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Cd doping at PVD-CdS/CuInGaSe₂ heterojunctions

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Abstract

We report on direct evidence of Cd doping of the CuInGaSe₂ (CIGS) surface in physical vapor deposited (PVD) CdS/CIGS heterojunctions by scanning transmission electron microscopy (STEM) and related techniques. We find Cd doping of the CIGS nearsurface region regardless of the presence or absence of Cu rich domains in the CdS for both zinc-blende (zb) and wurtzite (wz) CdS. However, we find that the Cd penetrates much farther into the CIGS when Cu-rich domains are present in the CdS. This suggests that Cu exchanges with Cd, increasing the concentration gradient for Cd in the CIGS and thus driving Cd into the CIGS surface. The Cd doping is clearly resolved at atomic resolution in aberration-corrected STEM-high angle annular dark field images. In zb-CdS/CIGS heterojunctions, Cd is shown to substitute for both Cu and Ga atoms, while in wz-CdS/CIGS heterojunctions Cd seems to predominantly occupy Cu sites. Cd doping in the CIGS surface layer suggests the formation of a p-n homojunction in the CIGS, which may account for the high device efficiencies, comparable to CBD-CdS/CIGS processed structures.

1. Introduction

CuInGaSe₂ (CIGS)-based thin film solar cells have been given considerable attention for several decades due to their long term stability and high solar conversion efficiencies[1-5]. Normally a thin buffer layer is deposited on the CIGS surface to form an expected p-nheterojunction and protect the CIGS surface from potential radiation damage induced by subsequent deposition of ZnO window layer. Chemical bath deposited (CBD) CdS is the most common and recognizably successful buffer layer employed in CIGS solar cells. The CBD process is simple and fast. However, it is incompatible with large scale in-line "dry" vacuum based film deposition technologies and generates a large amount of chemical waste. Thus, vacuum based deposition, e.g. physical vapor deposition (PVD) of CdS, would be favorable. Indeed, a PVD-CdS/CIGS flexible solar module with an aperture area of 7583 cm² from MiaSolé demonstrated a 16.3% efficiency under global AM1.5 solar illumination (999.3 W/m²) (measured by Fraunhofer ISE)[6]. Other groups typically have found PVD-CdS/CIGS solar cells to be inferior in efficiency compared to CBD-CdS/CIGS solar cells. Some authors[7] argued that the possible poorer coverage of PVD-CdS on CIGS surface may be responsible. Abou-Ras et al.[8] suggested that the absence of a Cd doping layer on the CIGS surface in PVD-CdS/CIGS heterojunctions, and thus the lack of a p-n homojunction, may explain the efficiency deficit. Indeed, Ramanathan et al. [9, 10] showed that Cd insertion into the CIGS surface may hold the key to the success of CBD-CdS/CIGS solar cells by comparing the efficiencies of a series of CIGS solar cell devices in which the CIGS surfaces were treated in different CBD solutions. Although the Cd-doped CIGS surface in CBD-CdS/CIGS junction has been experimentally verified [11, 12], no direct evidence of Cd doping on the CIGS surface in PVD-CdS/CIGS is available.

In this paper, we report the results of an extensive investigation of PVD-CdS/CIGS heterojunctions in samples fabricated under a single set of deposition conditions in the MiaSolé production line. Different regions of the heterojunctions exhibit two different CdS crystal structures (wurtzite and zincblende) and these structures may have either high or low Cu diffusion into the CdS from the CIGS. We have previously reported on the Cu distributions in similar samples [13]. This paper focuses on the distribution of Cd in regions dominated by each of these behaviors. Here, we present direct evidence of Cd doping in the CIGS near-surface region regardless of the presence of Cu rich domains in the CdS buffer layer for both crystal structures of CdS. We found that the Cd doping depth in the CIGS is much larger when Cu domains are present in the CdS, implying Cu migration into the CdS promotes Cd diffusion into the CIGS surface. Evidence of Cd migration into the CIGS surface in CBD-CdS/CIGS heterojunctions is also presented for comparison, although the Cd concentration is much lower than that in the CIGS surface in the PVD-CdS/CIGS junctions. The greater extent of Cd doping in the CIGS near-surface region in PVD-CdS/CIGS heterojunctions may contribute to formation of high efficiency devices similar to the beneficial effect of Cd doping in CBD-CdS/CIGS solar cells.

2. Experiment

The PVD-CdS/CIGS solar cell samples were provided by MiaSolé from their production line. All layers that comprise MiaSolé's solar cells are deposited sequentially onto a flexible stainless steel substrate in a single pass in an all-PVD process system without a vacuum break. One difference of this approach compared to most other manufacturing methods is the replacement of the CBD-CdS layer with a PVD-CdS deposition. The sample studied here was processed in MiaSolé's production equipment using process settings similar to manufacturing settings.

For comparison, stainless steel samples coated up to the CIGS absorber step identically to those with PVD-CdS were removed from the deposition tool and coated with CdS by CBD. The CBD process was performed in an aqueous solution of CdSO₄, NH₂CSNH₂, and NH₄OH, at a temperature of 65 °C for 16 min. The samples were rinsed in water, dried, and finished with a ZnO deposition sequence following a process similar to that used for the PVD samples. Every effort was made to ensure that the samples with CBD-CdS were as nearly identical to those with PVD-CdS as possible.

TEM samples were prepared by a lift-out technique in an FEI Focused Ion Beam instrument Helios Nano Lab 600i. A low voltage and small current of the Ga ion beam (1 kV, 8 *p*A) was used to clean the surface damage and remove any Ga ion beam implantation following the higher voltage and current ion beam milling step used to produce the sample. More detailed milling parameters can be found in Ref. [13]. The samples were stored in a dedicated TEM sample preservation capsule filled with dry N₂ to protect from gradual oxidation. Before being loaded into the TEM, the samples were further cleaned using a Fischione Model 1040 NanoMill specimen preparation system to further minimize the Ga-induced surface amorphous layer and other damage. The TEM sample was tilted to a [021] CIGS zone axis where clear high resolution images of the interface were obtained without any indication of overlap of the CdS and CIGS. In these samples, the CdS typically grows epitaxially on the CIGS, so a lattice image of the CIGS also provides a lattice image of the CdS. STEM-EDS maps were acquired in a FEI Titan TEM operating at 200kV at the National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley

National Lab. The EDS detector is a Super-X quad windowless detector with a collection solid angle of 0.7 steradian enabling elemental mapping, typically in several minutes. Atomic resolution STEM-high angle annular dark field images were collected in a probe-aberration-corrected JEM ARM 200CF at the University of Illinois at Chicago. The inner and outer acceptance angles were estimated to be 68 mrad and 280 mrad, respectively. EDS line profiles were constructed from areas selected from the lattice images so that composition and microstructure could be matched.

3. Results and discussion

3.1 CdS with Cu rich domains

Figure 1 shows STEM-EDS maps of epitaxial zinc-blende (zb) CdS on the CIGS with the same epitaxial relationship as reported in our previous paper[14]. A Cu rich layer about 10 nm thick is seen in the CdS buffer layer near the junction (Fig. 1b). In the PVD-CdS/CIGS heterojunctions we studied, Cu rich domains are consistently observed and sometimes can completely replace Cd, forming a pure copper sulfide compound[15]. The compound is very close to Cu₂S stoichiometry and its lattice is fully coherent with that of the CdS. At the same time, a Cd-containing region is found to extend beyond the S signal into the CIGS surface (Fig. 1c). Our results differ from the observations by Abou-Ras *et al.* [8], where no Cd was found on the CIGS side of the heterojunction. In Fig. 1e there is an O-containing region in the CIGS, roughly equivalent to the Cd-containing region in the CIGS. The O doping probably results from diffusion into the CIGS surface when the CIGS film was exposed to sputtering gas containing a mixture of O₂ and Ar. The presence of O in the CIGS surface is also confirmed by Auger electron spectroscopy (not shown).

Figure 2 shows an integrated composition line profile obtained from the area designated by the box outlined in white in Fig. 1b. The O and In signals are intentionally omitted to enhance the clarity of the other elements of interest. If the O signal is taken into account, the total anion concentrations (Se and O in the CIGS, and S and O in the CdS) in both layers are found to be \sim 50%. The region to the left of the vertical dotted line is CIGS with residual Cd. The two horizontal dotted lines mark the baselines of Cu and Ga in the bulk CIGS. The gradual increase of Cd concentration on the CIGS side is accompanied by the Cu and Ga concentrations decreasing, with Cu decreasing much more than Ga. This is very similar to the report by Cojocaru-Miredin et al.[16] for CBD- CdS where, using atom probe tomography, they found a Cu and Ga depleted region about 1 nm thick in the CIGS that was doped by Cd. However, they found no Cu rich domains in the CdS. The doping depth of Cd in the CIGS that we find is at least 15 nm, much larger than the 1 nm reported in Ref. [16]. Our results suggest that Cd ions may reside on Cu sites, forming Cd_{Cu}^+ , which act as donors and convert the *p*-type CIGS to *n*-type. In addition, our EDS line profiles suggest the substitution of Cd for Ga as well, forming Cd_{Ga} , which is an acceptor. Considering that the Cu concentration is about twice as high as Ga and Cu is more depleted, the overall doping effect would still yield an *n*-type CIGS surface.

We also investigated the wurtzite (wz) CdS phase with Cu rich domains. Figure 3 shows STEM-EDS maps of one such area with Cu domains (Fig. 3a). As in the case of the zb-CdS phase, there is appreciable Cd concentration in the CIGS near its surface for wz-CdS overlayers (Fig. 3b). There is also an O signal that seems to follow the Cd signal. A composition line profile from the white box is displayed in Fig. 4, where the Cd doping depth into the CIGS is seen to be ~18 nm. The Ga signal doesn't show much depletion,

contrary to the behavior of the zb case. Our theoretical calculations suggest that this difference can be explained by the difference in migration barriers of Ga interstitials in the two different phases[13]. Also in contrast to the zb-CdS/CIGS case, Cd ions apparently exclusively occupy Cu sites in the wz-CdS.

3.2 CdS with no Cu rich domains

In addition to the Cd doped CIGS surface accompanying Cu domains in the CdS phase, we also find that even in the absence of Cu migration into the CdS buffer, Cd can be present in the CIGS surface layer, but with much less doping depth. This is the case when significant O_2 is present during CdS deposition. Figure 5a displays a low-magnification STEM-high angle annular dark field (HAADF) image of zb-CdS/CIGS heterojunction where a bright band in the CIGS surface is clearly seen as indicated by two arrows, implying that the bright band should have higher average atomic number, *Z*, than the CIGS below, since image intensity in the HAADF image follows a dependence of Z^{1.7[17]}.

To find out the underlying chemical difference responsible for the bright band, a composition EDS line profile was measured (Figure 5b). The two dotted lines mark the pure CIGS surface where the Se concentration is constant and Cd is observable above background. It is also worth noting that the Cu and Ga concentrations decrease while the Cd concentration increases, suggesting Cd resides on both Cu and Ga sites. This is in good agreement with the observation of Cd doping in CBD-CdS/CIGS by Cojocaru-Miredin *et al.*[16]. However, the Cd doping depth reported here is about 5 nm, larger than the 1 nm reported in Ref. [16]. Our results suggest that chemical migration behaviors similar to those in CBD-CdS/CIGS occurred in the PVD-CdS/CIGS heterojunction. The fact that the Cd doping in the CIGS surface occurs even with no Cu rich domains in the CdS phase suggest

that Cu vacancies are formed prior to the deposition of the CdS. A Cu depleted CIGS surface could be formed due to the reconstruction of the CIGS surface to reduce the electric dipole energy, as supported by density functional theory calculations by S. B. Zhang *et al.* [18]. The Cd doping depth in the CIGS surface, about 5 nm, is much smaller than the 15 nm in case of zb-CdS with Cu domains discussed in the previous section, suggesting that Cu migration into the CdS can promote Cd doping in the CIGS. Presumably the Cd ions fill Cu vacancies, and greater Cu migration into the CdS leaves more Cu vacancies behind.

Figure 6a depicts atomic resolution HAADF images along the [021] zone axis of the CdS/CIGS heterojunction, from a region containing the bright band in Fig. 5a. The Cd doped CIGS surface region of about 5 nm thickness is identified based on the intensity variation and the EDS compositional line profile in Fig. 5b. The interface between the CdS and the Cd doped CIGS is sharp and free of any dislocations. Filtered lattice fringes using a pair of (-111) CdS diffraction spots (these overlap with (112)-type reflections from the CIGS) are shown in Fig. 6b where the line indicates the interface. No misfit dislocations are found along the interface. In addition, the fringes are very coherent across the CdS and CIGS interface and of almost equal interplanar distance, suggesting good lattice match of the CdS and CIGS. The incorporation of O into the CdS enables large flexibility in tuning the lattice constant of the CdS and helps to form a coherent and defect-free hetero-interface with the CIGS. Further, we note that there is an array of dark domains about 7 nm away from the hetero-interface as shown by circles in Fig. 6a. EDS quantification suggests a composition in the marked area of: $(15 \pm 2.1)\%$ O, $(38 \pm 1.6)\%$ S, $(47 \pm 1)\%$ Cd. These highly oxidized CdS domains are well crystallized and show coherent lattice fringes with the surrounding CdS matrix. As indicated by the circles in Fig. 6b, a Frank dislocation loop is formed inside the dark domain circled in Fig. 6a. The formation of the dislocation loop may be related to the agglomeration of O atoms along the {111} type close-packed Cd(O,S) planes. Another individual dislocation is also found in the CdS as shown by an arrow in Fig. 6b.

Figure 7 presents an enlarged HAADF image of the area shown in Fig. 6a to give more insights into the CdS doped CIGS layer. The image is deliberately colored in DigitalmicrographTM to highlight each layer according to the intensity variation. In the CdS layer, columns of Cd atoms produce the majority of the intensity with tiny tails on one side representing the O and S atoms. The dumb-bell structure of the atom columns in the CdS is clearly observed in a corresponding STEM-annular bright field (ABF) image (not shown). This mode is more sensitive for light atoms [19, 20] and shows the reverse contrast to the image in Figure 7. The Cd doped CIGS layer, roughly marked by two lines, is about 5.5 nm thick, consistent with the EDS line profile shown above. The substitution of Cd for Cu and Ga, as indicated by the EDS composition profile, gives higher intensity in the HADDF image compared to the undoped CIGS (discussed below).

Cd doping of the CIGS surface is also confirmed in wz-CdS/CIGS heterojunctions with no Cu domains in the CdS. Figure 8a displays a typical atomic resolution HAADF image where the CdS shows complete epitaxy on {112} CIGS surface with the same epitaxial relationship as described previously for wz-CdS on CIGS[14]. The difference in height of the CIGS {112} surface across this image is about 2.4 nm, which is about seven CIGS {112} plane spacings. The height difference is from atomic steps that contribute to the strain relaxation between the wz-CdS phase and tetragonal CIGS. We identified six dislocations inside the wz-CdS, indicated by circles in Fig. 8a, by applying image filtering using the $(0002)_{CdS}$ and $\{112\}_{CIGS}$ contributions to the FFT patterns. While these dislocations contribute to misfit strain relaxation, most of these dislocations are not located at the interface and so should not affect carrier collection in the CIGS.

Figure 8b is a composition line profile extracted from the wz-CdS/CIGS heterojunction shown in Fig. 8a. The two dotted lines denote the Cd-doped CIGS region. Here, the concentration of Se and Ga are constant, but Cu is reduced. This is indicative of Cu vacancy sites filled by Cd atoms. The average Cd doping depth is at least 8 nm, determined from the EDS profile and the HAADF image (Fig. 8a) where Cd doped CIGS shows slightly higher image intensity. The doping depth (8 nm) here is also smaller than that in the CIGS surface in the wz-CdS/CIGS heterojunction with Cu rich domains (18 nm), supporting our observation that Cu migration from the CIGS into wz-CdS facilitates Cd doping of the CIGS surface.

3.3 Comparison with CBD-CdS

To put the above results in context, we compare the results for film stacks using identical absorber layers but with CBD-CdS rather than PVD-CdS. Figure 9a displays a typical high resolution TEM image of a CBD-CdS/CIGS heterojunction where CdS exhibits nanocrystalline structure and poor epitaxy on the CIGS surface compared to the PVD process. Figure 9b shows a STEM-EDS line scan across a CBD-CdS/CIGS heterojunction. We observe O in both the CIGS surface and CdS buffer layer (not shown). Cu was also found in the CBD-CdS, consistent with previous reports [11, 21], but in a more patchy manner rather than being organized into uniform Cu-rich layers[13]. In contrast to the PVD samples, a much lower concentration of Cd (4% vs. at least 10%, close to the PVD-CdS/CIGS interface) was found to be present in the CIGS. This difference could be

attributed to the poor crystallinity and epitaxy of CBD-CdS on the CIGS surface and/or lower growth temperature for the CBD process (Although the substrate temperature during PVD-CdS growth was not monitored it is likely to be higher than CBD-CdS). Another striking feature is that the S signal extends far into the CIGS, which is not seen in the PVD-CdS/CIGS heterojunctions. Sulfur diffusion into the CIGS was first observed by Heske *et al.*[22] where they found by using surface-sensitive X-ray emission and photoelectron spectroscopy that S and Se ions can undergo some degree of ion-exchange.

Recently it was shown [23] that the CBD-CdS/CIGS solar cells fabricated on flexible polyimide substrate can deliver 20.4% efficiency. The authors argued that the key of the success is that KF post deposition treatment of the CIGS surface before deposition of CBD-CdS results in a Cu and Ga depleted CIGS surface region where a p-n homojunction is generated by Cd incorporating into Cu vacancy sites and thus forming Cu_{Cd}^+ donors. Apparently Our PVD-CdS process is producing a CdS/CIGS hetero-interface similar to the KF post deposition treatment of the CBD-CdS/CIGS solar cells[23].

4. Conclusions

In summary, we provide the first direct evidence of a Cd doped CIGS surface layer at PVD-CdS/CIGS heterojunctions by STEM-EDS and STEM-HAADF. Cd doping in the CIGS surface layer occurred regardless of the presence of Cu rich domains in the CdS. However, Cu migration from the CIGS into the CdS enhances the Cd doping in the CIGS surface for both zb-CdS and wz-CdS phases. Atomic resolution STEM-HAADF images provided detailed supporting structural information of the Cd doped CIGS layers. For

comparison, STEM-EDS line profiles of a CBD-CdS/CIGS heterojunction also showed Cd doping of the CIGS surface layer, but at much lower concentration than in the PVD samples. Our results are in sharp contrast to the observation by Abou-Ras *et al.* [8], who found no Cd in the CIGS surface in a PVD-CdS/CIGS heterojunction. The disparity of results suggests that elemental intermixing between the CdS and CIGS can be very sensitive to the details of the growth conditions and should be discussed on a case by case basis. The Cd doped CIGS surface, which is believed to play an important role in the performance of CBD-CdS/CIGS heterojunctions, is demonstrated in our PVD-CdS/CIGS heterojunctions and may account for the high efficiency of the PVD-CdS/CIGS solar cells fabricated using this process.

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Figures and captions



Figure 1. STEM-EDS maps of a zb-CdS/CIGS heterojunction showing Cu rich domains in CdS (b) and Cd doping in the CIGS surface layer (c). Note that oxygen is present on the CIGS surface (d) as well.



Figure 2. Composition line profiles extracted from the white box in Fig. 1b. The profiles of O and In are not shown for better display of the other profiles. Two horizontal dotted lines mark the baseline concentrations of Cu and Ga in the CIGS and the region to the left of the vertical line is nominally CIGS. Note that Cu and Ga concentration decreases with Cd concentration increasing in the CIGS, suggesting Cd is substituting for both Cu and Ga. The doping depth of Cd on the CIGS surface is at least 15 nm.



Figure 3. STEM-EDS maps of a wz-CdS/CIGS heterojunction showing Cu rich domains in CdS (a) and Cd doping in CIGS surface layer (b). Note in (c) that oxygen is present on the CIGS surface.



Figure 4. Composition line profiles extracted from the box in Fig. 3a. Two horizontal dotted lines marks the baselines of Cu and Ga in the CIGS and the region to the left of the vertical line is nominally CIGS. Note that Cu concentration decreases (Ga also slightly decreases close to the vertical line) with Cd concentration in the CIGS increasing, suggesting Cd mainly substitutes for Cu. The doping depth of Cd in the CIGS is about 18 nm.



Figure 5. Low magnification STEM-HAADF image (a) of a zb-CdS/CIGS heterojunction with no Cu domains in the CdS. Higher intensity in the bright band denoted by the two arrows indicates a higher average atomic number than the CIGS below. (b) Composition line profiles from the zb-CdS/CIGS heterojunction indicate Cd doping to ~5 nm depth in the CIGS.



Figure 6. An atomic resolution HAADF image (a) of the zb-CdS/CIGS heterojunction shown in Fig. 5a. The line indicates the interface between the CdS and Cd doped CIGS surface layer in which the intensity is slightly higher than in the undoped CIGS layer below. The white dotted circle marks a highly oxidized domain, which is coherent with the surrounding CdS matrix. (b) Filtered lattice fringes using one pair of {111} reflections of CdS and {112} reflections of CIGS (their lattice spacings are almost the same and the diffraction spots in FFT patterns overlap) shows a Frank dislocation loop in the highly oxidized domain. The arrow indicates another individual dislocation in the CdS.



Figure. 7 Colored HAADF image showing detail of the zb-CdS/CIGS heterojunction in Fig. 6. Two white lines mark the Cd doped CIGS surface region where the image intensity is higher than the undoped CIGS below.



Figure 8. Atomic resolution HAADF image (a) of a wz-CdS/CIGS heterojunction. The red line and yellow line indicate a 2.4 nm high step at the heterojunction. Six dislocations in the CdS are circled. (b) Corresponding compositional line profiles. Two horizontal dotted lines mark the baselines of Cu and Ga in the CIGS and the region defined by the two vertical lines indicates the Cd doped CIGS layer.



Figure 9. (a) A typical high resolution TEM image of a CBD-CdS/CIGS heterojunction showing the poor crystallinity and epitaxy of CBD-CdS compared to the PVD-CdS materials. (b) STEM-EDS line profiles of a CBD-CdS/CIGS heterojunction. Cd is found in the CIGS surface layer at much lower concentration than in the PVD-CdS/CIGS junctions. Note that unlike in the PVD samples, the S signal persists deep into the CIGS ~5 at. %.

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