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Effect of Cu/(Zn+Sn) ratio on the ZnSe position and performance of CZTSe solar cells

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ABSTRACT

$Cu_2ZnSnSe_4$ photovoltaic absorber layers were prepared by the vapor selenization of stacked Cu/Sn/CuZn/Mo/glass precursor films with different Cu/(Zn + Sn) compositional ratios (CZT = 0.8, 0.85 and 0.9). The absorber was ZnSe-free at CZT = 0.9 but the films obtained from CZT = 0.85 or 0.8 contained a ZnSe phase mainly at the bottom or top of the absorber film, respectively. Although the solar cell fabricated from the CZT = 0.9 absorber showed poor-shunt characteristics (efficiency = 1.94%), that produced from CZT = 0.85 exhibited significantly distorted current–voltage characteristics (efficiency = 4.23%). The CZT = 0.8 ratio showed the highest efficiency of 5.8% and normal pn diode behavior. This suggests that the existence or location of the ZnSe phase within the absorber is not related directly to the solar cell performance. Instead, the ZnSe phase may alter the defect distribution near the space charge region. Several aspects of the device behavior depending on the CZT ratio are discussed with respect to the relative position of the ZnSe phase.

1. Introduction

The commercialization of Cu(In,Ga) $(S,Se)_2$ (CIGSSe) solar cells, despite having the highest conversion efficiency among thin film-based photovoltaic technologies, has been limited by the lack of natural resources and the high material cost, particularly In and Ga [1]. $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cells have long been considered as an alternative to CIGSSe because earth abundant and cost-effective Zn and Sn can replace In and Ga [2]. Furthermore, CZTSSe has comparable material properties to CIGSSe. CZTSSe is a p-type semiconductor with a high optical absorption coefficient of 1×10^4/cm and a bandgap that can be controlled over the range, 1–1.5 eV, by adjusting the S/(S + Se) composition ratio [3,4].

CZTSSe-based absorber thin films can be synthesized by evaporation [5], sputtering [6,7], nanoparticle deposition [8], electrodeposition [9,10], spray pyrolysis [11], and hybrid solution-particle-based spin coating. Recently, IBM developed a hydrazine-based non-vacuum deposition process to produce Cu-poor and Zn-rich (Cu/(Zn + Sn) = 0.8, Zn/Sn = 1.1) CZTSSe thin films, and demonstrated a world-record efficiency of 12.6% [12]. Unfortunately, hydrazine is unsuitable as a solvent for the mass production of large area photovoltaic devices because of its toxicity and explosive nature [13].

Currently, large area CIGSSe photovoltaic modules are produced by a so-called two-step process, which consists of the deposition of metallic precursor thin films by magnetron sputtering with subsequent thermal annealing under a chalcogen environment. One of the advantages of using the two-step process is that the precursor films can have a range of metal stacks. The stacking order of the constituent elements, Cu, Zn and Sn, can strongly affect the void formation, grain size, adhesion, and composition of the absorber film [14]. For example, larger CZTSSe grains could be obtained from a Sn/Zn/Cu/Mo stack due to the direct contact of Cu and Zn compared to the Zn/Sn/Cu/Mo stack. In addition, the conversion efficiency was higher when a Sn/Cu/Zn/Mo stack was used because of the improved adhesion of CZTSSe to Mo due to the absence of direct contact of Cu and Mo, as well as the larger grains due to Cu/Zn direct contact. Capping the precursor top with Cu can reduce the loss of Zn or Sn during high temperature annealing process, making it favorable for composition control of the absorber film.

The existence of secondary phases, such as $Cu_2Sn(S,Se)_3$ or Zn(S,Se), which strongly affect the solar cell performance, might also be affected by the stacking order of the metal precursor. For example, residual (Cu,Sn)-chalcogenide with metallic conductivity

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will deteriorate the device shunt and result in a poor fill factor. Although a Zn-rich precursor has been generally adopted to prevent the formation of secondary phases [15,16], the off-stoichiometric condition may promote the formation of other secondary phase of Zn(S,Se) [17]. Many studies have examined the variation of the solar cell performance with the existence of Zn(S,Se) as a separate phase in CZTSSe absorber films [18–21]. On the other hand, the effects of the Zn(S,Se) phase remaining in the absorber are not completely understood. For example, the ZnS surface layer was reported to be responsible for FF loss due to the high series resistance [22], enhancement of the open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill-factor (FF) by implementing a thin Zn-rich layer on the absorber surface [23]. In addition, Zn(S,Se) was suggested to have little or no effect on the device performance except for decreasing the effective volume of the absorber [16].

Despite the importance of Zn(S,Se) phase control for high efficiency devices, it is extremely difficult to detect the Zn(S,Se) phase using a routinely used analytical tool, such as XRD, because the major diffraction peaks of CZTSSe overlap with those of Zn(S,Se) [24,25].

In the case of selenization of the Cu–Zn–Sn precursor film stacked with individual layers of each element, the formation of a ZnSe secondary phase might be favorable. Therefore, in this study, the effects of the [Cu]/([Zn]+[Sn]) compositional ratio (CZT ratio) on the location of the ZnSe phase and the device performance were exploited. The phase was identified using a simple technique combining slope polishing with micro-Raman analysis.

2. Experiment

$Cu_2ZnSnSe_4$ (CZTSe) absorber films were prepared on ~600-nm-thick Mo sputtered sodalime glass (SLG) substrates by selenizing Cu–Zn–Sn metallic precursor films. The precursor films were deposited by DC-magnetron sputtering with Cu-50 at%Zn alloy, pure Sn and pure Cu targets, 3 inches in diameter. The base pressure prior to deposition was less than 1×10^{-6} Torr to minimize the H_2O vapor, and the working pressure was 5 mTorr. The 500 nm thick precursor films with a Cu/Sn/CuZn/Mo stacking order, in which the top Cu layer capped all the layers to prevent Sn loss during the high temperature annealing process, was deposited at a DC powers of 10 W, 50 W and 100 W, respectively. The compositional ratio of Zn/Sn was fixed to unity, and CZT with composition ratios of 0.8, 0.85 and 0.9 was varied by controlling the top Cu layer thickness. The actual composition of the precursor films were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). To achieve the CZTSe absorber films, the precursor films were selenized using Se vapor at 500 °C for 10 min. The metallic compositions of the selenized films were confirmed to be similar to the precursor films without significant loss of Sn or Zn. A p-n diode was constructed by depositing a 50 nm thick CdS buffer layer by chemical bath deposition and 80 nm i-ZnO by RF-magnetron sputtering, and a 500 nm (Ga,Al):ZnO transparent conducting oxide layer was deposited by DC-magnetron sputtering. The current collecting grid of 0.1 μm Ni and 1.65 μm Ag was deposited by electron beam evaporation through a shadow mask.

The morphology of the films was examined by scanning electron microscopy (SEM, Hitachi S-4800). The CZTSe films were analyzed by X-ray diffraction (XRD; PANalytical MPD for thin film) in ω-scan mode to examine the crystalline properties and to determine the existence of a secondary phase along the absorber thickness direction. To investigate the depth distribution of the different phases, CZTSe devices were polished mechanically with a dimple grinder (Gatan Inc., model 645) until the Mo back contact layer was exposed. The Raman measurements were carried out with the 441.6 nm-line of a He–Cd laser (blue laser) as the excitation source. A laser beam with a power of 1 mW was focused to a ~1 μm diameter using a 40 × microscope objective (0.8 N A.). The signal was dispersed with an iHR-550 spectrometer and detected with a liquid nitrogen-cooled back-illuminated charge-coupled-device. The current density-voltage (J–V) characteristics of the CZTSe solar cells were evaluated using a solar simulator (K3000, McScience) under AM1.5, 100 mW/cm^2 illumination at 25 °C. The external quantum efficiency (QE) was measured using an incident-photon-to-electron conversion efficiency measurement system (PEC-S20, Jasco) at 25 °C. The effective carrier concentration and depletion width were obtained from the C–V (4200-SCS, Keithley) curves measured at a 30 kHz modulation frequency of a 30 mV DC bias over the range, −1.0 V to +1.0 V, at room temperature in the dark.

3. Result and discussion

Fig. 1 presents cross-sectional SEM images of the three absorber films. The images were taken after device fabrication. CZTSe absorber films showed a well-developed columnar structure with a grain size greater than 1 μm. Although the grain size appeared to decrease marginally with decreasing CZT ratios, all the films showed a thick Mo selenide layer of ~1.2 μm with similar residual Mo layer thickness of ~0.2 μm. The thick MoSe formation suggests that precursor selenization was complete. Although the images were taken under the combined mode of Z-contrast and secondary election emission, it was difficult to distinguish any secondary phase, such as ZnSe, which often appears as a white contrast. A deep valley was pronounced in the case of CZT = 0.9 compared to the lower CZT samples. The irregular thickness of absorber is commonly observed in selenized absorber layers, particularly under Cu-rich conditions, and may induce a shunt path through the valley region. Fig. 2 shows the grazing incident XRD (GIXRD) data for the three CZTSe films, which was intended to reveal the phase distribution along the thickness direction. The incident angle, ω, was varied from 0.1 to 10°. For all three absorbers, only the CZTSe (JCPDS 01-070-8930), ZnO, $MoSe_2$, and Mo peaks were identified without any secondary phases, which are summarized in Table 1. On the other hand, the XRD peaks of the secondary phase, such as ZnSe (JCPDS 03-065-9602) or Cu_2SnSe_3 (JCPDS 03-065-4145), overlap with those of CZTSe. Therefore, it is difficult to determine if the absorber films are free of secondary phases. The diffraction patterns also contain Ag and ZnO peaks because they were taken from complete devices.

To resolve the depth distribution of any secondary phase across the whole thickness of the absorber films by Raman spectroscopy, the films were polished mechanically to have a small slope using a dimple grinder, which is commonly used to thin a material. Fig. 3 shows a photograph of the sample with an approximately 1 mm wide dimple formed by slope polishing.

The 1.5 μm thick absorber film was tapered successfully to reveal a slanting surface with a width of a few hundred micrometers. The phase distribution all the way down to the back contact can be identified by scanning a laser spot, few μm wide, along the slanting surface by micro-Raman analysis. Fig. 4 shows the Raman depth profiles obtained from the three different absorbers with a protecting layer of CdS (300 cm^{-1}) [26] on top. Overall, CZTSe (171, 194 cm^{-1}) [27], ZnSe (250 cm^{-1}) [27] and $MoSe_2$ (240 cm^{-1}) [28] peaks were clearly resolved but no Cu-related secondary phases, such as Cu_xSe or Cu_2SnSe_3, were detected. The Raman signals were excited using a blue laser, which is sensitive to the ZnSe phase but the signals obtained using the red or green laser were similar in terms of the Cu-related secondary phases. ZnSe was found to exist at both the bulk and surface of the absorber selenized from the CZT = 0.8 precursor, whereas only near back contact was observed