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Comparison of chalcopyrite and kesterite thin-film solar cells

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ABSTRACT

In this study, we investigate methods of improving the efficiency of $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTS)-based solar cells by comparing $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGSe)- and CZTS-based absorber layers. In particular, the CZTS-based absorber exhibits lower current characteristics than the CIGSe absorber layer in terms of the band gap alignment and electron-hole recombination at the CdS-absorber interface. Moreover, we demonstrate that defects are one of the causes of the voltage loss. In order to improve the efficiency of CZTS-based solar cells, it is important to control the band gap alignment at the CdS-absorber layer interface and to suppress the formation of secondary phases inside the absorber.

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Introduction

After the announcement of the Paris agreement to reduce carbon dioxide emissions in 2015, the role of renewable energy sources has become very important. Against this background, the renewable energy market can be expanded by solar photovoltaics through improvements related to high-efficiency and high-energy-density solar cells. For instance, thin-film solar cells, such as CdTe and $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGSe) solar cells, have high power conversion efficiencies (PCEs) of 22.1% and 22.3%, respectively [1]. However, the PCE is only 12.6% for thin-film solar cells based on CZTS and related materials (e.g., $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe), and $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTSSe)) [2]. A PCE of over 15% is required in order to make cost-effective CZTS-based solar cells competitive against the CIGSe counterparts [3,4].

To achieve such a high PCE, it is important to survey various PCE improvement methods for CZTS-based solar cells by analyzing the characteristics of CIGSe solar cells with similar structures. Many previous research results have been reported regarding CZTS-based solar cells, and have focused on various features such as grain crystallinity [5,6], secondary phases [6–12], defects

[6,11–15], and Na content [16,17]. Furthermore, these factors have been correlated with voltage and current characteristics. In the case of CZTSSe solar cells with a PCE of 12.6%, the open-circuit voltage (V_{OC}) is 0.513 V, the short-circuit current density (J_{SC}) is 35.2 mA/cm^2 , and the fill factor (FF) is 69.8% [2]. On the other hand, in the case of CIGSe solar cells with a PCE of 20.3%, V_{OC} is 0.74 V, J_{SC} is 35.4 mA/cm^2 , and FF is 77.5% [18]. According to this comparison with CIGSe characteristics, these low J_{SC} and V_{OC} values must be improved in order to enhance the PCE of CZTS-based solar cells. In particular, concerning CZTSe cells with a PCE of 11.6%, a J_{SC} value of 40.6 mA/cm^2 was reported [19], so there does in fact exist a means of enhancing J_{SC} . Therefore, we may conclude that the improvement of V_{OC} constitutes a relatively more important task at present.

In this study, we compare the characteristics of CIGSe-based chalcopyrite and CZTS-based kesterite thin-film solar cells, and present methods of improving the current–voltage (C – V) characteristics of CZTS-based solar cells. These improvements can be expected to enable the realization of low-cost, high-efficiency CZTS-based thin-film solar cells.

Experimental

In order to conduct this comparison between CIGSe- and CZTS-based solar cells, three samples were fabricated: a CIGSe sample using evaporation, a CZTS sample and a CZTSSe sample using a

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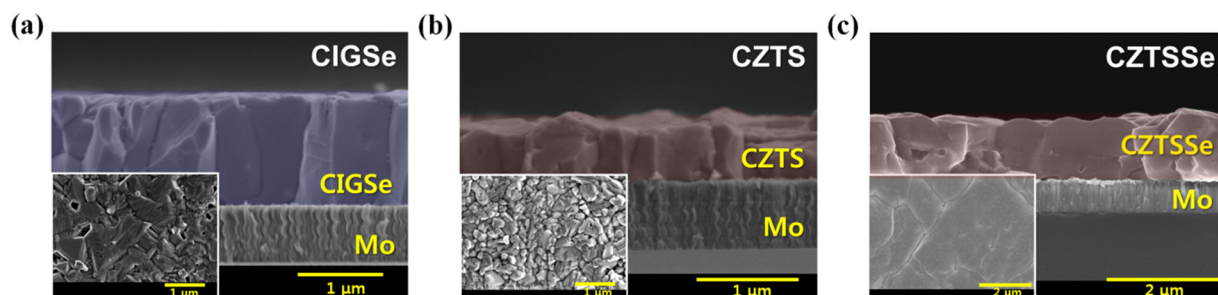


Fig. 1. Cross-sectional and surface SEM images of various absorber layers. (a) In CIGSe, the thickness of the absorber layer is 1.27 μm . (b) In CZTS, the thickness of the absorber layer is 0.6 μm . (c) In CZTSSe, the thickness of the absorber layer is 1.13 μm .

sputtering process. All three solar cell device structures consisted of a soda lime glass (SLG) substrate, a 600-nm-thick Mo layer as a back contact, an absorber layer, a 50-nm-thick CdS buffer layer deposited via a chemical bath, a 50-nm-thick intrinsic ZnO layer deposited via sputtering, a 300-nm-thick Al-doped ZnO (AZO) layer as a transparent conducting oxide layer deposited via sputtering, and a 500-nm-thick Al collection grid deposited via thermal evaporation. The CIGSe absorber layer was grown on the Mo layer via a three-stage co-evaporation process involving Cu, In, Ga, and Se [20,21]. In the first step, an $(\text{In,Ga})_2\text{Se}_3$ precursor was deposited on the substrate for 1500 s at about 420 $^\circ\text{C}$. A pyrometer was used to measure the temperature of the SLG. In the second step, the Cu-rich CIGSe films were grown with Cu and Se fluxes at about 550 $^\circ\text{C}$. In the third step, small amounts of In and Ga were evaporated in order to convert the Cu-rich CIGSe films to Cu-poor CIGSe films. By way of contrast with the CIGSe absorber fabrication process, the CZTS and CZTSSe absorber fabrication processes were carried out in two steps, which included an annealing step for chalcogenization after the initial absorber precursor deposition step. Precursors for the CZTS and CZTSSe absorber layers were deposited on the Mo layer using 99.99% pure Cu (70 nm, 150 W of DC power), SnS (120 nm, 200 W of RF power), and ZnS (140 nm, 200 W of RF power) sputtering targets with a stacking order of Cu/SnS/ZnS/Mo. This stacking order was determined from our previous work [22]. The CZTS precursor film was sulfurized at atmospheric pressure in a quartz furnace with two heating zones for the CZTS absorber. The sulfur source was evaporated in a 300 $^\circ\text{C}$ heating zone, and the samples were subsequently heated to 540 $^\circ\text{C}$ for 30 min. For the CZTSSe absorber layer, precursor films deposited using sputtering were selenized in a nearly sealed quartz furnace at 570 $^\circ\text{C}$ for 20 min [5]. The remaining device layers, as described above, were subsequently added using the aforementioned processes.

The samples were characterized using a solar simulator, external quantum efficiency (EQE) measurements, scanning electron microscopy (SEM), depth-resolved Raman spectroscopy, scanning transmission electron microscopy–energy dispersive spectrometry (STEM-EDS), and admittance spectroscopy (AS). $C-V$ characteristics were measured under a simulated air mass 1.5 global spectrum (AM 1.5 G) and 100 mW/cm^2 illumination (1 sun) using a solar simulator (Newport Co., model 94022A). The EQE values were obtained using an SR 830 DSP lock-in amplifier system (McScience Co.). Images of the cross-sectional structures and the surface morphology of the films were obtained using SEM (Hitachi Co., model S-4800).

Table 1
Device characteristics of the thin-film solar cells.

Cell	Absorber	Absorber process	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)	R_{S} (Ωcm^2)	E_{g} (eV)	$E_{\text{g}}/q-V_{\text{OC}}$ (V)	Area (cm^2)
CIGSe	CIGSe	Evaporation	0.659	32.13	73.82	15.63	0.40	1.185	0.526	0.211
CZTS	CZTS	Sputtering	0.574	17.39	56.37	5.63	0.86	1.515	0.941	0.185
CZTSSe	CZTSSe	Sputtering	0.387	33.18	60.98	7.82	0.44	1.091	0.704	0.185

To investigate the phase distribution in the absorber layers, each sample was mechanically polished using a dimple grinder until the Mo back contact layer was exposed; depth-resolved Raman spectroscopy measurements were then performed using the 632.8 nm line of a He-Ne laser and the 514.5 nm line of an Ar^+ laser as excitation sources. The laser beams (power of 1 mW) were focused to a $\sim 1 \mu\text{m}$ in diameter using a 50 \times microscope objective (0.8 N.A.) for the visible laser and a 40 \times objective (0.5 N.A.) for the UV laser. The signal was dispersed using an iHR-550 spectrometer and detected using a liquid-nitrogen-cooled back-illuminated charge-coupled device. EDS (Bruker Co., model QUANTAX-200) measurements were performed to map out the distribution of the secondary phases. AS measurements were performed over the temperature range of 90–300 K using an E4980A LCR meter (Agilent Co.), which probed frequencies from 20 Hz to 2 MHz. The measurements were conducted using a temperature tolerance of ± 0.05 K or less. The $C-V$ characteristics (Keithley, model 4200-SCS) were measured using 50 mV and 100 kHz AC excitation with DC bias from -4.5 V to 0 V.

Results and discussion

Fig. 1 shows SEM images of the absorber layers. In CIGSe (Fig. 1a), the thickness of the absorber layer is 1.27 μm , and the grains are well grown. The thicknesses of the absorber layers of CZTS (Fig. 1b) and CZTSSe (Fig. 1c) are 0.6 μm and 1.13 μm , respectively. As with CIGSe, the grains of CZTS and CZTSSe are well grown. Table 1 and Fig. 2 show the various characteristics of these thin-film solar cells. As shown in Fig. 2a, CIGSe shows high V_{OC} , J_{SC} , and FF values with a PCE of 15.63%. On the other hand, CZTS and CZTSSe show low J_{SC} values for high V_{OC} values, as well as high J_{SC} values for low V_{OC} values. Moreover, the FF is lower than that of CIGSe in both cases. In Fig. 2b, CZTS and CZTSSe show lower EQE characteristics compared to CIGSe at wavelengths under 500 nm. In Fig. 2c, E_{g} is 1.185 eV for CIGSe, 1.515 eV for CZTS, and 1.091 eV for CZTSSe. In what follows, these differences between the CIGSe, CZTS, and CZTSSe characteristics are investigated at the level of the CdS-absorber interface and inside the absorber layer.

CdS-absorber interface

In CZTS-based thin-film solar cells, J_{SC} can be improved for band gaps in the range of 1.1–1.4 eV [23]. This is correlated with the influence of the band edge shifts on the doping properties of the absorber layer [24]. However, an absorber is difficult to be doped n-type if the conduction band level is too high [24,25]. As the

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