Nanoscale Doping Profiles within CdTe Grain Boundaries and at the CdS/CdTe Interface Revealed by Atom Probe Tomography and STEM EBIC

Jonathan D. Poplawsky^{a,*}, Chen Li^b, Naba R. Paudel^c, Wei Guo^a, Yanfa Yan^c, and Stephen J. Pennycook^d

^aCenter for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA

E-mail: PoplawskyJD@ornl.gov

^b Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA

Current affiliation: Department of Lithospheric Research, University of Vienna, Vienna, Austria

^cThe University of Toledo, Department of Physics and Astronomy, McMaster Hall, 2nd Floor Rm 2017, Toledo, OH, 43606, USA

^dNational University of Singapore, Department of Materials Science and Engineering, Singapore

Keywords: CdTe, Atom Probe Tomography, Scanning Transmission Electron Microscopy, Electron Beam Induced Current, Thin Films

Abstract: Segregated elements and their diffusion profiles within grain boundaries and interfaces resulting from post deposition heat treatments are revealed using atom probe tomography (APT), scanning transmission electron microscopy (STEM), and electron beam induced current (EBIC) techniques. The results demonstrate how these techniques complement each other to provide conclusive evidence for locations of space charge regions and mechanisms that create them at the nanoscale. Most importantly, a Cl dopant profile that extends ~5 nm into CdTe grains interfacing the CdS is shown using APT and STEM synergy, which has been shown to push the pn-junction into the CdTe layer indicative of a homojunction (revealed by STEM EBIC). In addition, Cu and Cl concentrations within grain boundaries within several nms and μ ms from the CdS/CdTe interface are compared, Na segregation of <0.1% is detected, and S variations of ~1-3% are witnessed between CdTe grains close to the CdS/CdTe interface. The segregation and diffusion of these elements have a direct impact on the material properties, such as band gap energy and n/p type properties. Optimization of the interfacial and grain boundary doping will lead to higher efficiency solar cells.

1. Introduction

CdTe based solar cells are currently one of the leading commercialized thin-film solar technologies in terms of price per watt and total watts installed per year. The advantage of thin-film CdTe technology over traditional Si is the ability to reduce costs associated with semiconducting material, thus reducing the total module price. However, unlike Si, there is a large efficiency gap between the record CdTe efficiency (21.5%) and the theoretical efficiency (~33%) [1]. If this gap can be bridged without increasing the production costs, the price per watt of the manufactured modules will reduce significantly. Despite improvements in recent years, the main issue limiting the efficiency of CdTe solar cells is the low value for the open circuit voltage (V_{oc}) (877 mV for the record cell), which is 61% of the band gap, while a similar band gap material, GaAs, has a record cell V_{oc} that is 79% of its band gap [1]. The introduction of Cu into the material is one factor in increasing the V_{oc} due to p-type doping and a better ohmic back contact, but the Cu incorporation begins to self-compensate the p-type doping above a certain incorporation concentration, thus making heavy p-type doping difficult [2-6]. Overall, the low V_{oc} has been attributed to low p-type doping concentrations in the CdTe absorber, a poor back contact, a poor junction with CdS, and electron-hole recombination at point defects, interfaces, and grain boundaries (GBs) [7]. Despite the low V_{oc} , CdTe solar cells have been able to achieve a short-circuit current (J_{sc}) close to the theoretical maximum, which is significantly enhanced by the $CdCl_2$ heat treatment (HT) [7,8]. Although Cl segregation at grain boundaries (GBs) and the CdTe/CdS interface after this treatment has been identified using scanning transmission electron microscopy (STEM) electron energy loss spectroscopy (EELS) and STEM energy dispersive x-ray spectroscopy (EDS) techniques, quantification of this segregation is difficult, and low levels of segregation that can be responsible for doping are undetectable with these experiments [9-12]. APT has been used in several papers to characterize CdTe solar cells with higher detection limits, particularly GBs in the CdTe layer, but there has not been a detailed evaluation of the CdS/CdTe interface for this material system to date [6,13-18]. To this end, several regions of fully treated ($CdCl_2$ and Cu) and untreated CdTe devices have been analyzed using atom probe tomography (APT) and compared to SEM electron beam induced current (EBIC) and STEM techniques (including STEM EBIC) to better quantify, understand, and correlate the segregation of Cu and Cl to the device properties, such as the position of space-charge-regions. These results exemplify the advantages of APT over traditional high-resolution characterization methods, and show how APT can be complimentary to other techniques, such as STEM and EBIC, to answer important material questions and verify other significant results.

2. Experimental Section

2.1 APT

APT is a technique that has been widely used for the characterization of metallic materials for more than 3 decades [19,20]. Recently, the local electrode atom probe (LEAP) with laser pulsing capabilities was invented and commercialized, which has enabled APT to characterize semiconducting and insulating materials at a larger scale. APT is a time of flight (TOFF) mass spectrometry technique, in which the material of interest is formed into a needle shape and evaporated one atom at a time, while each atom is projected onto a 2 dimensional position sensitive detector. The information from the detector can be reconstructed by a computer, which results in a data set that includes the 3D atomic positions with up to sub-nm resolution, the identity of each atom, and a low background noise, in which down to 10 ppm of an element can be detected [19]. For CdTe, the background noise can be higher than

normal for typical APT experiments because most of the elements evaporate as complex molecules with several mass-to-charge (m/q) peaks. In addition, slight thermal tails, due to the insulating properties of these materials at low temperature, also increase the background [14,16]. Despite these, the background noise is much lower than all other 1 nm or lower resolution techniques. The combination of high resolution and low background noise give this technique its unique properties and edge over traditional high-resolution techniques for the characterization of solar cell materials, specifically the location of dopant profiles in GBs and interfaces.

An FEI Nova 200 dual beam focused ion beam (FIB) was used to lift out and prepare atom probe needles. The wedge lift out geometry was used to mount multiple samples on a Si microtip coupon, which enables for the fabrication of multiple needles from one lift-out [21]. A 5 kV final polishing step was used to minimize Ga damage and sharpen the needle within the region of interest. The very narrow needle dimensions (~50 nm tip radius, 5 degree shank angle, 100-500 nm long) and respectively large grain size of CdTe (1-4 μm) make it challenging to encompass a GB in the center of the needle. To this end, several needles were fabricated and evaporated in the atom probe to obtain a few high quality data sets with the desired ROI. The sample preparation method used for the CdS/CdTe interface requires a few additional steps beyond the standard sample preparation methods, and therefore, a more detailed sample preparation description can be found in reference [22].

APT was performed with a local electrode atom probe (CAMECA instruments LEAP 4000X HR) equipped with an energy compensated reflectron lens. The APT needles were run at a base temperature of 30 K, applying 355 nm wavelength ~10 ps laser pulses of 3 pJ, a repetition rate of 100 kHz, and a detection rate of 0.5-1.0%. Data reconstruction and analysis was performed with IVAS 3.6.8. Peak overlaps between $^{130}\text{Te}^{2+}$, $^{126}\text{Te}^{2+}$ and $^{63}\text{Cu}^+$, $^{65}\text{Cu}^+$ do exist, but the Cu content could be realized via the peak decomposition method, which is explained in more detail in reference [22].

2.2 Sample Growth

All CdTe layers for the samples used in this study were grown by the closed spaced sublimation (CSS) method in the superstrate configuration, which is a high temperature growth method (~600 C substrate temperature). The CdS/CdTe cells were grown on $\text{SnO}_2\text{:F/SnO}_2$ -coated low-iron-soda-lime glass substrates (TEC15M), supplied by NSG North America. Roughly 80 nm thick CdS window layers were grown by radio frequency magnetron sputtering using a 4N purity (99.99%) target supplied from Materion. The Cu impurity level of this material was measured to be 0.69 ppm by using spectrographic analysis. After CdS, 4–5 μm CdTe absorber layers (4–5 μm) were prepared by CSS using a 99.999% purity CdTe source materials also supplied by Materion. The Cu impurity level of this source was measured to be <1 ppm using spectrographic analysis by Materion. Further details of the optimized growth conditions, such as substrate temperature, have been reported elsewhere [23].

2.3 STEM

A 5th order aberration corrected Nion UltraSTEM 200 equipped with a Gatan Enfium EELS Spectrometer was used for the STEM ADF and EELS measurements, which was operated at an accelerating voltage of 200 kV and a beam current of ~30 pA. For STEM EBIC measurements, the probe current was increased by an order of magnitude to increase the signal to noise ratio. The specimens were thinned using argon ion milling at liquid nitrogen temperature to avoid damage and diffusion due to excessive heating. An ~63 mrad inner

angle was used for the HAADF detector with an ~36 mrad EELS collection angle. Cl L23, Cd M45, and Te M45 edges were used for the EELS elemental maps.

2.4 EBIC

The SEM-EBIC measurements were done using a Hitachi S4800-CFEG equipped with a Gatan SmartEBIC system. All EBIC specimens were cross-section argon ion milled at liquid nitrogen temperatures using a Gatan Illion+ system to ensure a smooth, relatively damage free surface. The argon beam acceleration voltage of 5 kV allowed for <10 nm of the surface to be damaged, as calculated using SRIM simulations [24,25]. After cross-section argon ion milling, the devices were mounted on the Gatan EBIC stage, and connected to a Stanford Research Instruments SR570 low-noise current amplifier. A 3kV accelerating voltage and beam current of ~30-50 pA was used to ensure a high-resolution probe, while maintaining low-injection conditions [26]. These low accelerating voltage conditions make the EBIC signal sensitive to the magnitude of local electric fields so that space charge regions at the CdS/CdTe interface and GBs can be easily imaged [27]. All EBIC measurements represent the short circuit carrier extraction efficiencies because they were all done without a bias. Further details of the SEM EBIC experiments can be found in the experimental and supplementary materials sections of reference [8].

3. Results and Discussion

3.1. CdTe Grain Boundaries

An APT needle containing a triple junction CdTe GB interfacing with a CdS grain was successfully extracted from a CdTe device and run in the LEAP using a slightly modified FIB liftout technique [21]. A detailed explanation of the liftout procedure for the CdS/CdTe interface is explained in reference [22]. A top and side view of the reconstructed dataset can be seen in **Figure 1**(a) and (b). Each dot in this data set represents a single atom, which are colored and labeled as Na, Cl, S, or Te atoms. Also, a 22% S isoconcentration surface, which separates the dataset into a region >22% S and <22% S, is representative of the CdS/CdTe interface approximate location [28]. To better visualize this 3D dataset, a video of the dataset rotating can be found here: [provide link to video]. There are over 2.5 million atoms collected in this dataset, and therefore, a lot of compositional information is contained within this dataset, including elemental segregation at GBs and the CdS/CdTe interfaces as well as S concentration variations between the CdTe grains. Included in Figure 1 are the Cl atom APT 1D line profiles extracted from regions indicated by the arrows in the insets as well as one STEM EELS 1D line profile (Figure 1 (e)) of a similar GB close to the interface. Gaussian functions have been fit to these profiles to reveal the Cl concentration (atomic %) and width of the GBs. The function used to fit the equation is:

$$f(x) = Ae^{-\left(\frac{x-x_0}{width}\right)^2}, \quad (1)$$

where A is the concentration, x is the position in nm, and $width$ is the GB width. The three GBs close to the CdS/CdTe interface were calculated to have widths between 2.0 and 2.7 nm, while the STEM EELS Cl profile shown in Figure 1(e) has a calculated width of 0.34 nm. It is clear that the APT data contains a GB widening artifact, which is not surprising because there could easily be an evaporation field difference between the GB and the grain interior causing a local magnification effect [15,29]. The distorted composition profile due to the local magnification effect can be corrected by reducing the width of the line profile to the actual

GB width, while maintaining the same integrated Cl counts. To do this, several Cl STEM EELS line profiles of random GBs were fit with Gaussian functions to reveal the average width of the Cl profile. Using this method, the GB width was calculated to be 0.51 ± 0.15 nm. The APT GB width was normalized to the STEM EELS data, which revealed that the Cl composition in the GBs of the APT data set was miscalculated by a factor of ~4-5 times. By applying the appropriate correction factor obtained from the STEM EELS data, the Cl concentration within the three analyzed GBs was calculated to be between 11-13%, which is in good agreement with the STEM EELS dataset, showing ~16% Cl. Also included in Figure 1 are the Cl concentrations after adding the + and – standard deviations (noted as σ_+ and σ_-) for the normalized APT profiles. This error is not linear because the correction factor for the Cl profiles is $\propto 1/(0.51 \pm 0.15 \text{ nm})$ from estimating the GB width from the STEM EELS data. The standard deviations of the adjusted solute concentration can be referenced in the figures.

One advantage of APT over STEM EELS data is the very low noise level, in which the APT noise level for Cl (~0.1-0.2%) is almost 50 times lower than the STEM EELS data set (~5%). This allows for the ability to quantify differences of solute segregation within GBs that are in different parts of the cell with high accuracy. To this end, a GB close to the back contact (200-500 nm from the back contact) of a fully treated cell was run in the LEAP. A 1D line profile from the resulting dataset (Figure 1(f)) shows significantly less Cl segregation (7.4%) than the GBs close to the CdS/CdTe interface (11-13% Cl). Note that the non-corrected 1.4% Cl composition of the back contact grain boundary is in good agreement with other published Cl GB segregation APT results, while the uncorrected values of 2.4-3.0% for GBs close to the CdS/CdTe interface show much different values [6,14,16]. The decreased GB Cl content towards the back of the device could reduce and potentially negate the n-type doping properties of the GBs, which would inhibit the device from shorting through the GB [10]. In addition to the Cl segregation in the back contact GB, significant Cu segregation (up to 2.2% at the GB) was detected by using a manual peak decomposition of the extracted GB region (see reference [22]), while no Cu could be detected using this method within GBs close to the CdS/CdTe interface. Peak decomposition was necessary because there exist mass spectrum peak overlaps between the Cu^+ and some Te^{2+} isotopes ($^{63}\text{Cu}^+$ with $^{126}\text{Te}^{2+}$ and $^{65}\text{Cu}^+$ with $^{130}\text{Te}^{2+}$). In addition to GBs in fully treated devices, several APT needles were prepared for a non-Cu, non- CdCl_2 treated device, in which no Cl or Cu could be detected in the GBs. Therefore, Cl and Cu segregation only occurs in these regions after each respected treatment. Images and profiles of these data can be found in reference [22].

The aforementioned results are very consistent with SEM EBIC measurements of three CdTe devices that were exposed to (1) a CdCl_2 HT, but no Cu treatment, (2) a Cu treatment, but no CdCl_2 HT, and (3) neither a CdCl_2 HT nor a Cu treatment shown in **Figure 2**. These cells were used in a previous study and the performance parameters can be found elsewhere [8]. Without either treatment, the GBs and the CdS/CdTe interface do not show any significant EBIC contrast, and therefore, are not photoactive under short circuit conditions. This is an indication that the GBs and CdS/CdTe interface are regions with high recombination before treatment. After the CdCl_2 HT, the GBs close to the CdS/CdTe interface along with the CdS/CdTe interface produce the highest currents where most of the Cl is segregating, while the Cu treatment only shows an enhancement in GB EBIC for GBs away from the CdS/CdTe interface where most of the Cu is segregating, as shown by the APT data. The enhanced EBIC currents within and around these regions has been shown to be due to localized space-charge regions as a result of GB and interface n-type doping in the p-type CdTe layer [8,10]. The APT results confirm that this change in the material after the CdCl_2 and Cu treatments is due to Cu and Cl segregation in the GBs and Cl segregation at the interface, which allows for higher collected short-circuit currents.

In addition to Cu and Cl segregation in GBs, the low noise level of the APT data allows for the detection of 1-2% S variations between the CdTe grains close to the CdS/CdTe interface. **Figure 3** shows the 1D S concentration profiles of the 3 GBs shown in Figure 1 (a) and (b). Above each profile, an arrow is drawn over the GB to indicate the location of the profile to easily compare the S concentration of each grain. It is clear that the 3 CdTe grains in the dataset contain variations in S content (~5% for grain 1, ~4% for grain 2, and ~3% for grain 3). There is also a slight S segregation in the GBs that is more obvious for GB2 due to the small change in S concentration between the grains. Also, S segregation in GBs away from the CdS/CdTe interface is more obvious because those grains contain $<<1\%$ S, as shown in the referenced papers [6,16]. The S concentration fluctuation between grains is evidence that the CdTe grain orientation interfacing the CdS grain affects the S diffusion properties. Therefore, S diffusion from the CdS grains occurs at different rates with respect to the CdTe grain orientation. The different S concentrations in the CdTe grains result in variations in the band gap close to the interface, such that the higher sulfur concentrations exhibit reduced bandgaps due to the bowing effect [30-33]. Therefore, each CdTe grain has a unique band gap close to the CdS/CdTe interface that slightly tweaks each grain's absorption properties including the wavelength range of absorption. This only occurs ~0.5-1 μm from the interface where most of the S diffusion takes place, while the typical CdTe band gap of ~1.44 eV will be recovered as the S diffusion dissipates. A similar concentration of S segregation in CdTe grains interfacing the CdS has also been detected for a non-treated CdTe device (see Figure 3 in reference [22]). Therefore, significant S diffusion occurs within the grains during the closed space sublimation (CSS) growth, and cells not exposed to the CdCl_2 HT also experience significant S diffusion into the CdTe grain. When comparing these results to the EBIC images in Figure 2, it can be concluded that the S diffusion is not a major contributor to increasing the carrier collection at the CdS/CdTe interface because the interface is photoactively dead before the CdCl_2 treatment, even though there is significant S diffusion. The mechanism responsible for the enhanced J_{sc} and EBIC current at the CdS/CdTe interface is due to Cl segregation. A detailed evaluation of the mechanism will be revealed later.

The Na concentration profiles shown in **Figure 4** is the perfect example to demonstrate the significant advantage of the characteristic high resolution and sensitivity of APT, in which less than 1 at. % of Na can be detected within sub nm regions. Such low concentrations can be detected because Na only has one isotope, it does not evaporate as a complex molecule at this concentration, and its small mass makes the m/q peak appear before the heavier Cd and Te ions, where thermal tails increases the noise level. These factors make Na the most detectable element in the CdTe dataset. Detection of Na is significant because Na segregation in GBs and interfaces has proven to be a key mechanism in the improvement of CIGS solar cells, while the benefit or disadvantage of Na segregation is hardly discussed for CdTe solar cells [34,35].

To better understand the role of Na segregation, a GB close to the interface was run in the atom probe for a non-treated CdTe device (Figure 3 of reference [22]). The results show that approximately the same concentration of Na segregates in GBs close to the interface of CSS grown CdTe devices without any treatment compared to those with treatment. Therefore, the Na must diffuse from the glass substrate during the CSS growth. The EBIC measurements in Figure 2 have shown that after the Cu or CdCl_2 treatments, the carrier collection properties of the GBs are enhanced compared to the grains, while before either treatment, the GBs are non-photoactive and contain a large number of recombination centers [8,36]. Because Na is present in the GBs before and after these treatments, Na must not improve these regions of the solar cell. Whether or not Na segregation inhibits carrier collection at the GBs is unable to be determined from these sets of data. Therefore, Na segregation is not needed to make a high efficiency solar cell, but, at the same time, may not negatively affect the device performance.

3.2. CdS/CdTe Interface

The CdS/CdTe interface is of great interest because these two layers form the pn-junction responsible for creating the internal electric field to allow for proper solar cell operation. Previous STEM EELS experiments have been performed on the CdS/CdTe interface, but the noise level was too high to quantify the Cl segregation in this region [9]. By including APT results with STEM EELS data, an improved analysis of the CdS/CdTe interface was possible.

Figure 5 includes a (a) STEM EELS profile, (c) 22% S isosurface proxigram of (b) an extracted interface from grain 2, and (d) a simultaneously taken STEM annular dark field (ADF) and STEM EBIC profile of the CdS/CdTe interface. A local magnification effect of GBs in this material for APT was discussed previously. Naturally, one would assume that the same type of effect could occur for the CdS/CdTe interface, but the ~5 nm S profile of the APT data (Figure 5(c)) matches that of the STEM EELS data (Figure 5(a)), and therefore, the APT profile is a good representation of the material, and does not contain a local magnification artifact. This can be explained by the similar evaporation fields of CdS and CdTe and the z-direction evaporation of the CdS/CdTe interface, which will make the APT reconstruction more accurate compared to an orthogonal GB. Note that the STEM EELS and APT data show a rapid ~5 nm S diffusion with the S concentration dropping from ~45 at. % to ~5 at. % (depending on the grain) within ~5 nm. A second more widely known diffusion mechanism is not shown in its entirety due to the short length of the APT needle. In this second mechanism, S diffusion occurs over several 100's of nms into the CdTe grain from the CdS/CdTe interface [37,38]. Auger depth profiles presented by Enriquez *et al.* show >10% S ~200 nms inside the CdTe grain, while the APT data show that this S diffusion starts at an ~5% S concentration ~5nm from the interface. Compositional analysis using Auger depth profiling can be compromised by preferential sputtering, which isn't an issue with APT, making the APT experiment more reliable for the depth dependence of the S diffusion at the nanoscale. Both APT and STEM have revealed a rapid S diffusion mechanism in addition to the more commonly reported long diffusion. An APT 1D line profile of an untreated cell in reference [22] shows the long S diffusion in more detail due to the length of the needle.

By comparing the STEM ADF image to the STEM EELS profile (Figure 5(a)), it can be seen that the CdTe grain grows incoherently on top of the CdS grain (not epitaxially), in which there is a clear structural interface that occurs where S begins to diffuse in the STEM EELS profile. Therefore, most of the ~5 nm S diffusion occurs within the CdTe grain, in which the S concentration reaches a minimum of ~3-6 at. % ~5 nm into the CdTe grain. This is shown in more detail by Li *et al.* [9]. Unlike the STEM EELS dataset, the APT line profile reveals that there is significant Cl (~4 %) and minimal Na segregation (~0.2 %) around the interface, in which most of the Cl and Na is segregating within the CdTe grain. Proxigrams of all the APT CdS/CdTe interfaces shown in Figure 5(b) revealed Cl segregation ranging from ~3-6 % and Na segregation from 0.1-0.9 % depending on the interface, and therefore, the crystalline orientation of the interface plays a role in the solute segregation composition. More importantly, Cl substitution for Te ions within bulk CdTe is an n-type dopant, and therefore, a thin layer of the CdTe grain could be doped n-type close to the CdS if Cl substitutes Te in this region. To better understand the doping properties of the Cl segregation, a STEM EBIC experiment has been performed to directly image the junction position with respect to the CdS/CdTe interface, with the results presented in Figure 5(d).

Previous SEM EBIC average line profiles has revealed that the maximum current occurs in the vicinity of the CdS/CdTe interface, but the resolution of this technique is not high enough to resolve EBIC currents within the ~5nm Cl doping profile shown by APT [8]. Therefore, a higher resolution EBIC technique was needed (STEM EBIC). Cross-sectional

STEM EBIC is a much more challenging experiment than SEM EBIC due to the thin section of material, which was ~ 1 mean free path thick for the 200 keV beam used in this experiment (~ 100 nm) [39]. This significantly reduces the EBIC signal compared to SEM measurements, and is difficult to extract from the noise. Also, special sample preparation techniques needed to be developed to contact the anode and cathode separately without shorting the device (separated by ~ 4 μm), which is discussed in more detail in Figure 4 of reference [22]. The EBIC and ADF images shown in Figure 5(d) were taken during the same electron beam scan to allow for the correlation of the Z-contrast image with the currents generated by the electron beam. The corresponding EBIC and ADF line profiles along the same region show that the EBIC current continues to increase until an inflection point several nanometers inside the CdTe layer. Due to the near surface generation of carriers for the thin specimen, this inflection point is indicative of the location of the maximum internal electric field of the material (the pn-junction) [27], which can be linked to the Cl segregation in this region shown by the atom probe results. Therefore, APT has revealed a Cl dopant profile of a small portion of the CdTe grain close to the CdS/CdTe interface forming a thin homo-junction inside the CdTe absorber layer.

4. Conclusion

Atom probe tomography has been shown to be a useful tool for determining and quantifying solute segregation concentrations in GBs and interfaces for CdTe solar cells. This technique has been complemented with STEM, EBIC, and STEM-EBIC measurements to understand the role of certain atomic specie segregation and diffusion, such as Cl, Cu, S, and Na, in increasing the efficiency of these solar cells, and provide information about doping mechanisms at the nanoscale. It has been shown that Cl segregates with a higher concentration in random GBs close to the CdS/CdTe interface compared to those close to the back contact, while a significant amount of Cu segregates only in CdTe GBs away from the CdS/CdTe interface. Less than 1 at. % of Na segregation has been detected in the GBs close to the interface, which occurs during the CSS growth of the CdTe layer, and not during either treatment fabrication step. All GBs before either treatment are non-photoactive, and therefore, Na does not make GBs photoactive, while Cu and Cl activate the GBs. S diffuses during the CSS growth into the CdTe grains, such that a $\text{Cd}_x\text{S}_{1-x}\text{Te}$ alloy layer is formed several 100's of nm into the CdTe grains, where x can have a value between 0.90 and 0.95 close to the interface. The S content in this alloy layer reduces as the CdTe grain grows further away from the CdS/CdTe interface until it reaches $\sim 0\%$ close to the back contact. In addition to this slow S diffusion, there exists a rapid S diffusion that occurs mostly in the CdTe grain, in which the S content reduces from ~ 45 at. % to ~ 5 at. % in ~ 5 nm of material. Only the APT technique was capable of detecting and quantifying the Cl concentration in this region, which can dope a thin layer of the CdTe grain forming a homojunction a few nms inside the CdTe grain at the CdS interface. A STEM EBIC system was developed and used to confirm the pn-junction location being inside the CdTe grain. Overall, the combination of APT, STEM, EBIC, and STEM-EBIC techniques has shown to be a powerful tool to understand the underlying mechanisms of CdTe solar cell operation at the nanoscale.

Acknowledgements

This research was supported by the US Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy, Foundational Program to Advance Cell Efficiency (F-PACE), grant number DE-FOA-0000492, by the Office of Basic Energy Sciences (BES), ORNL's Materials Science and Engineering Division, and by ORNL's Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility.

- [1] M.A. Green, K. Emery, Y. Hishikawa, W. Warta, E.D. Dunlop, Solar cell efficiency tables (Version 45), *Prog. Photovolt: Res. Appl.* 23 (2014) 1–9.
- [2] M.J. Romero, D.S. Albin, M.M. Al-Jassim, X. Wu, H.R. Moutinho, R.G. Dhere, Cathodoluminescence of Cu diffusion in CdTe thin films for CdTe/CdS solar cells, *Appl. Phys. Lett.* 81 (2002) 2962.
- [3] L. Kranz, C. Gretener, J. Perrenoud, R. Schmitt, F. Pianezzi, F. La Mattina, P. Bloesch, E. Cheah, A.C. Abreve, C.M. Fella, H. Hagendorfer, T.J. ger, S. Nishiwaki, A.R. Uhl, S. Buecheler, A.N. Tiwari, Doping of polycrystalline CdTe for high-efficiency solar cells on flexible metal foil, *Nat. Commun.* 4 (1AD) 1–7.
- [4] J.V. Li, J.N. Duenow, D. Kuciauskas, A. Kanevce, R.G. Dhere, M.R. Young, D.H. Levi, Electrical Characterization of Cu Composition Effects in CdS/CdTe Thin-Film Solar Cells With a ZnTe:Cu Back Contact, *IEEE J. Photovolt.* 3 (2013) 1095–1099.
- [5] S.-H. Wei, S.B. Zhang, First-Principles Study of Doping Limits of CdTe, *Physica Status Solidi (B)*. 229 (2002) 305–310.
- [6] L. Kranz, C. Gretener, J. Perrenoud, D. Jaeger, S.S.A. Gerstl, R. Schmitt, S. Buecheler, A.N. Tiwari, Tailoring Impurity Distribution in Polycrystalline CdTe Solar Cells for Enhanced Minority Carrier Lifetime, *Adv. Energy Mater.* 4 (2014) 1301400.
- [7] M. Gloeckler, I. Sankin, Z. Zhao, CdTe Solar Cells at the Threshold to 20% Efficiency, *IEEE J. Photovolt.* 3 (2013) 1389–1393.
- [8] J.D. Poplawsky, N.R. Paudel, C. Li, C.M. Parish, D. Leonard, Y. Yan, S.J. Pennycook, Direct Imaging of Cl- and Cu-Induced Short-Circuit Efficiency Changes in CdTe Solar Cells, *Adv. Energy Mat.* 4 (2014) 1400454.
- [9] C. Li, J. Poplawsky, N. Paudel, T.J. Pennycook, S.J. Haigh, M.M. Al-Jassim, Y. Yan, S.J. Pennycook, S-Te Interdiffusion within Grains and Grain Boundaries in CdTe Solar Cells, *IEEE J. Photovolt.* 4 (2014) 1636–1643.
- [10] C. Li, Y. Wu, J. Poplawsky, T.J. Pennycook, N. Paudel, Grain-Boundary-Enhanced Carrier Collection in CdTe Solar Cells, *Phys. Rev. Lett.* 112 (2014) 156103.
- [11] C. Li, J. Poplawsky, Y. Wu, A.R. Lupini, A. Mouti, D.N. Leonard, N. Paudel, K. Jones, W. Yin, M. Al-Jassim, Y. Yan, S.J. Pennycook, From atomic structure to photovoltaic properties in CdTe solar cells, *Ultramicroscopy*. 134 (2013) 113–126.
- [12] T. Paulauskas, C. Buurma, E. Colegrove, Z. Guo, S. Sivananthan, M.K.Y. Chan, R.F. Klie, Atomic-resolution characterization of the effects of CdCl₂ treatment on polycrystalline CdTe thin films, *Appl. Phys. Lett.* 105 (2014) 071910.
- [13] D.R. Diercks, J. Li, J.D. Beach, C.A. Wolden, B.P. Gorman, Atom probe tomography for nanoscale characterization of CdTe device absorber layers and interfaces, *IEEE Photovoltaic Spec. Conf.*, 40th. (2014) 0085–0089.
- [14] P.-P. Choi, O. Cojocaru-Mirédin, D. Abou-Ras, R. Caballero, D. Raabe, V.S. Smentkowski, C.G. Park, G.H. Gu, B. Mazumder, M.H. Wong, Y.-L. Hu, T.P. Melo, J.S. Speck, Atom Probe Tomography of Compound Semiconductors for Photovoltaic and Light-Emitting Device Applications, *Microsc. Today*. 20 (2012) 18–24.
- [15] O. Cojocaru-Mirédin, P.-P. Choi, D. Abou-Ras, S.S. Schmidt, R. Caballero, D. Raabe, Characterization of Grain Boundaries in Cu(In,Ga)Se₂ Films Using Atom-Probe Tomography, *IEEE J. Photovolt.* 1 (2011) 207–212.
- [16] D.J. Larson, D.A. Reinhard, T.J. Prosa, D. Olson, D. Lawrence, P.H. Clifton, R.M. Ulfig, T.F. Kelly, V.S. Smentkowski, Atom Probe Tomography Analysis of Grain Boundaries in CdTe, *Microsc Microanal.* 18 (2012) 928–929.
- [17] J. Li, D.R. Diercks, T.R. Ohno, C.W. Warren, M.C. Lonergan, J.D. Beach, C.A. Wolden, Controlled activation of ZnTe:Cu contacted CdTe solar cells using rapid

- thermal processing, *Sol. Energy Mater. Sol. Cells.* 133 (2015) 208–215.
- [18] D.R. Diercks, B.P. Gorman, Nanoscale Measurement of Laser-Induced Temperature Rise and Field Evaporation Effects in CdTe and GaN, *J. Phys. Chem. C.* (2015) 150824150956008–9.
 - [19] D.J. Larson, T.J. Prosa, R.M. Ulfig, B.P. Geiser, T.F. Kelly, *Local Electrode Atom Probe Tomography*, Springer, New York, NY, 2013.
 - [20] M.K. Miller, R.G. Forbes, *Atom Probe Tomography: The Local Electrode Atom Probe*, Springer, New York, NY, 2014.
 - [21] K. Thompson, D. Lawrence, D.J. Larson, J.D. Olson, T.F. Kelly, B. Gorman, In situ site-specific specimen preparation for atom probe tomography, *Ultramicroscopy.* 107 (2007) 131–139.
 - [22] J.D. Poplawsky, C. Li, N.R. Paudel, W. Guo, Y. Yan, S.J. Pennycook, Methods for STEM EBIC and Atom Probe Tomography of the CdS/CdTe Interface in CdTe Solar Cells, *Data in Brief.* (2015) 1–5.
 - [23] N.R. Paudel, Y. Yan, Fabrication and characterization of high-efficiency CdTe-based thin-film solar cells on commercial SnO₂:F-coated soda-lime glass substrates, *Thin Solid Films.* 549 (2013) 30–35.
 - [24] J.R. Michael, P.G. Kotula, Low Energy Ga⁺ and Ar⁺ Ion Milling for Improved EBSD Sample Preparation, *Microsc Microanal.* 14 (2008) 976–977.
 - [25] J.F. Ziegler, M.D. Ziegler, J.P. Biersack, SRIM–The stopping and range of ions in matter (2010), *Nucl. Instrum. Methods Phys. Res., Sect. B.* 268 (2010) 1818–1823.
 - [26] M. Nichterwitz, T. Unold, Numerical simulation of cross section electron-beam induced current in thin-film solar-cells for low and high injection conditions, *J. Appl. Phys.* 114 (2013) 134504.
 - [27] H.P. Yoon, P.M. Haney, D. Ruzmetov, H. Xu, M.S. Leite, B.H. Hamadani, A.A. Talin, N.B. Zhitenev, Local electrical characterization of cadmium telluride solar cells using low-energy electron beam, *Sol. Energy Mater. Sol. Cells.* 117 (2013) 499–504.
 - [28] O.C. Hellman, J.A. Vandenbroucke, Analysis of three-dimensional atom-probe data by the proximity histogram, *Microsc. Microanal.* 6 (2000) 437–444.
 - [29] F. Vurpillot, A. Bostel, D. Blavette, Trajectory overlaps and local magnification in three-dimensional atom probe, *Appl. Phys. Lett.* 76 (2000) 3127–4.
 - [30] N.R. Paudel, Y. Yan, Enhancing the photo-currents of CdTe thin-film solar cells in both short and long wavelength regions, *Appl. Phys. Lett.* 105 (2014) 183510.
 - [31] K. Ohata, J. Saraie, T. Tanaka, Optical Energy Gap of the Mixed Crystal CdS_xTe_{1-x}, *Jpn. J. Appl. Phys.* 12 (1973) 1641–1642.
 - [32] N.W. Duffy, L.M. Peter, R.L. Wang, Characterisation of CdS|CdTe heterojunctions by photocurrent spectroscopy and electrolyte electroreflectance/absorbance spectroscopy (EEA/EER), *J. Electroanal. Chem.* 532 (2002) 207–214.
 - [33] K. Wei, F.H. Pollak, J.L. Freeouf, D. Shvydka, A.D. Compaan, Optical properties of CdTe_{1-x}S_x (0≤x≤1): Experiment and modeling, *J. Appl. Phys.* 85 (1999) 7418.
 - [34] A. Rockett, J.S. Britt, T. Gillespie, C. Marshall, C. Marshal, M. Al-Jassim, F. Hasoon, R. Matson, B. B, Na in selenized Cu(In, Ga)Se₂ on Na-containing and Na-free glasses: distribution, grain structure, and device performances, *Thin Solid Films.* 372 (2000) 212–217.
 - [35] A. Rockett, The effect of Na in polycrystalline and epitaxial single-crystal CuIn_{1-x}Ga_xSe₂, *Thin Solid Films.* 480–481 (2005) 2–7.
 - [36] O. Zywitzki, T. Modes, H. Morgner, C. Metzner, B. Siepchen, B. Späth, C. Drost, V. Krishnakumar, S. Frauenstein, Effect of chlorine activation treatment on electron beam induced current signal distribution of cadmium telluride thin film solar cells, *J.*

- Appl. Phys. 114 (2013) 163518.
- [37] J.P. Enríquez, E.G. Barojas, R.S. Gonzalez, U. Pal, S and Te inter-diffusion in CdTe/CdS hetero junction, Sol. Energy Mater. Sol. Cells. 91 (2007) 1392–1397.
- [38] S.G. Kumar, K.S.R.K. Rao, Physics and chemistry of CdTe/CdS thin film heterojunction photovoltaic devices: fundamental and critical aspects, Energy Environ. Sci. 7 (2014) 45–102.
- [39] R. Egerton, Electron Energy-Loss Spectroscopy in the Electron Microscope, Springer Science & Business Media, 2011.

Figure 1. (a) The top and (b) side view of a 3 dimensional reconstructed APT dataset containing a triple point CdTe GB that is terminated at the CdS/CdTe interface. Na, Cl, S, and Te ions are displayed along with a 22% magenta S iso-concentration surface, which separates the CdS and CdTe layers. (c) A STEM ADF image of a CdTe GB terminating at the CdS interface with an outline of an APT needle to demonstrate the location of the APT needle in the device. This image is not the same GB shown in (b). (d) The APT Cl concentration profiles of each GB within the dataset displayed in (a) and (b), showing slight variations in the Cl content. (e) A STEM EELS profile of a CdTe GB within a fully treated CdTe device, and (f) an APT Cl concentration profile of a GB close to the back contact.

Figure 2. EBIC images of a (a) non-treated, (b) Cu treated, and (c) CdCl₂ heat-treated CdTe devices. The scale bars in the EBIC images are 3 μ m and are located at the CdS/CdTe interface.

Figure 3. The APT S concentration profiles across the three GBs shown in Figure 1 (a). The sensitivity and resolution of APT allow for the detection of ~1-3% S variations between grains as well as ~1% S segregation at the GBs.

Figure 4. The APT Na concentration profiles across the three GBs shown in Figure 1 (a). The sensitivity and resolution of APT allow for the detection of <1% Na segregation within each GB.

Figure 5. (a) A STEM-EELS profile of the CdS/CdTe interface showing an ~ 5 nm S diffusion profile that occurs mostly inside the CdTe grain, also shown by Li *et al.* ^[9] (b) The extracted region of interest that was used to make the proximity histogram shown in (c). The APT S, Cl, and Na profiles from the interface extracted from the APT dataset. (d) Line profiles taken from simultaneous collection of STEM-EBIC and ADF images during the same electron beam raster. The red dashed line and arrow indicate the inflection point of the EBIC line profile, which identifies the pn-junction. The black dashed line and arrow indicate the approximate location of the CdS/CdTe interface verified by the Z-contrast ADF image. The insets in (d) are the corresponding EBIC and ADF images from which the line profiles were taken.

Figure 2

Figure 3

Figure 5