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Surface potential on grain boundaries and intragrains of highly efficient $Cu_2ZnSn(S,Se)_4$ thin-films grown by two-step sputtering process

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ABSTRACT

$Cu_2ZnSn(S,Se)_4$ (CZTSSe) thin-film solar cells are prepared by stacking sputtering of precursors and annealing at Se atmosphere. We achieved the highest conversion efficiency of a CZTSSe thin-film solar cell with 8.06%. Local electrical properties of the CZTSSe films were investigated by Kelvin probe force microscopy. We studied samples which show conversion efficiencies between 3.17% and 8.06%. The CZTSSe thin-film with the highest efficiency exhibits predominantly downward potential bending at grain boundaries (GBs) and upward potential bending at intragrains (IGs). On the other hand, the film with the lowest efficiency shows the opposite behaviors that downward potential bending at GBs and upward potential bending in many regions of IGs. The downward potential bending allows minority carrier collection and reduces recombination at GBs, consequently, enhance current in the solar cell devices. However, some of the GBs possesses deep-level traps so they behave as a hurdle for charge transport, which can be compensated with the carrier motion in the IGs. The results suggest that the potential variations on the GBs and IGs are significantly linked to the carrier transport and device characteristics in the solar cells.

1. Introduction

$Cu_2ZnSn(S,Se)_4$ (CZTSSe) attracts great attention for replacing $Cu(In,Ga)Se_2$ (CIGS) for solar cell applications. CZTSSe absorber material is considered to be low cost because In of CIGS is rare in the earth. The CZTSSe is desirable for absorbers material and has a stable state [1,2]. CZTSSe has a high absorption coefficient and susceptible to tune its band gap with changing the ratio of S and Se. The highest conversion efficiency of CZTSSe is reported as 12.6% using a hydrazine-based non-vacuum process by Mitzi's group of IBM [3]. For sputtering process, 9.3% has been achieved by Clemens' group of Stanford University [4]. RF and DC sputtering with compound and metal targets is a promising tool of manufacturing for CZTSSe solar cells, which is already demonstrated in CIGS solar cells. It is reported that compound sources such as ZnS and SnS_2 can improve adhesion between a substrate and CZTS thin-film, grain growth and composition control of the films [5–12].

Stacking orders of the precursors during the sputtering orchestrate all the possible phase formation of the kesterite CZTSe and other secondary phases [6]. A dense morphology without voids is observed on the surface staking orders in the $Cu/SnS_2/ZnS/Glass$ [7]. A thicker layer showed an explicitly decreased circuit current density and fill factor because of the high series resistance in the CZTS thin-film solar cell [13]. It is reported that CZTS thin-film solar cell have similar properties with CIGS [14,15]. Therefore, it is critical to investigate the various absorber layer conditions for enhancing the conversion efficiency of CZTSSe to more than 20% conversion efficiency. In particular, the grain boundaries (GBs) in CIGS have unique electrical behavior compared with other photovoltaic thin-film solar cells. The GB of the single crystal thin-film solar cells acts as a defect and a recombination center [16]. The GBs of CIGS helps in minority carrier separation, resulting in suppression of the recombination due to the effect of sodium and the large relaxation of atomic structure at GBs in CIS pull the defect states and thus do not create deep level inside the band gap [17–20]. Persson et al., reported the structural barrier model showed that Cu depletion at GB may create hole barrier by reduced of coupling between Se-p and Cu-d state at GBs [21].

Two controversial views on GBs have been discussed in CIGS thin films, which are not completely established in CZT(S,Se) thin-films.

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One of the views is that GBs acts as an efficient carrier collection region [22,23]. The minority carrier collection takes place at GBs in CZTSSe thin-films by Kelvin probe force microscopy (KPFM) and conductive atomic force microscopy (C-AFM) measurements. A similar explanation has been addressed in CIGS thin-film results [22]. The other view is represented that GBs is acting as a recombination center. Li et al. reported that in GBs in CZTSe thin-film localized defect states can be induced and high density of defect states is formed in CZTSe by theoretical calculations [24]. Yin et al., suggested that there are three types of chemical bonds Cu-Se, Sn-Se, and Zn-Se bond in CZTSe [25]. However, GBs of CZTSe induce wrong atomic bonds, so it results in deep defect states inside the band gap that enhance the recombination of photo generated carriers. Therefore, we need to identify the roles of GBs and carrier transport near GB in CZTSSe thin-films. In this study, we achieved 8.06% conversion efficiency of CZTSSe thin-film solar cell based on a compound source. In a previous study, we reported the recombination mechanism of GBs on CZTSe thin-films grown by co-evaporation, which achieved ~3% conversion efficiency [23]. In this paper, we investigated the roles of GBs and IGs in sputtered CZTSSe thin-films by local electrical and device characterization, especially different conversion efficiency samples between low efficiency of 3% and high efficiency of 8%. From these results, we can describe the efficient current trapping near GBs and explain the improving of J_{SC} in high efficiency of CZTSSe thin-film.

2. Experimental

Precursor films were coated on Mo-deposited SLG substrates. The stack of Cu/SnS/ZnS precursor layers was sequentially deposited by sputtering from 99.99% pure Cu, ZnS, and SnS targets [9]. In the second step, the as-grown precursors were annealed with Se metal in a furnace at a substrate temperature of 570 °C and maintained for 10 and 20 min. Before the annealing process, the sealed furnace was evacuated to low 10^{-3} Torr to remove moisture and impurities. Ar gas was then introduced in the sealed furnace and the pressure was allowed to reach the atmosphere. The absorber layers were deposited with different thicknesses of 1.2, 1.4, 1.6, and 1.8 μm-thick after selenization. To fabricate the solar cells, the obtained absorber layers were covered with a 50 nm thick CdS buffer layer by chemical bath deposition. A 50 nm intrinsic ZnO layer and a 300 nm Al-doped ZnO layer were then deposited by RF sputtering. Finally, a 500 nm Al collection grid was deposited on the top of the device by thermal evaporation. Solar cell factors, series resistance and shunt resistance of CZTSSe thin-films are shown in Table 1. The final composition of Cu/(Zn+Sn) ~0.94 and Zn/Sn ~1.05 of CZTSSe thin-films were obtained by energy dispersive spectrometry (EDS). The morphology and grain size of the CZTSSe thin-films were investigated by FE-SEM (JSM-6700F). The accelerating voltage of 10 kV was used for this measurement.

Current–voltage measurements were carried out to estimate the solar cell parameters. CZTSSe thin-film solar cells were measured using a solar simulator. From the *J–V* curves, we calculated the ideality factor of each sample. The X-ray diffraction (XRD) result shows that (112) preferred orientation of all CZTSSe thin-films as indicated in supplement Fig. 2. However, crystalline orientation of each grain on the surface was not confirmed.

We investigated the local electrical properties of the CZTSe thin films by KPFM, which is a commercial atomic force microscopy (Nano focus Inc, n-Tracer). A Pt/Ir-coated tip was used for measuring the CZTSSe thin-films with Mo-coated soda lime glass. From KPFM measurement, we can obtain the surface potential and topography were decided under a non-contact mode by applying AC voltage with an amplitude of 1 V (peak to peak) and frequency of 80 kHz to obtain clear images and sufficient sensitivity. The AC voltage will make an oscillating force to the tip. The feedback loop controlled the DC potential to nullify the contact potential difference component by applying a DC bias to the tip, so we can obtain the two dimensional surface potential images [26]. The topography images were obtained using the non-contact mode at a resonant frequency of the probe of about 83.25 kHz. The scanning rate was with 0.5 Hz to minimize topological signal and samples were not damaged during these measurements. A lock-in amplifier was operated with a sensitivity of the 200 mV/nA. In order to understand the role of GB in effect the device performances of the CZTSSe thin-film solar cell, local electrical characterization has been applied. Hafemister et al., reported whether GB is advantageous to the cell performance depending on band bending [27]. From the surface potential and device performance results, it is essential to understand the polycrystalline thin-film solar cell performances.

Table 1
Solar cell factors, series resistance and shunt resistance of CZTSSe thin-film solar cells.

Sample	Thickness (μm)	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF* (%)	Efficiency (%)	R_{sh} (Ω cm^2)	R_s (Ω cm^2)	*A*
D1	1.20	36.10	0.41	54.62	8.06	166.63	0.72	1.85
D2	1.40	36.74	0.38	55.03	7.74	136.80	0.86	1.68
D3	1.60	27.28	0.38	37.61	3.93	34.27	0.86	4.06
D4	1.80	25.43	0.35	35.29	3.17	32.41	0.97	4.53

3. Results and discussion

3.1. Device performance

The sputter deposited CZTSSe samples have a different absorber layer thickness. D1 has the thinnest thickness of about 1.2 μm and D4 has the thickest thickness of about 1.8 μm, as shown Table 1. However, another set of CZTSSe samples prepared under different growth conditions which are not presented in this paper. Contrary to the samples in this paper, the samples show the highest conversion efficiency in the CZTSSe sample with 1.4-μm thickness. Therefore, the conversion efficiency would not depend simply on the film-thickness. Grain size of D1 and D2 is around 2.5–4 μm and compact grain growth on the surface. However, D3 and D4 film show about a 1–2 μm smaller grain size than that in D1 and D2. These results show that a longer selenization formed a larger grain and compact grain growth for CZTSSe thin-films. The highest conversion efficiency of the CZTSSe thin-film solar cell of the absorber layer was 1.2 μm. The result of efficiency is increased, the thickness is decreased. The thickest D4 has the lowest conversion efficiency and high series resistance as shown Table 1. The minority carrier lifetime is longer at a lower series resistance [28]. Minority carriers in the high resistance CZTSSe absorber layer do not transport sufficiently. Thus, we can deduce that a thick absorber layer reduces J_{SC} of the CZTSSe thin-film solar cell as shown in Table 1. D1 and D2 have a higher J_{SC} than D3 and D4, because the thickness of the absorber layer is thinner than that of D3 and D4. The best solar cell of D1 has an efficiency of 8.06% with a V_{OC} of 0.41 V, a J_{SC} of 36.10 mA/cm^2, and a fill factor of 54.62%, as shown in Table 1. Samples thicker than 1.4 μm of the absorber layer show poor J_{SC} and *FF*. The high series resistance and low shunt resistance reduce the fill factor and device performances. A thick CZTSSe film has low conversion efficiency and low J_{SC}. Because the minority carrier could not reach the absorber layer, the thick layer could be detrimental to carrier separation. The fill factor of D2 is significantly different from that of the D3. The diode equation of thin-film solar cell can be described *J–V*