the following intensity correlation analysis: The “double counting” in the former case would be offset in the correlation plots by the increased error bars associated with the individual points. The latter situation will only occur if adjacent grains are indistinguishable using the current techniques and will therefore not directly affect the analysis of the images, however, suitable care will be taken to not overgeneralize the findings.

The In 3d and Ga 2p images are reproduced—along with the region boundaries—in Figures 2(a) and 2(b), respectively, with the image contrast set such that the regions of relatively high and low intensity are represented by saturated colors. Note that this is a strictly visual cue and does not reflect the intensity distribution used in the analysis below. However, by comparing Figure 2(a) with Figure 2(b), the anticorrelation of the In 3d and Ga 2p photoemission intensity becomes quite obvious.

For each ROI, the mean intensity and standard deviation were determined. The individual intensity values were rescaled by dividing by the average intensity value for all regions; the distributions and correlations of the relative intensities of the In 3d and Ga 2p photoemission among the regions are analyzed in Figures 2(c)–2(e). Of the 104 defined ROIs, 12 were determined to be dominated by shadowing effects—based on having unusually low intensity in the In 3d, Ga 2p, Se 3d, and Na 1s (not shown) maps—and were removed from the statistical analysis. The gray markers in Figure 2(c) show the intensities of the removed data points (also indicated as white regions in Figures 2(a) and 2(b)). The normalization procedure was repeated without the contributions of the 12 excluded regions, and it is these renormalized values that are displayed in Figure 2(c) (Note: the overall effect of the renormalization was extremely small).

The intensities of the In 3d and Ga 2p photoemission in defined ROIs are normally distributed, as can be seen in the quantile-quantile (Q-Q) plots in Figures 2(d) and 2(e), in which a theoretical normal distribution is compared to the actual measured distribution of intensities (a linear relationship indicates a normal distribution). The correlation plot in Figure 2(c) includes a linear-regression fit (taking into account the error bars of both variables) that suggests a direct anticorrelation between the In 3d and Ga 2p intensities. No correlation is observed between the Se 3d intensities and the intensities of the In 3d or Ga 2p lines.

Assuming that the intensity variations are directly related to the sample composition (specifically, the value of $x = \text{Ga}/(\text{In} + \text{Ga})$), the images can be interpreted in terms of changes in the chemical and electronic surface structure. Adapting a previously described¹⁴ formula and assuming a uniform Se content, the *bulk* band gap of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ is given by

$$E_g = (1.00 + 0.13x^2 + 0.55x)[\text{eV}]. \quad (1)$$

The Ga/(In+Ga) bulk composition was reported to be ~ 0.25 ;² a similar surface stoichiometry is assumed here. If the variations in photoemission intensity are then used as a representation of the deviations from the composition average (i.e., rescaling the points in Figure 2(c) such that the average Ga 2p intensity was 0.25, and the average In 3d

FIG. 2. (a) In 3d and (b) Ga 2p photoemission count rate difference. Red and blue regions represent relatively low and high count rates, respectively. The whitened areas are regions of uniformly low intensity that were removed from the analysis. (c) Correlation plot showing the relationship between the normalized Ga 2p and In 3d photoemission intensities [using the regions defined in (a) and (b)]. Gray points correspond to whitened regions (not used to calculate the correlation). The error bars represent one standard deviation. (d) and (e) Q-Q plots of expected normal distributions of the In 3d and the Ga 2p normalized photoemission intensities vs. the measured intensities, with mean (μ) and standard deviations (σ).

intensity was 0.75), the calculated band gaps are normally distributed with a standard deviation of ca. 40 meV. Note that this variation in the band gaps can be estimated with a fair degree of accuracy even with some uncertainty in the

nominal overall composition (and hence the mean band gap value) because of the dominance of the linear term in Eq. (1) for plausible values of x (assuming, also, that the surface band gap varies similarly with x as does the bulk band gap). We find that the band gap at the surface of the investigated CIGSe absorber can vary up to 40 meV in between grains. In the absence of a spatially resolved probe of the bulk composition, we will proceed with the analysis under the assumption that the degree of variability in surface composition is reflective of corresponding variations in the bulk composition, although this relationship could be influenced by varying deposition conditions and/or surface oxidation.

In addition to the grain-size scale variations described above, close inspection of the defined ROIs in Figures 2(a) and 2(b) reveals that the Ga 2p/In 3d anticorrelation occurs on much smaller scale (<100 nm) as well. Several instances of such a variation occur within single grains; the small size and resulting poor statistics of these regions prevent us from attempting to tabulate or quantify these instances; we speculate that these regions may correspond to the theoretically predicted In-Ga segregation,¹² which would in turn lead to strain-induced decreases in the band gap.

The effects of varying band gaps such as we show here have previously been discussed in detail;^{6–8} the main effect on device performance is an increase in saturation current density and a corresponding decrease in the open circuit voltage, V_{OC} . Similarly, a variation in the absorber surface band gap will influence the conduction band alignment, and thus the likelihood of interface recombination, at the heterojunction formed between the absorber and the front contact in a device.

The current study indicates that, at least in the samples studied here, the band gap variations occur on the μm (i.e., grain size) scale, with the alloy composition in each individual grain being relatively homogeneous. Smaller scale variations (i.e., segregation of In- or Ga-rich phases within a grain) are significantly less apparent here, suggesting that strain-induced band gap variations presumably play a smaller role within each grain.

Although the impact will depend on the relative alignments of the respective valence band maxima and conduction band minima, the observed differences in band gap between adjacent CIGSe grains can have an influence on the lateral charge carrier transport. The possible energy barrier resulting from the variation in band gap described here is in fact consistent with the barrier heights observed in similar CIGSe samples ($0.1 < x = \text{Ga}/(\text{In} + \text{Ga}) < 0.3$) determined via simple transport and Hall measurements (≈ 20 – 70 meV).⁴ This correlation has impact on the analysis of the operation of CIGSe-based solar cell devices, as it implies that the grain boundaries—potentially a separate source of energy barriers—can be made to have little or no influence on the lateral charge carrier transport in optimized devices, in agreement with the reported benign/beneficial role that grain boundaries play in polycrystalline chalcopyrite absorbers.⁹

The increasing barrier height reported as $\text{Ga}/(\text{In} + \text{Ga})$ decreases,³ however, cannot likely be explained in terms of a stoichiometry-related energetic barrier, because of both the decreasing dependence of the band gap on composition as x approaches zero and an expected decrease in size of the absolute deviation from the nominal composition.

In summary, we have presented a study of spatially resolved surface composition of polycrystalline $\text{Cu}(\text{In,Ga})\text{Se}_2$ as determined using x-ray excited photoelectron emission microscopy (X-PEEM). Regions of uniform In 3d and Ga 2p photoemission intensity having dimensions in the range of the expected grain size of ca. 0.5 – 1.0 μm were observed; corresponding regions in the X-PEEM maps show a direct anticorrelation between the intensities of the two signals. Using the relative photoemission intensity as a marker for departures from a nominal stoichiometry, estimates of the changes in the band gap were made; the band gaps were found to be normally distributed with a standard deviation of 40 meV. Such variations are predicted to have negative effects on the open circuit voltage of a device, therefore, limiting device performance. In addition, band offsets between adjacent grains could create barriers to charge transport; a barrier of ca. 40 meV would be easily overcome by carriers at normal operating temperature, however, the offset could affect the outcome of low-temperature characterization techniques.

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