

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 near-surface 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 [1–6]. Normally a thin buffer layer is deposited on the CIGS surface to form an expected *p-n* heterojunction 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) [7]. Other groups typically have found PVD-CdS/CIGS solar cells to be inferior in efficiency compared to CBD-CdS/CIGS solar cells. Some authors [8] argued that the possible poorer

coverage of PVD-CdS on CIGS surface may be responsible. Abou-Ras et al. [9] 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. [10,11] 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 [12,13], 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 [14]. This paper focuses on the distribution of Cd in regions dominated by each of these behaviors. Here, we present direct evidence of Cd doping

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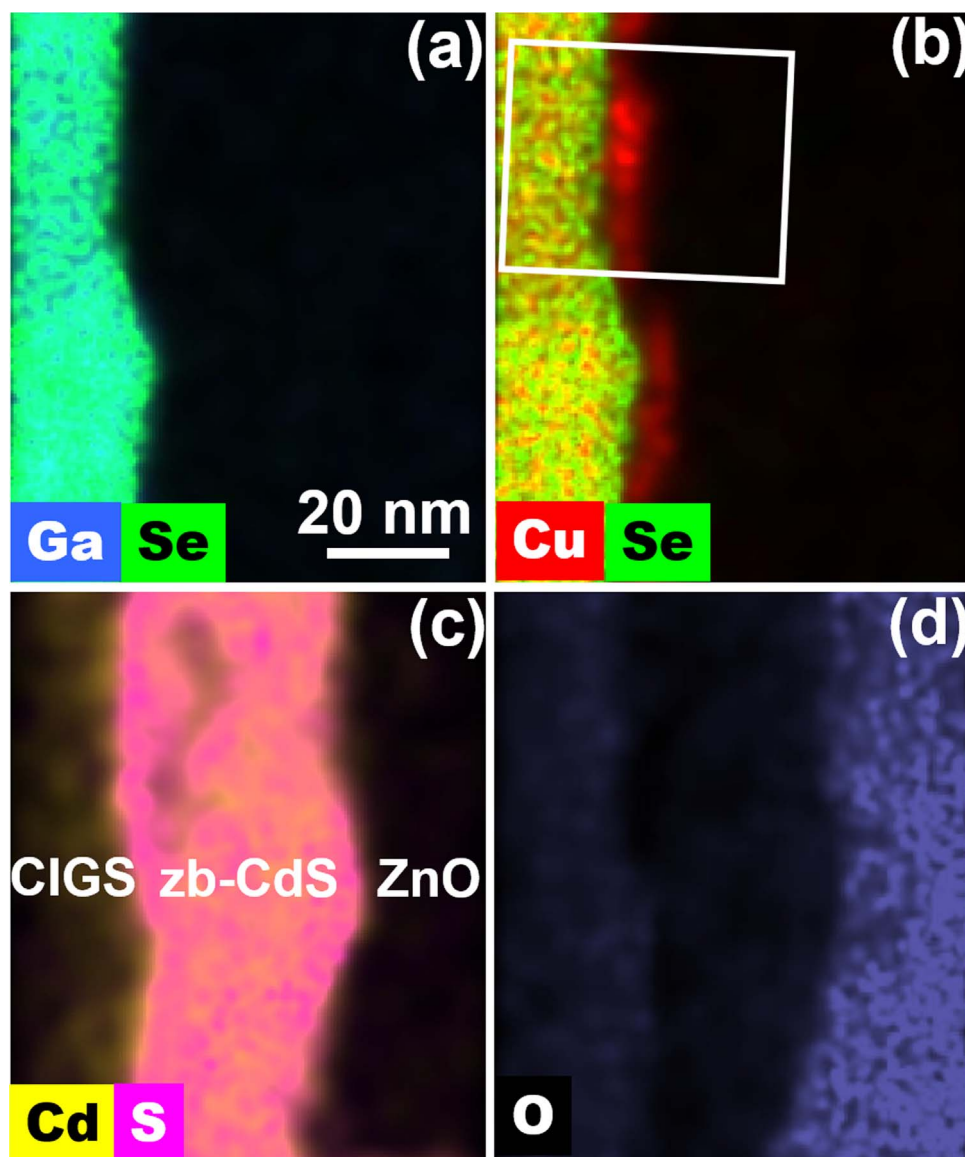


Fig. 1. STEM-EDS maps of a zb-CdS/CIGS heterojunction showing Cu rich domains in CdS (b) and Cd doping in the CIGS surface layer (c). Note that oxygen is present on the CIGS surface (d) as well.

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 [15].

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 pA) 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. [14]. 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

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