Beyond 11% efficient Cu$_2$ZnSn(Se,S)$_4$ thin film solar cells by cadmium alloying

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ABSTRACT

Cd-alloying CZTSSe (sulfur about 1%) film was prepared by selenizing CZTS precursor with CdS on the top. The XRD and Raman spectra indicated that Cd alloyed into CZTSSe lattice and the calculated Cd/(Cd + Zn) ratio was 0.13. Some small grains with increased Sn/Cu ratio existed near back contact. Grain growth enhanced after Cd alloying, resulting in a more homogenous Sn/Cu ratio along thickness direction. SIMS profile of solar cell confirmed Cd incorporation in bulk while also a higher Cd content near absorber surface. Corresponding to microstructure, electrical properties were also modified by Cd alloying. In the absorber bulk, the trap energy levels and density of Cd-alloying sample were 38 meV and 1.47 $\times 10^{16}$ cm^{-3}, while 118 meV and 6.98 $\times 10^{15}$ cm^{-3} for reference sample. The dominant recombination was in bulk, instead of at interface as in reference sample. Back contact was improved owing to a smaller series resistance and a smaller rise of R$_s$ at low temperature. J-V curve observed an improvement of V$_{oc}$ and J$_{sc}$. The EQE curve indicated sharper absorption edges and band gap reducing from 1.00eV to 0.95 eV. As a consequence, a highest efficiency of 11.2% for CZTSSe solar cells was achieved.

1. Introduction

Kesterite Cu$_2$ZnSn(SSe)$_4$ (CZTSSe) is a promising absorber for thin film solar cells due to the advantages of excellent photovoltaic performance in theory and earth abundant elements [1,2]. The band gap of CZTSSe can be linearly tuned from 1.5eV to 1.0 eV by varying S/(S + Se) ratio [3]. Currently, the record efficiency for CZTSSe (sulfur around 20%) and CZTSe solar cells are 12.6% [4] and 11.6% [5], respectively, which are still relatively low compared to the 22.6% of CIGSe [6] and 22.1% of CdTe thin film solar cells [7].

The performance of kesterite thin film solar cells is limited in three aspects: 1) interface between buffer layer and absorber, 2) bulk defect and grain boundary in absorber, and 3) interface between absorber and Mo back contact [8]. Among them, the properties of absorber should be the foundation. Apart from optimizing process parameters, adding element for alloying could also be effective to modify the properties of absorber. Cadmium is such a promising element. Previous reports on Cd in thin film solar cells mainly lie in chalcopyrite CIGSe [9,10], CISe [11] and CGSe [12]. During chemical bath deposition (CBD) of CdS, Cd

could diffuse into absorber in a depth from 10 nm to 100 nm, forming n-type Cu-poor layer. Thus, a buried homo-junction would form near the surface of absorber, reducing interface defect at hetero-junction. There are just a few reports on Cd in kesterite CZTSSe. In contrast, it is focusing on alloying Cd into absorber. In the reported work, Cd alloying seems to enhance grain growth [13–15] and alter effective doping density [13,14]. A reduction of ZnS phase [13] and band tail [15] in CZTS is also reported.

The efficiency of CZTSSe solar cells could be boosted by optimizing the content of Cd alloying. Since Cd is believed to occupy Zn site in kesterite absorber, Cd content is described by Cd/(Cd + Zn) ratio. The first case in literature is the Cd in CZTS. The optimal ratio of Cd/(Cd + Zn) is determined as 0.4, achieving a highest efficiency of 9.82% [13]. Recently, Hao group has reported an 11.5% efficiency using the same ratio [15]. The second case is Cd in CZTSSe (sulfur around 36%). The optimal Cd content is 0.05 with efficiency increased from 5.41% to 8.11% [14]. In the aspect of fabrication, Cd alloying has been achieved in solution based processing using cadmium acetate for CZTS [13] and cadmium chloride for CZTSSe [14], or during heat treatment by

sulfurizing a CBD CdS on the top of co-sputtered Cu/ZnS/SnS precursor [15]. However, there are just limited reports about the effect of Cd on performance of kesterite solar cells. More investigation is needed to understand the effects of Cd alloying on kesterite solar cells, including CZTSSe in full range of S content and from different processing methods.

Recently, a sputtering method based on quaternary target has been proposed as an alternative to fabricate CIGSe and CZTS solar cells [16,17]. In this work, we provide a new case of Cd alloying to increase the conversion efficiency in CZTSSe (sulfur around 1%) solar cells based on sputtering from a quaternary target. The layer structure for Cd alloying was SLG/Mo/CZTS precursor/CBD CdS. The Cd-alloying absorber CZTSSe was obtained after selenization. The incorporation and distribution of Cd was examined by XRD, Raman and SIMS. The impacts of Cd alloying on the device performance and bulk defects of CZTSSe solar cell were investigated by current-voltage curve, external quantum efficiency (EQE) and thermal admittance spectroscopy. As a result, the highest efficiency was improved from 8.5% to 11.2%.

2. Experimental

The CZTS precursors were deposited on $1'' \times 3''$ Mo-coated glass by sputtering a quaternary CZTS target with purity of 99.99% (Cu:Zn:Sn: S = 1.8:1.1:0.9:3 at%). For Cd-alloying samples, a 50-nm CdS film was deposited on top surface of CZTS precursor using chemical bath deposition (CBD). The precursors were then placed in a quartz box (30 cm $\times$ 30 cm) inside a vacuum chamber with base pressure of 2.0 $\times 10^{-3}$ Pa. Pure Ar gas with pressure of 1×10^4 Pa at room temperature ($\sim 25\,°C$) was first flowed into chamber before heating. The heating rate of substrates was 10 °C/min. The supply of selenium would begin by inletting 30 vol% H_2Se in Ar gas with a flow rate of 20 sccm without outlet when the temperature reached 300 °C. Samples were kept at 560 °C for 30 min. Subsequently, the supply of selenium would stop and the samples would cool down naturally. The Cd-alloying CZTSSe absorber were thus obtained. More details about the selenization processing were explained in our previous work [17]. After selenization, samples were followed by 50 nm CdS by chemical-bath deposition and 50 nm i-ZnO/ 400 nm AZO layer from sputtering, and Ni-Al grid from electron beam evaporation using our standard processing [16]. CZTSSe solar cells with total area of 0.65 cm^2 (active area of 0.50 cm^2 measured by optical camera) was defined by mechanical scribing. No antireflective coating was used.

The microstructures of films were characterized by x-ray diffraction (XRD, Rigaku D/max 2500V) with Cu Kα irradiation (λ = 0.15418 nm) and Raman scattering spectroscopy (Raman, LabRAM HR Evolution) with laser wavelength of 532 nm. The morphologies were observed by field emission scanning electron microscopy (FE-SEM, MERLIN VP Compact). The depth profiles of element distribution for solar cells were recorded by time-of-flight secondary ion mass spectroscopy (TOF-SIMS, ION-TOF GmbH). Current-voltage characterization was performed using a $6'' \times 6''$ beam solar simulator from Newport (with simulated AM 1.5G illumination and calibrated by standard Si solar cell) and a Keithley 2400 source meter. External quantum efficiency (EQE) was performed using a QT500 AD quantum efficiency testing system (Crow Tech Corp.) with a xenon light source, a monochromator and lock-in amplifier. Admittance spectroscopy measurements were carried out in the temperature of 130–300 K under dark condition with a LCR meter (HP 4284A), which applied an AC voltage of 50 mV by varying the frequencies from100 Hz to 1 MHz.

3. Results and discussions

3.1. Cd alloying

XRD and Raman spectra of absorbers are performed to check whether Cd exists in absorber and figure out the Cd content, as shown in

Fig. 1. XRD patterns of both samples are attributed to CZTSe. In spite of this, absorber is still described as CZTSSe (sulfur about 1%) [17]. Compared to the reference absorber, the (112) peak from Cd-alloying one shifts from 27.12° to 27.06°, indicating an increase of interplanar spacing. This could be the reflection of Cd alloying into the CZTSSe lattice due to the larger radius of Cd than that of Zn. According to Cd alloying in CZTS, kesterite structure would not change when Cd/(Cd + Zn) ratio is less than 0.6 [13]. The Cd/(Cd + Zn) ratio can be roughly estimated to be about 0.15 using the thickness and density of CZTS and CdS. It is thus rational to assume a solid solution after Cd alloying. According to the Vegard's Law, the calculated ratio of Cd/(Cd + Zn) in absorber is 0.13 by the shift of (112) peak, which is consistent with the estimated value. The lattice constants of a and c are estimated to be 5.711–5.717 Å and 11.340–11.342 Å, respectively.

In Fig. 1c, Raman peaks at 170 cm^{-1}, 194 cm^{-1}, 230 cm^{-1} and 249 cm^{-1} are attributed to CZTSe [18]. No obvious peak from secondary phase is observed. For the Cd-alloying absorber, the Raman spectrum exhibits a slight shift to lower wavenumber, shown by a small vertical line. Since the Raman shift is negatively correlated to the mass of atoms, heavier Cd atom at Zn site in CZTSSe would result in a shift toward lower wavenumber. This indicates that the Cd is really incorporated into the CZTSSe bulk, in agreement with XRD results.

3.2. Effects of Cd alloying on microstructure

Fig. 2a and b show the cross-section image of resulting solar cells. After Cd alloying, the grain size of CZTSSe increases from hundreds of nanometer to micron level. The small grains near the back contact disappear, resulting in a near single-grain layer. Small voids near back contact are observed for two samples. This indicates that Cd alloying enhances grain growth, which is in accordance with reported results [13–15]. Large grains help to reduce potential defect at grain boundary which might cause a recombination loss for J_{sc}. The enhanced grain growth might benefit from lower melting point after Cd alloying. Most solid solution exhibits a lower melting point when a compound is alloyed with one having lower melting point. In this case, the melting point of CZTSe is 805 °C while that of CCTSe is a lower value 780 °C [19]. When CZTSe and CCZTSe films are annealed at a same temperature, low-melting-point CCZTSe films would obtain larger grains.

To link the morphology with elements distribution, TOF-SIMS profile of CZTSSe solar cells are recorded in Fig. 2c and d. The intensity for each element is normalized and the intensity at half maximum in the front and back of absorber is defined as interface, as indicated by dash line. The Cd content in Cd-allying absorber is higher in that in reference sample, in agreement with XRD and Raman results. A gradual dropping of Cd signal from CdS to absorber is also observed, which result in relatively high Cd content near the absorber surface (indicated by blue arrow). Furthermore, the Sn/Cu ratio near back contact is higher than that in the bulk for reference sample, while this ratio is more homogeneous in the Cd-alloying one. This higher Sn/Cu ratio at back contact might correspond to the fine grains in Fig. 2a. This suggests that the enhancement of grain growth also leads to a more homogeneous distribution of composition. The highest Cd signal is from the bottom of CZTSSe absorber for both samples. Since no Cd is detected in reference absorber by XRF, one possibility is that Cd ion from solution goes through grain boundary or voids inside the absorber and accumulates near Mo side as Cd related cluster or CdS particle, during the deposition of buffer layer CdS.

3.3. Effects of Cd alloying on device performance

Efficiency in this work refers to the active area one. The efficiency of twelve reference solar cells is in the range of 3–8%. While the efficiency of CZTSSe solar cells with Cd-alloying is from 8% to 11%. Fig. 3a shows the J-V curve of the highest efficiency of CZTSSe solar cells with and without Cd alloying. Short circuit current density and open circuit