Performance enhancement of Cu$_2$ZnSn(S,Se)$_4$ solar cell by inserting Sb and Sb$_2$Se$_3$ doping layer at the bottom of CZTS precursor

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Abstract
In this work, CZTSSe thin film is prepared by selenizing CZTS precursor with Sb and Sb$_2$Se$_3$ doping layer at the bottom. The XRD and Raman results demonstrate that kesterite CZTSSe thin film with preferred crystalline quality is prepared. XPS and EDS results indicate that the inserted Sb and Sb$_2$Se$_3$ atoms do not occupy the lattice of CZTSSe. Both Sb and Sb$_2$Se$_3$ will transfer into semi-liquid phase Sb$_2$Se$_3$ during selenization process, which diffuses into the surface of the absorber from the bottom of the absorber and finally volatilizes at the elevated temperature. The semi-liquid phase Sb$_2$Se$_3$ effectively promotes the grain growth of CZTSSe. CZTSSe thin film with Sb$_2$Se$_3$ doping layer has a better crystalline quality than that with Sb doping layer, which exhibited a best PCE of 4.0%, featuring 361.1 mV Voc, 23.1 mA cm$^{-2}$ Jsc and 48.2% FF.

1. Introduction
As energy consumption and environmental pollution become more and more serious, solar energy has received much attention as a clean energy source [1]. Since the realization of commercial production in silicon-based solar cells in the 1950s, light absorbing material has become a hot research field [2]. Currently, the mainstream compound semiconductor thin films such as Cu(In,Ga)Se$_2$ (CIGS), CdTe and Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) have been intensively studied and gradually become promising options for next generation photovoltaics [3]. Even though the satisfactory merits of CIGS and CdTe thin film solar cells, most of the required elements for producing CIGS and CdTe are limited by its low abundance in earth (In) and toxicity (Cd), which largely restricted its large scale production [4]. Among the most promising p-type absorbers, kesterite CZTSSe with the property of non-toxic and environmentally friendly has witnessed rapid development in the past decades from the initial power conversion efficiency (PCE) of 0.66% to the world champion 12.6% [5, 6]. Nowadays, CZTSSe thin film solar cell fabricated on flexible substrates has opened a wide range of application for roll-to-roll production, which can be easily integrated into various buildings and structures. The word record PCE of flexible CZTSSe thin film solar cell fabricated on willow glass has been refreshed to 6.9%, which is still far from those rigid substrate relied devices [7]. The main factor dragging the progress pace of device performance is the open circuit voltage (Voc) deficit in CZTSSe absorber. It is well known that the Voc deficit is caused mainly by charge pair recombination and the recombination can be suppressed by improving the crystallinity of CZTSSe. Researchers find that cationic substitution or partial substitution of Cu, Zn or Sn in CZTSSe can not only suppress the formation of secondary phase (ZnS) and anti-occupation defects (Cu$^{2+}$ and Zn$^{2+}$) but also improve the crystallinity of CZTSSe [8]. For these factors, various cationic substitution strategies have been carried out to replace the metallic atoms in CZTSSe. Currently, to replace the location of Cu in CZTSSe, the introduction of Ag is mostly reported, which can also adjust the optical band gap of CZTSSe [9]. For the substitution of Zn, elements such as Cd, Fe, Mn and Co have been intensively reported [10–13]. The study of replacing the location of Sn in
CZTSSe with a cationic is mainly related to Ge and Si [14]. Among all the potential metallic elements, the study of Sb related CZTSSe is seldom reported, which has been verified a positive effect in promoting the grain growth of CIGS [15].

Herein, the e-beam evaporated Sb layer and Sb$_2$Se$_3$ layer were introduced as different doping sources to prepared CZTSSe thin films. PCE enhancement was observed after incorporating Sb layer and Sb$_2$Se$_3$ layer in CZTS precursor. The detailed physical mechanism of Sb and Sb$_2$Se$_3$ doping layer on performance enhancement for flexible CZTSSe thin film solar cell are investigated systematically.

2. Experimental details

50 μm thick Ti foil was selected as the flexible substrate. Firstly, the substrates were immersed in acetone, ethyl alcohol and deionized water for ultrasonic cleaning for 10 min, respectively. After that, diluted acid solution with HNO$_3$ and HF was used to further removing the oxide layer from the substrate surface and the polishing time was 60 s. The Mo back contact layer with the thickness of 800 nm and the square resistance of 0.8 ohm/square was sputtered on Ti substrate. For two kinds of Sb incorporation sources, 20 nm Sb thin film was prepared by e-beam evaporation system. The base vacuum and evaporation rate was $4 \times 10^{-4}$ Pa and $1 \text{ Å s}^{-1}$, respectively. Additionally, Sb$_2$Se$_3$ thin film was prepared by 40 nm Sb layer followed by selenization process. For the selenization process, 5 mg Se pellets were placed into the quartz tube and the evaporated 40 nm Sb layer was selenized at 360°C for 20 min in a nitrogen atmosphere. The thickness of Sb$_2$Se$_3$ was about 90 nm. After that, all the samples were transferred into the magnetron sputtering system for CZTS precursor preparation. The CZTS precursor was co-sputtered with a sandwich structure. The top and bottom layer was co-sputtered with Zn and CZTS targets, the middle layer was sputtered with Cu and CZTS targets. The thickness of CZTS precursor was about 450 nm. Detailed sputtering process can be referred to our previous report [16]. The CZTS precursor with Sb and Sb$_2$Se$_3$ layer were selenized at 580°C for 10 min in a nitrogen atmosphere. The CZTSSe thin film with Sb and Sb$_2$Se$_3$ layer in CZTS precursor are labeled as S1 and S2. The schematic illustration for the fabrication of Sb and Sb$_2$Se$_3$ incorporated CZTSSe thin films is presented in figure 1. Flexible CZTSSe thin film solar cells with the traditional structure of Ti/Mo/CZTSSe/CdS/i-ZnO/ITO/Ag were fabricated. After 60 nm CdS was prepared by chemical bath deposition, 50 nm i-ZnO and 200 nm ITO were subsequently sputtered on CdS. Finally, Ag grid was evaporated on ITO and the effective area of each isolated cell was 0.2 cm$^2$.

The structural information of thin films was determined by x-ray diffraction (XRD, Bruker D8 Advance equipped with Cu-K$_\alpha$, radiation source) and Raman spectroscopy (Renishaw inVia, 532 nm laser). The micromorphology of Sb, Sb$_2$Se$_3$, and CZTSSe thin films was performed by scanning electron microscopy (SEM, Hitachi S4800) and the elemental analysis of CZTSSe thin film was carried out by energy dispersive spectroscopy (EDS, Hitachi S4800, 20 kV) mounted on SEM. The surface roughness of CZTSSe thin film was measured by atomic force microscopy (AFM, FSM FM-Nanoview 6600). X-ray photoelectron spectroscopy (XPS, Escalab 250Xi) was used to determine the valence states of Sb. Finally, the current density-voltage curve of

Figure 1. Schematic of Sb and Sb$_2$Se$_3$ incorporation process of CZTSSe thin films.
flexible devices was carried out by Keithley 2400 sourcemeter with AM 1.5 G illumination, the power density of the solar simulator was 100 mW cm\(^{-2}\).

3. Results and discussion

The structural information of Sb and Sb\(_2\)Se\(_3\) thin film is examined by XRD and the result is shown in figure 2(a). As we can see from the XRD pattern, two visible peaks located at 23.57° and 48.35° are well matched with the (003) and (006) peak of Sb (JCPDS No.: 35-0732). For Sb\(_2\)Se\(_3\) thin film, the characteristic peak located at 27.65° can be attributed to the (230) peak of Sb\(_2\)Se\(_3\) (JCPDS No.: 15-0861). Other binary or ternary phases are not observed in figure 2(a), indicating the phase purity of the obtained Sb and Sb\(_2\)Se\(_3\) thin film.

The XRD patterns of CZTSSe, CZTSSe with Sb and CZTSSe with Sb\(_2\)Se\(_3\) doping layer are shown in figure 2(b). Visible peaks located at 27.42°, 45.62° and 53.9° are well matched with the (112), (204) and (312) peak of kesterite CZTSe (JCPDS No.: 52-0868) for all the samples [17]. A gradual increased diffraction intensity is observed in figure 2(b), indicating a superior crystalline quality of the CZTSSe absorber after inserting the Sb and Sb\(_2\)Se\(_3\) doping layer in CZTS precursor. Besides, CZTSSe thin film with Sb\(_2\)Se\(_3\) doping layer in precursor has a higher diffraction intensity than that with Sb layer in precursor. Other impurity phases are not observed in figure 2(b), which guarantees the purity of absorber layers. We find that there exists a slight diffraction peak shift in XRD results after inserting Sb or Sb\(_2\)Se\(_3\) layer in CZTS precursor, which maybe be due to the existence of Sb or Sb\(_2\)Se\(_3\). During the selenization process, especially for CZTSSe, the formation of binary phases such as ZnS, ZnSe and CuSe are more likely to occur. These potential binary phases will result in a severe reduction in crystallinity and carrier lifetime of CZTSSe absorber. Besides, their diffraction peaks are quite close to that of CZTSSe. Therefore, the purity of the obtained CZTSSe thin films needs to be distinguished. Raman spectra of CZTSSe, CZTSSe with Sb and CZTSSe with Sb\(_2\)Se\(_3\) doping layer are depicted in figure 3. Dominant vibration peaks located at 174.38 cm\(^{-1}\), 195.55 cm\(^{-1}\) and 232.53 cm\(^{-1}\) can be attributed to CZTSSe [18]. The other peak located at 326.85 cm\(^{-1}\) is classically reported for CZTS [19]. Similarly, the Raman intensity of CZTSSe with Sb\(_2\)Se\(_3\) doping layer is higher than that with Sb doping layer, which is in accordance with the XRD results. The higher intensity of CZTSSe thin film with Sb\(_2\)Se\(_3\) doping layer in XRD and Raman results shows that introducing a Sb\(_2\)Se\(_3\) doping layer in CZTS precursor can play a better positive role in enhancing the crystalline quality of CZTSSe than introducing a Sb doping layer. The detailed explanation of this phenomenon will be discussed later. Other binary and ternary peaks are not observed in figure 3, further demonstrating the purity of the obtained CZTSSe thin films.

The SEM images of evaporated Sb thin film, Sb\(_2\)Se\(_3\) thin film and CZTSSe thin films are shown in figure 4. For the evaporated Sb thin film, the SEM image reveals a relatively uniform distribution of small grains with the size of 50–100 nm. The surface morphology of the Sb\(_2\)Se\(_3\) thin film depicted in figure 4(b) shows a relatively loosen distribution of grains with the size of 400 nm. The increased grain size is a manifestation of grain nucleation and growth process during selenization. The SEM images of CZTSSe, CZTSSe with Sb and CZTSSe with Sb\(_2\)Se\(_3\) doping layer are shown in figures 4(c)–(e), respectively. CZTSSe without Sb incorporation presents a compact distribution of grain on its surface in figure 4(c). An obvious increase in uniformity and grain size (300–500 nm for S1, 800–100 nm for S2) is observed after inserting a Sb and Sb\(_2\)Se\(_3\) doping layer in CZTS precursor, which suggests an increased crystallinity of CZTSSe thin films. The increased grain size with decreased grain boundary can effectively suppress the recombination losses of carriers, which is desirable for high efficiency solar cells [20]. The SEM images with the cross section view are shown in figures 4(f)–(h). A near...
single-grain layer throughout the entire CZTSSe absorber is formed at the CZTSSe-Mo interface (marked with red dot circle) after introducing Sb$_2$Se$_3$ thin film, which indicates a better interface quality, helping to reduce potential defect at grain boundary and resulting in less recombination for increasing short circuit current density ($J_{sc}$). The AFM images of CZTSSe thin films are presented in figure 5. The surface roughness of CZTSSe with Sb and Sb$_2$Se$_3$ doping layer is 40.89 nm and 14.94 nm, respectively. Due to decreased surface roughness, a better coverage of the subsequent CdS layer on CZTSSe absorber is easier to form, finally reducing the interface state density [21].

We find that there exists a slight diffraction peak shift in XRD results after inserting Sb or Sb$_2$Se$_3$ layer in CZTS precursor, which can be explained by the possible existence of Sb and Sb$_2$Se$_3$. However, there is no shift in Raman results. We think the un-shifted peaks in Raman results can be explained by the Raman test itself which is only a superficial measurement with a depth of $\sim$150 nm. As previously reported by Zhang et al, Sb prefers to
substitute the atomic location of Sn in CZTS\textsuperscript{22} and the atomic radius of Sn is very close to Sb, so that the first possibility for the slight shift in XRD could be attributed to the similar atomic radius of Sn and Sb. The second possibility is that Sb does not enter into the lattice of CZTSSe during the selenization process at all. To exclude one of the above reasons, the XPS valence states of Sb is determined and the core-level spectrum of Sb 3d in CZTSSe thin films is shown in figure 6. Obviously, no peaks concerning Sb element are detected in XPS results, indicating that the evaporated Sb or Sb\textsubscript{2}Se\textsubscript{3} atoms do not remain in the CZTSSe absorber. Then the other issue comes. Where does Sb or Sb\textsubscript{2}Se\textsubscript{3} exist? The formation sequence of CZTSSe are listed from equations (1)–(5). Cu\textsubscript{2}S/Cu\textsubscript{2}Se and SnS\textsubscript{2}/SnSe are firstly formed in the selenization process of Cu/Sn with S/Se. After that ternary compound of Cu\textsubscript{2}SnS\textsubscript{3}/Cu\textsubscript{2}SnSe\textsubscript{3} is formed during the reaction of Cu\textsubscript{2}S/Cu\textsubscript{2}Se and SnS\textsubscript{2}/SnSe\textsubscript{2}. Finally, the Cu\textsubscript{2}SnS\textsubscript{3}/Cu\textsubscript{2}SnSe\textsubscript{3} will react with Zn to form the kesterite CZTSSe. At the moment when selenium vapor reaches the bottom Sb doping layer, a reaction between Sb and Se is easy to take place, and consequently a Sb\textsubscript{2}Se\textsubscript{3} thin film forms. Since the melting point of Sb\textsubscript{2}Se\textsubscript{3} is 611 °C, logically speaking, Sb\textsubscript{2}Se\textsubscript{3} will not transfer into a quasi-liquid phase or vapor phase at the highest selenization temperature of 580 °C. Yan et al reported that the melting point of Sb\textsubscript{2}Se\textsubscript{3} mixed with Se will become lower than 450 °C when the content of selenium is excess\textsuperscript{15}. The atomic ratio results of CZTSSe thin films is shown in table 1, and the Se/(S + Se) ratios are 83.7% and 87.9% for CZTSSe thin films with Sb and Sb\textsubscript{2}Se\textsubscript{3} doping layer, respectively. Both of the samples present a state of rich selenium. Thus the Sb\textsubscript{2}Se\textsubscript{3} will reasonably diffuse into the surface of the absorber from the bottom of the absorber in the form of a quasi-liquid phase and finally volatilize at the elevated temperature. As we can see in table 1, the atomic percentage of Sb in CZTSSe thin film is 0.01% and 0% for S1 and S2, respectively, which further verifies the disappearance of Sb by evaporation in Sb\textsubscript{2}Se\textsubscript{3} vapor state. During the selenization process, the

| Cu % | Zn % | Sn % | S % | Se % | Sb % | Se/(S + Se) |
|------|------|------|-----|------|------|-------------|
| S1   | 19.35| 15.21| 12.28| 8.63 | 44.52| 0.01        | 0.837       |
| S2   | 21.44| 13.87| 12.13| 6.34 | 46.22| 0           | 0.879       |

Figure 5. AFM images of CZTSSe thin films with (a) Sb doping layer and (b) Sb\textsubscript{2}Se\textsubscript{3} doping layer.

Figure 6. The core-level XPS spectrum Sb 3d in CZTSSe thin films.
grain growth of CZTSSe benefits a lot from the semi-liquid Sb$_2$Se$_3$, which can be verified in the crystalline quality and morphology discussion in XRD and SEM cross-section morphology. As previously discussed, CZTSSe thin film with Sb$_2$Se$_3$ doping layer has a better crystalline quality than that with Sb doping layer, the crystalline quality difference in CZTSSe can be explained by the equation (5). For sample S1, the formation of other ternary impurity phases such as Cu$_2$SbS$_3$ and Cu$_2$SbSe$_3$ is likely to take place before the reaction of Sb with the forthcoming Se vapor, which largely weakens the role of Sb$_2$Se$_3$ in promoting grain growth and passivating the grain boundary defect density. However, for sample S2, which already contains a Sb$_2$Se$_3$ layer under CZTS precursor, the formation process of Sb$_2$Se$_3$ can be ignored and its role in promoting grain growth can be much stronger.

\[ \begin{align*} 
\text{Cu} + S/Se & \rightarrow \text{Cu}_2S/Cu_2Se \\
\text{Sn} + S/Se & \rightarrow \text{Sn}_2/\text{SnSe}_2 \\
\text{Cu}_2S/Cu_2Se + \text{Sn}_2/\text{SnSe}_2 & \rightarrow \text{Cu}_2\text{Sn}_3/Cu_2\text{SnSe}_3 \\
\text{Cu}_2\text{Sn}_3/Cu_2\text{SnSe}_3 + \text{Zn} & \rightarrow \text{CZTSSe} \\
\text{Sb} + Se & \rightarrow \text{Sb}_2\text{Se}_3 
\end{align*} \]

To determine the device performance of the obtained flexible CZTSSe thin film solar cells, the J-V curves are recorded and they are shown in figure 7. The detail performance parameters of flexible CZTSSe thin film solar cells are listed in table 2. For the device without Sb incorporation, the poor PCE of 2.8%, featuring 315.8 mV Voc, 21.7 mA cm$^{-2}$ Jsc and 42.0% fill factor (FF), can be attributed to the small grain size with high boundary density, which brings severe carrier recombination, decreasing Jsc. For the devices with Sb doping layer and Sb$_2$Se$_3$ doping layer in CZTS precursor, an obvious PCE enhancement is observed. The best device performance with a PCE of 4.0% is obtained for the flexible CZTSSe thin film solar cell with Sb$_2$Se$_3$ doping layer. This desirable device performance benefits a lot from the semi-liquid Sb$_2$Se$_3$ during selenization process. The pre-deposited Sb$_2$Se$_3$ doping layer exists as quasi-liquid phase at elevated temperature and plays an effective role in promoting grain growth, reducing potential defect at grain boundary and decreasing a recombination loss for Jsc. Additionally, the decreased surface roughness of CZTSSe thin film after inserting a Sb$_2$Se$_3$ layer can also provide a better coverage with the subsequent CdS layer, making it easier to form a sharp CZTSSe/CdS heterojunction. The EQE curves of flexible CZTSSe thin film solar cells are shown in figure 8(a). For the flexible device without Sb incorporation, the poor EQE values in visible and near infrared region indicate the presence of a considerable amount of other recombining defects and severe bulk recombination in CZTSSe absorber,
reducing the ability of collecting carriers, which is responsible for the poor PCE of 2.8%. While for the solar cells with Sb and Sb$_2$Se$_3$ thin film in the precursor, the EQE spectra show enhancements in the visible and near infrared region, implying an increased ability in collecting photons. Additionally, the band gaps of these samples obtained by differential calculation are shown in figure 8(b), which indicates that the band gap of CZTSSe thin film (∼1.203 eV) after introducing Sb and Sb$_2$Se$_3$ thin film is not affected.

4. Conclusions

A significant enhancement in PCE for flexible CZTSSe thin film solar cells by inserting Sb and Sb$_2$Se$_3$ doping layer in CZTS precursor is reported. XRD, XPS and EDS results demonstrate that the introduced Sb and Sb$_2$Se$_3$ atoms do not occupy in the lattice of CZTSSe absorber. No matter Sb or Sb$_2$Se$_3$ is inserted in the bottom of the CZTS precursor, both of them will transfer into Sb$_2$Se$_3$ quasi-liquid phase, which diffuses into the surface of the absorber from the bottom of the absorber and finally volatilizes from the surface at the elevated temperature. During the selenization process, Sb$_2$Se$_3$ plays an effective role in promoting grain growth, reducing potential defect at grain boundary and finally improving the device performance. It is also found that CZTSSe thin film with Sb$_2$Se$_3$ doping layer has a better crystalline quality than that with Sb doping layer. Finally, a best PCE of 4.0% is obtained for the flexible CZTSSe thin film solar cell resulted from Sb$_2$Se$_3$ insertion into the bottom of the CZTS precursor.

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