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3-D Point Defect Density Distributions in Thin Film Cu(In,Ga)Se₂ Measured by Atom Probe Tomography

Adam Stokes^{*a,b}, Mowafak Al-Jassim^b, David R. Diercks^a, Brian Egaas^b, and Brian Gorman^a

^a*Colorado School of Mines, 1500 Illinois St., Golden, Colorado, U.S.A*
adstokes@mines.edu, ddiercks@mines.edu, bgorman@mines.edu

^b*National Renewable Energy Laboratory, 15013 Denver W Pkwy, Golden, Colorado, U.S.A*
mowafak.aljassim@nrel.gov, brian.egaas@nrel.gov

*Corresponding Author: Adam Stokes, (831) 428-1719

Abstract

This paper will discuss the findings of an ordered vacancy compound (OVC) phase that exists deep into the bulk of a high-efficiency Cu(In,Ga)Se₂ (CIGS) absorber that is shown to be a result of many ordered defect pairs of $2V_{\text{Cu}} + (\text{In,Ga})_{\text{Cu}}$ as determined by atom probe tomography (APT). To date, literature has shown that absorbers grown with the three-step process exhibit the OVC Cu(In,Ga)₃Se₅ (135 phase) only within the first few nanometers from the CdS/CIGSe interface and at grain boundaries. In this contribution, we have found a small volume ($100 \text{ nm} \times 100 \text{ nm} \times 300 \text{ nm}$) of an OVC phase to exist about 400 nm into the absorber. We show through concentration and density profiles that the concentration change from the stoichiometric Cu(In,Ga)Se₂ to the OVC is indeed a result of many ordered defect pairs. We use this volume to perform point defect density distributions to give unique insight to the band structure at the nanoscale.

Introduction

Polycrystalline Cu(In,Ga)Se₂ (CIGS) thin-film solar cells have achieved a record efficiency of 21.7%, making them the most efficient thin-film photovoltaic device ^[1]. Despite the excellent efficiencies demonstrated by the technology, the overall picture of the composition at surfaces, grain boundaries, and even within grains still remains ambiguous. During the mid-1990s, a considerable effort was made to structurally and electrically characterize a group of secondary phases, the so-called ordered vacancy compounds (OVC)

[2–10]. Found to solely exist at the surface of the Cu(In,Ga)Se_2 (112-phase) absorber and predicted to exist at the grain boundaries, the OVCs were explored to determine whether or not their inclusion was advantageous to device performance. Several studies have shown that OVCs—most notably, CuIn_3Se_5 , CuIn_5Se_8 , $\text{Cu(In,Ga)}_5\text{Se}_8$, and $\text{Cu(In,Ga)}_3\text{Se}_5$ —exist within the first five nanometers from the surface of the absorber [4,11,12]. The compositional change was attributed to a low energy of formation of Cu vacancies and In-on-Cu antisites (In_{Cu}) [2,5,13]. The formation energy was theorized to be lower, possibly even negative, when rows of these defects were stacked on top of each other.

The valence-band maximum (VBM) of CIGS solar cells consists of the anti-bonding hybridized states of Cu-d and Se-p orbitals, called p-d repulsion [2,5]. Intuitively, a copper-poor phase (i.e. $\text{Cu(In,Ga)}_3\text{Se}_5$) would reduce the repulsion between these and thereby reduce the VBM. On the other hand, the conduction-band minimum is only weakly influenced, resulting in an overall increase in bandgap to around 1.3 eV [14]. The reduction in the VBM may act as a hole-barrier and thereby reduce recombination at Cu-poor interfaces even when an abundant amount of defects are present. Furthermore, a thin layer of CuIn_3Se_5 on the surface of the 112 phase has been predicted to improve device performance by making an improved heterojunction of the n- CuIn_3Se_5 and p- CuInSe_2 [6,10]. This is presumed to also be true for the CIGS 112 phase and $\text{Cu(In,Ga)}_3\text{Se}_5$ (135 phase) of the Cu(In,Ga)Se_2 absorber as long as the bandgap remains similar to that of CuInSe_2 , which is indeed the case for high-efficiency devices.

Various studies on CIGS using secondary-ion mass spectrometry (SIMS), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS) have been used to identify the chemistry of CIGS devices but have not found an OVC deep into the bulk [11,12,14–17]. However, atom probe tomography (APT) may offer more insight on a nanometer scale than the above-mentioned characterization techniques. This is due to both the high spatial resolution (sub-nanometer level) and chemical sensitivity (10s of ppm) [18]. The volume analyzed using APT is roughly $100 \text{ nm} \times 100 \text{ nm} \times 500 \text{ nm}$ for the case of a typical CIGS specimen, which, when compared to other techniques listed above, is much smaller, and more able to capture nano-

domains. In this work, APT is used to quantify OVCs in high efficiency CIGS grown by the three step process.

Experimental

The CIGS absorber layers were grown on a Mo-coated soda-lime glass using a modified three-stage process[19,20]. The samples were prepared for APT and transmission electron microscopy (TEM) analysis using an FEI Helios 600i DualBeam focused ion beam / scanning electron microscope (FIB/SEM) similar to the technique described in Ref [21]. A final 2 kV cleaning step was used to reduce the damage to approximately the outer 2 nm of the sample. This is verified by isolating the Ga regions that have monoisotopic ^{69}Ga used in the FIB source from the regions with the naturally occurring ^{69}Ga and ^{71}Ga isotopic ratios within APT reconstructions. The end radii of the specimens analyzed ranged from 50–100 nm. APT data were collected using a LEAP 4000X Si instrument manufactured by Cameca Instruments, Inc. using laser energy of 5 pJ, a base temperature of 40K, a detection rate of 0.5%, and a laser pulse rate of 250kHz. Laser energy and base temperature were optimized to get equal evaporation rates of the constituent elements for an accurate chemistry profile of the device that well represents the stoichiometry of CIGS (please see supplemental section for details). A Philips CM200 TEM was used to capture the sample specimens' dimensions before and after APT using the hardware described in Ref [22] which allowed for more accurate 3D reconstructions.

Three sample specimens from adjacent regions of a 19%-efficient CIGS solar cell as measured by the National Renewable Energy Laboratory were analyzed. Each atom probe specimen was milled perpendicular to the surface of the absorber. A schematic of the geometry and location of Specimen 1 is shown in Figure 1a and b. The beginning of each specimen starts roughly $50\text{ nm} \pm 50\text{ nm}$ below the CdS/CIGS interface identified by TEM images.

An overlay of the TEM images before and after APT analysis Figure 1c was taken of one of the samples to assist in the reconstruction parameters. The dark regions are of the image taken after APT, whereas the lighter gray section is the image taken before APT. This allowed for quantification of the sample volume analyzed from the field evaporation process of APT by adjusting the image compression factor, efficiency, and ion volume, which greatly assist in the accuracy of the reconstruction. A mass spectrum acquired from Specimen 1 is also shown in Figure 1d.

Results and Discussion

Concentration profiles along the central axis were taken for three specimens (see Figure 2). Each data point gives the concentration statistics taken from a 1-nm-thick x 20 nm x 20 nm slice perpendicular to the central axis. The x-axis shows the distance that each slice is from the top of the specimen. The 0-nm point corresponds to the slice farthest away from the Mo layer. In each case, the beginning of the specimen is estimated from TEM images to be 50 ± 50 nm away from the CIGS/CdS interface.

A clear, significant change in stoichiometry is shown for Specimen 1 in Figure 2. For a ~80-nm section, the composition of the constituent elements are as follows: $14.3 \pm 0.3\%$ Cu, $13.9 \pm 0.3\%$ Ga, $18.1 \pm 0.5\%$ In, and $52.7 \pm 0.7\%$ Se. These concentrations closely resemble the $\text{Cu}_2(\text{In,Ga})_4\text{Se}_7$ OVC (15.4% Cu, 30.8% In+Ga, 53.8% Se). The concentration profiles at the bottom of the specimen, or furthest from the CdS/CIGS interface, resemble that of the traditional 112 phase ($24.1 \pm 0.3\%$ Cu, $10.2 \pm 0.3\%$ Ga, , $16.2 \pm 0.2\%$ In, $48.5 \pm 0.7\%$ Se). The change in composition from the beginning of the specimen to the 112-phase is gradual, taking roughly 300 nm for the transition. Considering that both phases have the chalcopyrite structure and the lattice constants are quite similar, one might expect this sort of gradual and diffuse phase transition. Curiously, the increase in Cu concentration from 80–225 nm coincides with a decrease in Ga concentration, which might indicate a movement of Cu into Ga sites (Cu_{Ga}). The other two specimens, FIB extracted from regions within several microns of Specimen 1, have standard 112-phase concentration profiles. This sug-

gests that the concentrations measured in Specimen 1 are not an artifact of the analysis technique as the same parameters were used on Specimens 2 and 3. Additionally, this provides an indication of the size and localized nature of this other phase.

Different compositions of OVCs have been theorized and previously observed on absorber surfaces. A reasonable way to characterize the OVCs is not just by stoichiometry, but also by the number of ordered defect pairs thereby giving a more relatable quantity to properties of the phase, such as the band diagram. OVCs are predicted to be a result of stacking pairs of an ordered defect pair (ODP), namely, two Cu vacancies (V_{Cu}) and an In or Ga on a Cu site, $(In,Ga)_{Cu}$.

Therefore, for every pair there are three fewer Cu atoms in the lattice when compared to the stoichiometric 112 phase. Also, for every pair there is one more In or Ga atom in the lattice. Eq. 2 shows the relationship of Cu concentration (X_{Cu}) and number of ODPs per a given volume.

$$\frac{(25 - X_{Cu})}{3} = ODP \quad (2)$$

From this observation, one can correlate the number of Cu vacancies in an OVC phase with the deviation in composition from stoichiometric CIGS, where Cu makes up 25 at%. Eq. 2 shows the relationship of measured Cu concentration (X_{Cu}) to the expected number of ODPs for a given volume.

Using the above relations, the number of ODPs and Cu composition as a function of distance for Specimen 1 is shown in Figure 3. Based on this, the specimen begins with approximately the $Cu_2(In,Ga)_4Se_7$

phase and ends with the 112-phase. Interestingly, the change in composition is more dramatic below where the analysis reaches the $\text{Cu}_3(\text{In,Ga})_5\text{Se}_9$ stoichiometry. From that point, the change to the 112-phase occurs over a relatively short distance.

From equation (2) the expected In + Ga concentration can also be determined in a phase with ODPs for a known Cu concentration by the following formula:

$$X_{\text{In+Ga}}^{\text{Predicted}} = 25 + (\text{In, Ga})_{\text{Cu}} \quad (3)$$

Likewise, the Se concentration results from filling the other sites with Se, or:

$$X_{\text{Se}}^{\text{Predicted}} = 100 - (X_{\text{Cu}} + X_{\text{In+Ga}}^{\text{Predicted}}) \quad (4)$$

Figure 4 shows the predicted Se and In+Ga concentration profiles for an OVC using equation (5) and (6) versus their experimentally measured values. There is quite good agreement between the predicted values and the measurement, suggesting that the observed phases are OVCs. Additionally, since equation (2), (3), and (4) relate all of the atomic concentrations to each other and to the number of ODPs, then knowing the concentration of any of the species (X_{Cu} , $X_{\text{In+Ga}}$, or X_{Se}) allows the determination of the remaining species and the number of ODPs, and thus also V_{Cu} . The difference between the predicted concentration profiles to the actual concentration profiles is minimal regardless of position and magnitude of off-stoichiometric volumes.

Another method of determining the number of ODPs, uses a number density profile analysis. If indeed the change in concentration is due to ODPs, then the number density of atoms (number of atoms/volume) should also change due to a large number of Cu vacancies. Figure 5 shows the schematic for the density

analysis for all three specimens, where the region of interest (ROI) was divided into twenty 20 nm x 20 nm x 22 nm boxes to ensure good counting statistics (~400K ions per box). The same ROI used for the concentration profiles was used in the density analysis. For the off stoichiometric specimen, the relative number density from each box was related to the number density of the 112-phase, i.e. the cube furthest away from the CdS/CIGS interface which has, by definition, a change in density equal to zero; $\Delta\rho^{Total}=0$. For the other two specimens the last box, i.e. the box furthest away from the CdS/CIGS interface was used as the reference box as well.

In order to make a density correlation to V_{Cu} , there is a need to first account for a change in lattice volume due to the ordered defect pairs and also account for possible atom probe reconstruction errors. The lattice volume is slightly reduced as compared to the 112 phase as a result of the V_{Cu} 's [23]. The lattice volume shrinkage will correspondingly affect the number density due to more unit cells per unit volume. Also, during the APT reconstructions there could be localized changes in density due to evaporation differences of the ions as well as the errors associated with the reconstruction methodology and parameters. Any such errors should occur throughout the analysis and, therefore, just contribute to the uncertainty of the values. According to Eq. 1, the Se atoms do not change lattice sites between the 112 and 135 phases. Furthermore, the three-stage-process includes a Se-rich deposition profile throughout all three stages so the phase(s) are assumed to be free from Se vacancies or substitutions on Se sites. Additionally, the incorporation of Se in interstitial sites is assumed to be energetically unfavorable. Therefore, since the total number of atoms of Se in the unit cell do not change between the 112 phase and the OVC phases, one should expect the relative change in the Se number density to equal the relative change in volume of the unit cell coupled with the change in density due to any atom probe reconstruction artifacts as shown in Eq. 5. By using the Se atoms as a normalization parameter the change in number density due to V_{Cu} 's can be isolated from the remaining parameters previously discussed.

$$\Delta\rho^{\text{UnitCellVolume}} + \Delta\rho^{\text{APTUncertainty}} = \Delta\rho^{\text{Se}} \quad (5)$$

It should be noted that the difference between the overall change in number density for all species and that for just selenium should be zero for stoichiometric CIGS absorbers.

For the non-stoichiometric phases, a key assumption in the analysis is there are no relative changes in vacancies besides V_{Cu} or interstitial atoms, the only additional mechanism for a change in number density is from V_{Cu} . Therefore the total change in density is the sum of the APT uncertainty, lattice volume, and V_{Cu} mechanisms (See Eq. 6).

$$\Delta\rho^{\text{Total}} = \Delta\rho^{V_{\text{Cu}}} + \Delta\rho^{\text{UnitCellVolume}} + \Delta\rho^{\text{APTUncertainty}} \quad (6)$$

The total change in density as well as the change in density due to the Se atoms may be calculated from the experimental set up given in Figure 5. From Eq. 5 and 6, the change in density due to V_{Cu} 's from the number density method may be obtained (see Eq. 7).

$$\Delta\rho^{V_{\text{Cu}}} (\text{Density}) = \Delta\rho^{\text{Total}} - \Delta\rho^{\text{Se}} \quad (7)$$

Figure 6a shows the difference between the total and Se number densities for ROIs from stoichiometric CIGS in Specimens 2 and 3 (See Figure 2) represented by $\Delta\rho^{V_{\text{Cu}}} (\text{Density})$ given by Eq. 7. Cu concentrations within 0.75 at% of the ideal (25 at%) were considered as stoichiometric CIGS. The figure shows the difference between the total number density and Se number density is small, with the average equal to 0 for both specimens with a standard deviation of 0.49 for Specimen 2 and 0.45 for Specimen 3. These indicate

the uncertainty attributable to the atom probe analysis and reconstructions. V_{Cu} can now be measured from change in density due to using Eq's 5, 6, and 7 for the off-stoichiometric specimen (Figure 6b).

The $\Delta\rho^{V_{Cu}}$ may also be calculated based on the measured Cu concentration. Combining Eq. 2 and the fact there are two V_{Cu} 's per every ordered defect pair, the number of V_{Cu} 's per 100 atoms for a given volume may be calculated (Eq. 8).

$$\#V_{Cu}'s = \frac{2(25 - X_{Cu})}{3} \quad (8)$$

Therefore, the percentage of Cu vacancies $\#V_{Cu}'s$ (%), per a given volume is equal to the quotient of $\#V_{Cu}'s$ over the number of total lattice sites which in this case is the sum of Cu vacancies and one hundred.

$$\#V_{Cu}'s (\%) = \frac{\#V_{Cu}'s}{100 + \#V_{Cu}'s} \quad (9)$$

Finally, the percent change of density from stoichiometric CIGS is equal to the product of the percentage of Cu vacancies and the scalar quantity representing the change in density due to the change in unit cell volume as well as uncertainties associated with APT reconstruction (Eq. 9; Please see Eq. 7 and the preceding section for further discussion).

$$\Delta\rho^{V_{Cu}}(\text{Concentration}) = (1 + \Delta\rho^{\text{UnitCellVolume}} + \Delta\rho^{\text{APTUncertainty}}) \frac{\#V_{Cu}'s}{100 + \#V_{Cu}'s} \quad (10)$$

Combining Eq. 7 and 9 gives Eq. 10; the total change in density due to V_{Cu} derived from the “concentration experiment” and is denoted as: $\Delta\rho^{V_{Cu}}(\text{Concentration})$

$$\Delta\rho^{V_{Cu}}(\text{Concentration}) = (1 + \Delta\rho^{Se}) \frac{\#V_{Cu}'s}{100 + \#V_{Cu}'s} \quad (11)$$

Cu concentrations collected in the same ROI as the density profile were used to then calculate the predicted change in density due to Cu vacancies, which corresponds to the values of $\Delta\rho^{V_{Cu}}(\text{Concentration})$ in Figures 6a and b. For Specimens 2 and 3, which had relatively constant compositions throughout the analyses, Figure 6a depicts little change in the density as a function of distance for either method. This is not surprising since both of these specimens appear to be single phases very nearly that of the stoichiometric 112 phase. Scatter in the data in this figure demonstrates the variability attributable to the data collection and reconstruction processes. Figure 6b shows the comparison of both approaches for the change in density due to Cu vacancies for Specimen 1. The change in density due to V_{Cu} is shown to be significant at the beginning of the specimen, roughly 5.5%. This is much greater than the instrumental and reconstruction uncertainty. Additionally, the good agreement between the two approaches allows for making some conclusions. First, there is indeed coupling of defects into ODPs by the ratio of two V_{Cu} for every $(In,Ga)_{Cu}$, which was shown to accurately reproduce both the experimental change in density and the experimental concentration profiles (See Figures 4 and 6). Secondly, the agreement supports the validity of the assumption that there is a negligible change in density due to interstitials or vacancies other than V_{Cu} . Lastly, there are an appreciable amount of ODPs (up to 3.5 pairs per 100 lattice sites).

Conclusion

The band structure can begin to be analyzed since the point defects have been characterized and quantified at the nano-scale. For example it is predicted that the ODP's result in a change from a p-type to an n-type semiconductor by creating a donor state $\sim 100\text{meV}$ from the conduction band maximum as well as eliminating the acceptor state caused by the uncoupled Cu vacancy[4]. Also, since this method determines the concentration of V_{Cu} , the valence band maximum shift could be more precisely calculated by quantifying the change in Cu-d Se-p repulsion.

More generally, this new method has demonstrated the ability to use APT data for determining point defect densities at the nano-scale. However, this technique will not be able to identify all point defects. Pairs that result in either no change in number density or composition could not be derived. Most notably for CIGS, the pair of $\text{Cu}_{\text{In}}+\text{In}_{\text{Cu}}$ which has been shown to have a low energy of formation, ^[2,13] cannot be measured.

Due to the highly localized nature of the composition changes shown in this study, it is not surprising that other techniques have not measured OVC phases in the bulk of CIGS. Characterization techniques such as XRF, XPS, and SIMS, which have been used to examine CIGS, have a much larger sample volume than APT. As a result, the concentration profiles acquired are a statistical average of nano-domains and thereby do not capture the highly variable local chemistry shown in this study.

Three different APT specimens from adjacent regions of a high-efficiency CIGS device were analyzed. One had a shift in the composition profile through the depth of the analysis. Most notably, it varied from being deficient in Cu and enriched in Ga and transitioned to the stoichiometric 112 phase composition; the profiles from the other two specimens indicated only the 112 phase. These data indicate the existence of a localized phase in the bulk of the absorber not yet seen in literature. The composition data were used to assess the validity of an ordered defect pair structure: $2V_{\text{Cu}}+(\text{In,Ga})_{\text{Cu}}$. Furthermore, a second approach using the change in number density through the specimen provided nearly identical results to the compositional

method. Moreover, the data were used to calculate quantitative point defect densities for CIGS at the nano-scale for a first time. From the unique characterization of point defects at the nano-scale produced by this new method, further optimization of CIGS devices may be possible by providing feedback for the processing of the absorber layer for active enhancement or diminishment of these defects.

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Author Contributions

A.S., M. A. and B. G. designed the research and experiments. D. D. helped with analysis of the experiments and edits of the paper. B. E. made the solar cells. A.S. wrote the paper. All authors contributed with discussions.

Competing Financial Interests

The authors declare no competing financial interests.

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Figure 1| Location, dimensions and mass spectrum of the APT samples. **a,** One specimen's dimensions in nm are shown in the APT reconstruction. **b,** representative SEM image of the CIGS device structure. **c)** Bright field TEM images from before and after APT field evaporation are overlaid to quantify the sample volume analyzed. The dark section is after APT and the light section is before APT. In this case, the depth consisted of a 440-nm-long central axis. **d)** Mass spectrum acquired from Specimen 1.

Figure 2| Composition profiles of three specimens where one exhibits off stoichiometry. Composition profiles were along the central axis of three specimens from the same high-efficiency CIGS sample. Specimen 1 (a) shows a concentration profile of a Cu-poor and Ga-rich phase, then transitions to the 112 phase from 80–440 nm. Specimens 2 (b) and 3 (c) have concentration profiles that are of the 112 phase. Error bars in all cases are less than $\pm 0.24\%$ which are omitted for clarity. Errors of ± 0.24 at. % Se, ± 0.14 at. % Cu, ± 0.17 at. % In, and ± 0.14 at. % Ga were calculated as a convolution of standard deviation and statistical error (very small $< 0.01\%$) using a control sample.

Figure 3| Cu Concentration and Ordered Defect Pairs as a function of distance for specimen 1. The number of ordered defect pairs is predicted as a function of Cu concentration. The concentration profiles suggest the specimen begins near the $\text{Cu}_2(\text{In,Ga})_4\text{Se}_7$ stoichiometry and ends at the traditional $\text{Cu}(\text{In,Ga})\text{Se}_2$ stoichiometry. Error bars for Cu concentration profile are ± 0.14 at. % and were omitted for clarity.

Figure 4| Experimental concentration profiles of Se and In+Ga as a function of distance compared to predicted profiles on the basis of ordered defect pairs using the experimental Cu concentration profile. Error bars for Se and Ga+In concentration profiles (actual) are ± 0.25 at. % and ± 0.22 at. % respectively which were omitted for clarity.

Figure 5| Density analysis schematic. (a) the atom probe reconstruction enclosing the region of interest (ROI) (blue box). (b) The ROI was then divided into 20nm x 20nm x 22nm cubes (c) Each cube had approximately 400K ions enclosed (d) which were used for number density calculations.

Figure 6| Density profiles of stoichiometric CIGS and non-stoichiometric CIGS. a) Change in density as predicted from the concentration profiles (filled symbols) and density profiles (empty symbols) as a function of distance for specimens 2 and 3. The change in density due to V_{Cu} was predicted using Cu concentration profiles (See Eq.'s 8-11). Density profile analyses were conducted by measuring the change in density from a volume of a box compared to the box furthest from the CdS/CIGS interface as a function distance (See Figure 6 and Eq. 5-7). The regions analyzed for Specimens 2 and 3 were taken when Cu concentration was $25 \pm 0.75\%$. In these regions, it is shown that the difference in change of density of Se ions and total ions is small, average = $0 \pm 0.49\%$ for Specimen 2 and average = $0 \pm 0.45\%$ for Specimen 3. **b)** Change in density same as in part a) but for Specimen 1.

Graphical Abstract