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Compositional dependence of photovoltaic properties of $Cu_2ZnSnSe_4$ thin film solar cell: Experiment and simulation

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ABSTRACT

In this paper, we have investigated the influence of Cu composition on the properties of $Cu_2ZnSnSe_4$ (CZTSe) thin film, and the device performances of CZTSe solar cells. CZTSe thin films were fabricated by selenization of sputtered stacked metallic precursors, and the conversion efficiency of Cu-poor CZTSe solar cell is 4.83%. The device simulation on CZTSe solar cell combined with experimental data indicates that the Cu-poor sample with lower Zn_{Cu} donor defect concentration exhibits relatively high efficiency. The large open circuit voltage (V_{oc}) deficit and high series resistance (R_s) are responsible for the efficiency limitation of Cu-poor CZTSe solar cell. Large V_{oc} deficit and high R_s are likely to originate from $[Cu_{Zn} + Zn_{Cu}]$ defect cluster and the formed $MoSe_2$ between CZTSe and Mo films, respectively.

1. Introduction

Quaternary semiconductor CZTSe has attracted extensive attention recently due to its high absorption coefficients ($> 10^4\,cm^{-1}$), an optimal direct band gap and the abundance of elements in the earth's crust (Mitzi et al., 2011). And the highest device efficiency of CZTSe thin film solar cell, 11.6%, was obtained using a vacuum co-evaporation technique (Lee et al., 2014). However, this efficiency is still far away from its predecessor $Cu(In,Ga)Se_2$ (CIGS) solar cells, which have achieved 22.6% efficiency. Up to now, There are enormous efforts reported to improve Cu_2ZnSnS_4 (CZTS) based thin film solar cell performance, which may provide some guidance on how to improve CZTSe solar cells efficiency (Guo et al., 2014; Yan et al., 2016; Dalapati and Zhuk, 2017; Wang et al., 2017).

Recently, the device model for Cu_2ZnSnS_4 (CZTS) or CZTSSe has been first proposed and analyzed (Gokmen et al., 2014; Courel et al., 2014), which make device simulation for CZTSe solar cell become also feasible. It is certain that device model and simulation based on experiment data would help to explore loss mechanisms on CZTSe solar cell. Sputtering is an industry compatible and relatively low-cost vacuum deposition technique, the advantages and challenges associated with sputter-deposited CZTS based solar cells have been described elsewhere (Dalapati et al., 2015; Zhuk et al., 2017). In our previous work, CZTSe films with good crystallinity were successfully prepared by a sputtering metal precursor and post-selenization method (He et al., 2014).

Besides, our previous work (Li et al., 2017) and other literatures (Chen et al., 2013; Tanaka et al., 2010, 2014; Tao et al., 2016; Ruan et al., 2014; Yao et al., 2017; Kim et al., 2017) showed Cu-poor composition is necessary for high efficiency CZTS based solar cells. According to first-principles calculations of Chen et al. (2013), Cu poor and Zn rich conditions can prevent the formation of [2CuZn + SnZn] clusters and result in the higher CZTS or CZTSe solar cell efficiency. Tanaka et al. (2010) demonstrated that the increasing Zn content enhanced grain growth in the absorber layer and accordingly reduced the series resistance of CZTS solar cell. Yakushev et al. (2017) reported Cu deficiency and Zn excess can widen E_g due to an improved ordering of the Cu/Zn atoms. However, the existing literature about Cu content change mainly focus on the material characteristics of CZTSe thin films. The comprehensive study about the effect of Cu composition change on both the properties of CZTSe absorber film and the solar cell performance is still limited. In this work, we have systematically investigated the influence of CZTSe thin films with different Cu composition on the structure, morphology, secondary phase formation and photovoltaic properties of CZTSe films both from experiment and simulation.

2. Experimental section

Polycrystalline CZTSe thin films were deposited on Mo-coated soda-lime glass substrates using the sequential deposition of metallic

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precursor layers done by RF magnetron sputtering and a final selenization process, as described in our earlier publication (Tao et al., 2016) and the Cu compositions are manipulated by adjusting the sputtering time of Cu target. To fabricate CZTSe solar cells, CdS thin film as buffer layer was deposited by using chemical bath deposition (CBD) at 70 °C. Intrinsic ZnO (i-ZnO) and aluminum-doped ZnO (AZO) were deposited by RF-sputtering process at 120 °C. Note that no metal grid and antireflection coating was deposited on the thin film solar cells. The area of solar cell is about 0.25 cm^2 (0.5 cm × 0.5 cm), determined by mechanical scribing. The efficiency of CZTSe solar cells were measured by a solar simulator under the standard AM 1.5 spectrum, the light intensity of the solar simulator was calibrated with a standard monocrystalline Si reference solar cell. Besides, a probe station was used to measure solar cells, one probe contacts each small area of *ZnO:Al* film and the other probe contacts the Mo layer. The crystalline structures of the CZTSe thin films were analyzed by X-ray diffraction (XRD) using Cu Kα radiation (Bruker D8 Discover) from 10° to 70°. Raman scattering experiments were performed with a micro-Raman spectrometer (Jobin-Yvon LabRAM HR 800UV, the wavelength of 488 nm as excitation). The surface micrographs and the composition of thin films were determined by a field emission scanning electron microscopy (FESEM: Philips XL30FEG) with an energy dispersive X-ray (EDX) analyzer. Current–voltage characteristics of the devices were measured under AM1.5 global spectrum with their radiance set to 1000 W/m^2 (Xelamp; Newport). External quantum efficiency (EQE) measurements were performed by a single source illumination system (halogen lamp) combined with a monochromator. Capacity-voltage curves were carried out using a Keithley 4200 semiconductor characterization system at room temperature in darkness at a frequency of 20 kHz. Electrochemical impedance spectroscopy was carried out using an electrochemical workstation system (model: CHI660D, CH Instrument, USA). Photoluminescence (PL) spectroscopy (Bruker 80V equipped with a liguid-nitrogen-cooled Ge detector) was applied to Cu-poor sample.

3. Results and discussion

For the study of the Cu variation, precursor films were produced with Cu/(Zn + Sn) equal to 0.79, 0.98 and 1.15, as measured by EDX analysis. These sets of samples are referred to as Cu-poor, Cu-stoichiometric and Cu-rich respectively in this paper. As shown in Table 1, the deviations of metal composition are slight between the final films and the precursor. The evolution of the atomic composition of the films with selenization process was previously discussed elsewhere (Tao et al., 2016). Fig. 1(a) shows XRD patterns of CZTSe thin films with different ratio of Cu/(Zn + Sn). As shown in Fig. 1(a), all films are grown well with polycrystalline textures. For all samples several dominant peaks (1 0 1), (1 1 2), (1 0 3), (2 0 0), (2 1 1), (2 0 4), (3 1 2) and (4 0 0)/(0 0 8) planes are attributed to the CZTSe compound, in terms of the standard XRD patterns (JCPDS 52-868 for CZTSe). However, the XRD studies can give little information about what structure of CZTSe thin film is and the presence of ZnSe in the synthesized CZTSe, as the most intensive XRD peaks of these compounds overlap those of CZTSe phase. Cu- rich CZTSe films contain $Cu_{2-x}Se$ as the secondary phase can be seen from a small peak on the left side of the (2 0 4) peak Mousel et al. (2014). According to the quasi-ternary phase diagram, Cu-rich condition can easily induce the presence of $Cu_{2-x}Se$ (Siebentritt, 2013; Dudchak and Piskach, 2003). Fig. 1(b)–(d) exhibit SEM cross sections of Cu-rich, Cu-stoichiometric and Cu-poor CZTSe solar cells, respectively. And Fig. 1(e) shows EDX result of the bottom of the Cu-poor CZTSe layer, which indicated $MoSe_2$/Mo interface and ZnSe secondary phase were confirmed in Cu-poor sample. For all samples, CZTSe absorber layers consist of sufficient large grain sizes (> 1 μm in diameter) irrespective of Cu content. In addition, a $MoSe_2$ interfacial layer between CZTSe and Mo is visible for Cu-poor and Cu stoichiometric sample little ZnSe secondary phase was also detected at the bottom of CZTSe layer for Cu-poor solar cell. According to Fig. 1(c) and (d), it is obvious that Cu-poor sample have thicker $MoSe_2$ layer than Cu-stoichiometric sample. This is maybe due to the fact that the Sn content in the precursor of Cu-poor sample is higher than Cu-stoichiometric sample. The metal precursor with a Sn-rich composition can grow a thicker $MoSe_2$ thin film at CZTSe/Mo interface than one with a Sn-poor composition (Yao, 2016). $MoSe_2$ layer comes from the chemical interaction of Mo film as bottom electrode and Se vapor during selenization and the existence of ZnSe phase is mainly caused by Zn-rich condition in CZTSe films.

Table 1
Element composition values of CZTSe thin films determined from EDX analysis.

Sample ID	Precursor films		CZTSe thin films		
	Cu/(Zn + Sn)	Zn/Sn	Cu/(Zn + Sn)	Zn/Sn	Se/Metals
Cu-rich	1.15	1.17	1.19	1.15	1.05
Cu-stoichiometric	0.98	1.15	1.01	1.13	1.01
Cu-poor	0.79	1.19	0.82	1.17	0.99

Raman spectroscopy is also useful to analyze the structure and the phase purity of CZTSe samples besides XRD analysis. Fig. 2 shows the Raman spectra of CZTSe thin films with different ratio of Cu/(Zn + Sn). It is worthy to note that during the Raman measurement, two different zones in each film were measured and their spectra were perfectly identical, indicating the phase homogeneity of the thin films. In order to obtain the exact peaks, the measured spectra were fitted by the Lorentzian curves. As shown in Fig. 2, the intense peak at 196 cm^{-1} can be assigned to the A_1 mode of Kesterite structure (KS) and the intense peak at 192 cm^{-1} can be assigned to the A_1 mode of Stannite structure (ST) Tiwari et al., 2017. Moreover, several weaker peaks locate at about 170, 217 and 231 cm^{-1} which are identified with A_2, E and B mode (Dimitrievska et al., 2015), respectively. Furthermore, the intense peak at about 250 cm^{-1} can be assigned to ZnSe secondary phase for all CZTSe thin films (Li et al., 2010). The $Cu_{2-x}Se$ mode at 261 cm^{-1} also can be observed in Cu-rich sample (Salomé and et al., 2014). The detection for impurity phase is consistent with that of XRD and SEM in Fig. 1. As described above, KS and ST coexist in CZTSe films. In order to understand the evolution of structural transform ation, Q= $I(A_1^{Ks})/I(A_1^{ST})$ is defined, where I(A) is the intensity of the indicated Raman mode based on full spectrum fitting. The values of Q are plotted in Fig. 2(d). Q is equal to 2.51, 2.95 and 3.26 for Cu-rich, Cu-stoichiometric and Cu-poor, respectively. With the ratio of Cu/(Zn + Sn) decreasing, the values of Q are enhanced, which indicating that Kesterite structure are formed more easily in Cu-poor condition.

Solar cells with a device structure of Al:ZnO/ZnO/CdS/CZTSe/Mo/glass were prepared. J-V characteristics for the best cell from each sample series under simulated AM1.5 illumination are shown in Fig. 3(a). The detailed solar cell parameters are listed in Table 2. As expected from literature, the experimental results suggest that the Cu content would influence the photovoltaic performance. A champion efficiency is 4.83%, with V_{oc} = 347 mV and J_{sc} = 31.02 mA/cm^2. The series resistance (R_s) of Cu-poor sample is 4.34 $\Omega\,cm^2$ which is much larger than the record CZTSe solar cell (0.32 $\Omega\,cm^2$). Compared with the record CZTSe solar cell, higher R_s of our Cu-poor sample may be the major deficiency which takes down the Fill Factor (44.8%). $MoSe_2$/Mo interface and ZnSe secondary phase were confirmed in Cu-poor sample and they are responsible for high R_S (Wätjen et al., 2012; Colombara et al., 2014). When the Cu content is in a stoichiometric state, an efficiency of 2.11% solar cell was obtained. The V_{oc} and the J_{sc} are 214 mV and 31.99 mA/cm^2, respectively. However, increasing Cu content to Cu-rich condition leads to very low efficiency of 1.07%. The highest efficiencies were achieved in Cu-poor and Zn-rich conditions. The compositional condition agrees with those reported in the literature (Chen et al., 2013; Wang et al., 2014). Compared with Cu-poor sample, Cu-stoichiometric has almost identical J_{sc} and R_s values. Meanwhile it has severely lower shunt resistance (R_{sh}) than Cu-poor, which directly