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Improvement of CZTSSe thin film solar cell by introducing a three-layer structure precursor

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ABSTRACT

CZTSSe thin films based on three-layer precursors with Cu-poor and Zn-rich in top and bottom layer while stoichiometric in middle layer were prepared. Compared with CZTSSe thin film obtained from a stoichiometric single layer precursor, the crystallization of thin film from a three-layer precursor got enhanced. Element distribution and growth nuclei position in precursor played an important role on CZTSSe thin film formation and solar cell performance. The conversion efficiency of CZTSSe solar cell from a three-layer precursor attained an increase of 3.54% over that from a single layer precursor.

1. Introduction

$Cu_2ZnSn(S,Se)_4$ (CZTSSe) thin film absorber was considered to be a promising substitution of $Cu(In,Ga)Se_2$ as its abundant elements, large absorption coefficient [1] and more appropriate band gap varying 1.0–1.5 eV depending on Se/S ratio [2]. The preparation process of CZTSSe thin film includes precursor deposition and post selenization/sulfurization. Vacuum methods have advantages such as low contamination, large scale production potential in precursor deposition. Up to now, CZTSSe thin film solar cell prepared by sputtering has reached 10% efficiency [3].

Lots of work focused on stacked metal or binary sulfide layer precursor prepared by sputtering [4–7]. The stacking sequence, namely the preset element distribution in vertical direction in precursor, played an important role in post selenization/sulfurization process as it could affect the introducing of Se into thin film [5] or the growth nuclei position [6]. Stacked layer precursor may have problems like voids and defects due to its incomplete element diffusion in annealing process [7]. Zhong's work found that the elements even in a homogeneous precursor, especially Cu and Zn, have different diffusion preference in vertical direction during post annealing process, leading to inhomogeneous element distribution of as-prepared CZTSSe thin film [8].

Thus in this paper, we introduced CZTS precursor with a three-layer structure by co-sputtering CZTS target with Zn or Cu targets. Cu-poor and Zn-rich in top and bottom layer while stoichiometric in middle layer were used to suppress the negative effect of the opposite vertical diffusion preference of Cu and Zn in post selenization process. As the chemical-potential stability of single-phase CZTSSe is in a narrow range [9], the control of Zn and Cu amount in three layers should be strict. We selenized the precursor and fabricated solar cells using the obtained CZTSSe thin films. A comparison between CZTSSe thin films selenized from a three-layer structure precursor and a stoichiometric single-layer precursor was carried out. To the best of authors' knowledge, there is no report on the effect of controlling the element distribution in vertical direction in quaternary sulfide mixed precursor on growth of CZTSSe thin film, nor CZTSSe thin film preparation using CZTS target sputtering. With the help of element distribution control, the conversion efficiency increased from 0.97% to 4.51%.

2. Experimental details

CZTS precursor was deposited in a three-layer structure on 1.2 μm thick Mo-coated glass substrate by co-sputtering method. As the surface binding energy of Cu, Zn, Sn and S is different, CZTS precursor prepared by sputtering single stoichiometric CZTS target is copper-poor [10]. The top and bottom layers were prepared by

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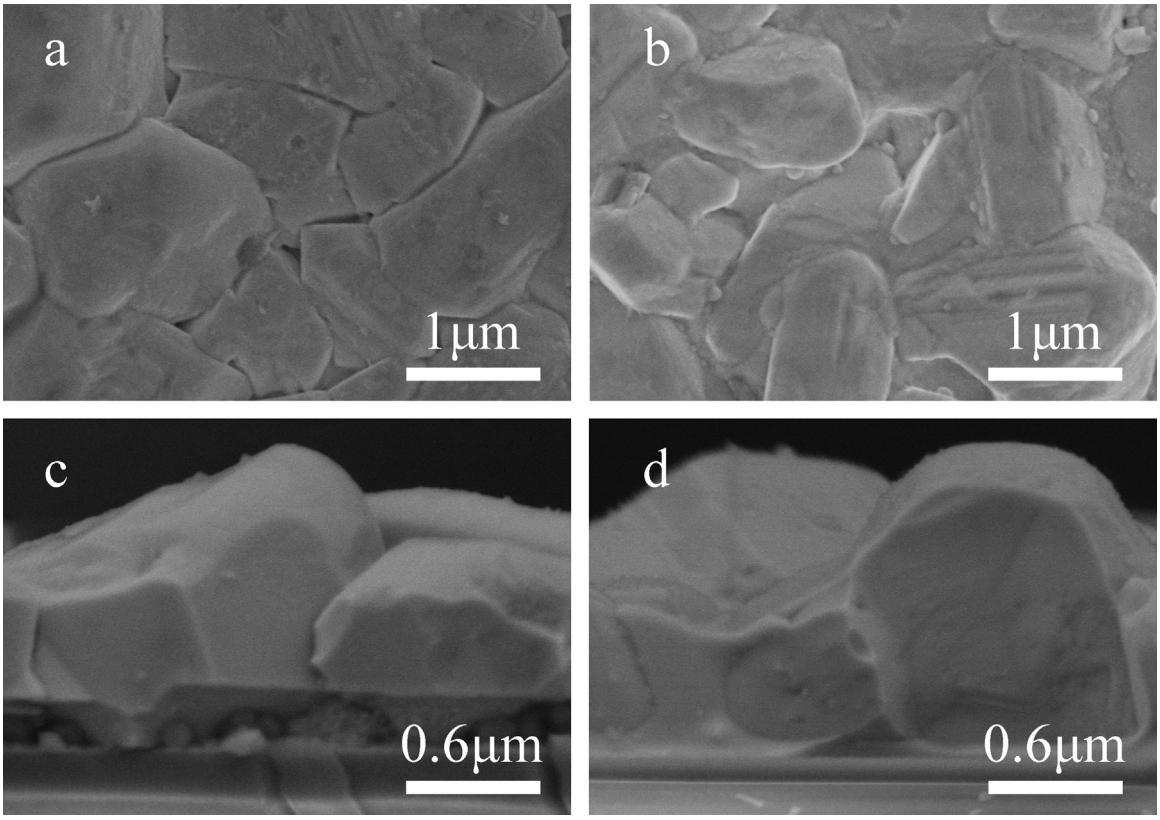

Fig. 1. Surface SEM images of CZTSSe thin films: (a) single layer; (b) three-layer. Cross-section SEM images of CZTSSe thin films: (c) single layer; (d) three-layer.

Table 1
Element composition of CZTSSe thin films.

Sample	Cu/%	Zn/%	Sn/%	S/%	Se/%
Single layer	24.47	12.70	13.53	19.90	29.41
Three-layer	23.77	13.40	13.98	18.76	30.09

co-sputtering CZTS and Zn targets and the middle layer was prepared by co-sputtering CZTS and Cu targets (all with 99.99% purity, purchased from mat-cn co., China). The deposition was carried out with 30 sccm Ar as working gas at the base pressure of 6.0×10^{-4} Pa. The sputtering powers for CZTS, Cu and Zn targets were fixed at 50 W, 20 W and 12 W RF, respectively. The thickness of top and bottom layer was 90 nm each and the middle layer's thickness was 600 nm. Stoichiometric single layer precursors by co-sputtering CZTS and Cu with the same total thickness were prepared for comparison. The precursors were placed with 20 mg Se powder in a nearly-sealed 40 cm^3 quartz tube, which was set in the heating zone of a tube furnace. The selenization process was maintained at 580 °C for 10 min. CZTSSe thin films were named as three-layer and single layer according to the structure of precursors.

X-ray diffraction (XRD, Rigaku Ultima-IV diffraction-meter with Cu–K_α radiation source) and Raman (Renishaw inVia, excitation laser wavelength of 532 nm) tests were used to analyze the structure and crystallization of the samples. The morphology and element analysis were studied by scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM and EDS, Hitachi S4800).

CZTSSe solar cells were fabricated in an ITO/i-ZnO/CdS/CZTS/

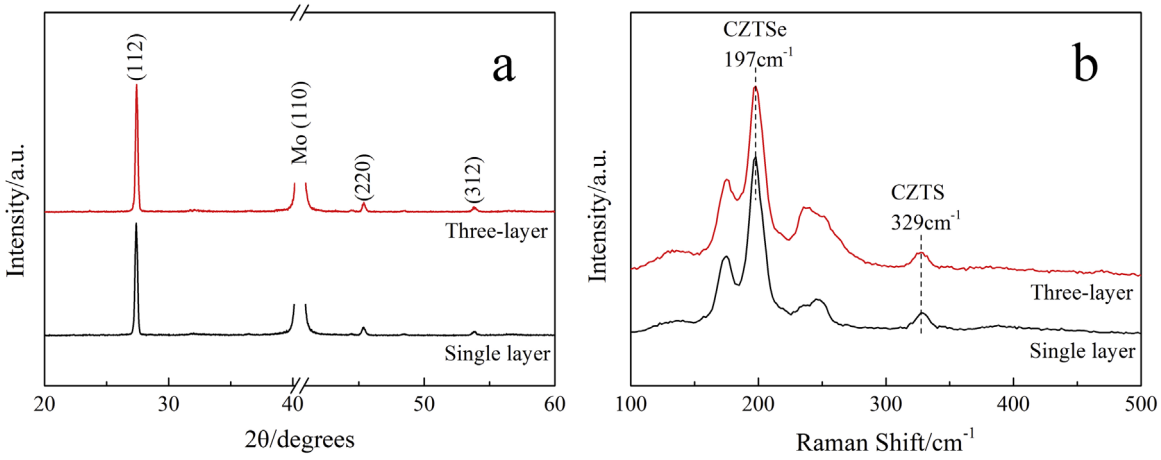

Fig. 2. XRD patterns (a) and Raman spectra (b) of CZTSSe thin films.