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# Effects of etching on surface structure of Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> absorber and performance of solar cell



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Hongmei Luan<sup>a,b</sup>, Bin Yao<sup>a,b,\*</sup>, Yongfeng Li<sup>a,b,\*</sup>, Ruijian Liu<sup>b</sup>, Zhanhui Ding<sup>a,b</sup>, Kun Shi<sup>b</sup>, Yan Li<sup>b</sup>, Zhenzhong Zhang<sup>c</sup>, Haifeng Zhao<sup>c</sup>, Ligong Zhang<sup>c</sup>

<sup>a</sup> State Key Lab of Superhard Material, and College of Physics, Jilin University, Changchun 130012, China

b Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, Changchun 130012, China

<sup>c</sup> State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, No. 3888 Dongnanhu

Road, Changchun 130033, China

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#### ABSTRACT

 $Cu_2ZnSn(S,Se)_4$  (CZTSSe) films with smooth surface were prepared by solution approach and etched (etched-CZTSSe) through using KMnO<sub>4</sub> in a H<sub>2</sub>SO<sub>4</sub> based medium followed by Na<sub>2</sub>S. Two types of solar cells with conventional structure were fabricated with CZTSSe and etched-CZTSSe as absorber, respectively. It is demonstrated by XRD, XPS, EDS and Raman measurement that the bulk CZTSSe is of kesterite structure while its surface contains a small amount of  $Cu_2ZnSn_3Se_8$  and ZnSe secondary phases besides kesterite CZTSSe. On the surface, the  $Cu_2ZnSn_3Se_8$  is completely removed after etching while the ZnSe is partially. It is found that the elimination or reduction of the secondary phases increase the shunt resistance greatly, leading to a larger opencircuit voltage ( $V_{oc}$ ) which results in the improvement of power conversion efficiency (PCE) for the etched-CZTSSe-based solar cell. The PCE has a maximum increase of 26% by etching. An intensive study has been made for the influencing mechanism of etching on the PCE of solar cells.

#### 1. Introduction

Kesterite Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> (CZTSSe) has been identified as a promising absorber material of alternative for Cu(In,Ga)(S,Se)<sub>2</sub> (CIGSSe), due to its earth-abundant and nontoxic elements, high absorption coefficient (>  $10^4$  cm<sup>-1</sup>), tunable band gap (1.0–1.5 eV) and a power conversion efficiency (PCE) as much as 33% predicted by Shockley-Queisser theory (Katagiri et al., 2009; Ki and Hillhouse, 2011; Mitzi et al., 2011; Ramasamy et al., 2012). In recent years, a great progress has been made in the preparation and performance of CZTSSe-based solar cell. The current record device (12.6%) of CZTSSe solar cell has been produced from a hydrazine solution process by the IBM research group (Wang et al., 2014). However, the record PCE of 12.6% is still smaller than the PCE of 22.6% (Jackson et al., 2016) of CIGSe solar cell, moreover, far below the Shockley-Queisser limit of 33% efficiency under terrestrial conditions (Wang et al., 2014). It has been demonstrated that the open-circuit voltage (Voc) deficit, equal to the difference between the band gap and V<sub>oc</sub>, is currently the biggest hurdle preventing CZTSSe devices from achieving higher efficiency (Altamura and Vidal, 2016; Gokmen et al., 2013; Mitzi et al., 2013). Although many factors, such as crystal quality, p-n junction (Hwang et al., 2017) and

electrode (Salomé et al., 2010), can influence the  $V_{oc}$  in a solar cell, carrier recombination near the charge-separating p-n junction play a dominant role. While carrier recombination in p-n junction is mainly determined by the band alignment (Altamura and Vidal, 2016; Bourdais et al., 2016), lattice mismatch and the secondary phases at p-n junction interface (Barkhouse et al., 2012; Yin et al., 2014).

A great deal of literature (Altamura and Vidal, 2016; Bourdais et al., 2016) has indicated that CZTSSe with a single kesterite structure is very hard to be obtained due to the extremely tiny composition region in which the kesterite CZTSSe is formed. Some secondary phases, such as  $Cu_2Sn(S,Se)_3$  (Mousel et al., 2013), Zn(S,Se) (Hsu et al., 2013), Cu(S,Se) (Tanaka et al., 2012), and Sn(S,Se) (Xie et al., 2014) are found very easily to be formed under the off-stoichiometry conditions. In general, the kesterite CZTSSe photovoltaic-grade absorber is prepared in the Znrich and Cu-poor condition. The best devices have the ratio of Cu/ (Zn + Sn) in the range of 0.7–0.9 and a ratio of Zn/Sn in the range of 1.1–1.25 (Lopez-Marino et al., 2013). Although the ratios can be controlled in bulk CZTSSe, it seems very difficult in its surface layer, resulting in an off-stoichiometric composition that is easy to form some secondary phases. These secondary phases can be retained at the interface of the CdS/CZTSSe heterojunction and potentially degrade the

\* Corresponding authors at: State Key Lab of Superhard Material, and College of Physics, Jilin University, Changchun 130012, China. *E-mail addresses:* binyao@jlu.edu.cn (B. Yao), liyongfeng@jlu.edu.cn (Y. Li).

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performance of CZTSSe-based solar cells. Therefore, it is essential and significant to characterize the secondary phases and elucidate their impact on the cell's performance as well as to look for an effective approach of removing or reducing those secondary phases for enhancing the performance of CZTSSe-based solar cell. Xie et al. (2014) reported that the SnSe secondary phase is detected by XRD (Li et al., 2016a,b). Tanaka et al. (2012) observed secondary phase of Cu<sub>2</sub>Se on the surface of CZTSSe by Raman spectroscopy and found that the amount of  $Cu_2Se$  can be lowered by adjusting the Cu/(Zn + Sn) ratio. Buffiere et al. (2015) used KCN to remove the secondary phase of Cu (S,Se) on the surface of CZTSSe. Edgardo Saucedo et al. (Fairbrother et al., 2014; Lopez-Marino et al., 2013) tried to clear away ZnSe secondary phase that was formed during annealing process in low pressure and temperature conditions with an etching method by using  $H_2O_2$ ,  $KMnO_4$ , or  $K_2Cr_2O_7$ , and found that  $KMnO_4$  is the most effective etching agent. These results indicate that the solution used for etching is not the same for different secondary phases. Although the characterization and elimination of surface secondary phases have been reported in some literature, few researches about the effect of secondary phases on the performance of CZTSSe-based solar cell are found and the corresponding influencing mechanism remains unclear or need to be further illustrated.

It is well known that X-ray photoelectron spectroscopy and Raman scattering spectroscopy are effective techniques to detect the composition and structure of surface layer. Chemical etching is one of approaches for removing surface secondary phases. Therefore, in our present work, we will clear the surface of CZTSSe film by chemical etching, characterize the surface structure before and after etching by XPS and Raman techniques and systematically study the influencing mechanism of etching on the performance of CZTSSe-based solar cells.

#### 2. Experimental

A precursor solution used for the preparation of Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) thin films was prepared by dissolving Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (1.198 g, 6 mmol),  $SnCl_2 H_2O$  (0.745 g, 3.3 mmol),  $ZnCl_2 H_2O$  (0.5043 g, 3.7 mmol), and thiourea (1.97 g, 26 mmol) into N, N-dimethyl formamide (10 mL, DMF) and then magnetically stirring for 2 h at room temperature. The CZTS precursor thin films were fabricated by spincoating the CZTS precursor solution onto the Mo-coated soda-lime glass substrates at a rotating rate of 3000 rpm for 3 min followed by drying in air at 300 °C, and the coating and drying processes were repeated 10 times. A detailed synthetic procedure of the CZTS films can be found elsewhere (Liu et al., 2015; Xiao et al., 2016). To get the suitable CZTSSe thin films, the as-prepared CZTS films and 200 mg of selenium powder were sealed in a graphite box (~55 mm in diameter and  $\sim$  40 mL in volume), followed by a selenization process at 550 °C for 15 min in a rapid thermal processing (RTP) furnace (MTI, OTF-1200X-4-RTP) under N2 flow (40 mL/min, keep the pressure at 1 bar) with a ramping rate of 5 °C/s, and finally cooled down to room temperature naturally. Subsequently, some CZTSSe films were etched by the KMnO<sub>4</sub> dissolved in dilute  $H_2SO_4$  (PH = 5) for 30 s followed by dipping in a Na<sub>2</sub>S (1 M) aqueous solution for 1 min. The KMnO<sub>4</sub> acidic solution is used to etch surface secondary phases, such as ZnSe, by following reaction (Lopez-Marino et al., 2013; Xie et al., 2014):

 $8H_2SO_4(aq) + 2KMnO_4(aq) + 5ZnSe(s) = 5Se$ (s) +  $5ZnSO_4(aq) + 2MnSO_4(aq) + K_2SO_4(aq) + 8H_2O(l)$ 

The Na<sub>2</sub>S is used to solubilize the Se produced by above reaction, so that the Se can be rinsed out from the surface. In addition, the Na of Na<sub>2</sub>S might diffuse into the polycrystalline CZTSSe films to passivate surface and grain boundaries, which is beneficial to improvement the PCE of solar cell.

For convenience, these CZTSSe films with an etching process are denoted as etched-CZTSSe. The CZTSSe-based solar cells with a

conventional structure of glass/Mo/CZTSSe/CdS/i-ZnO/ITO/Al were fabricated by using the CZTSSe or etched-CZTSSe as absorber layers. Then CdS buffer layer were prepared by chemical bath deposition, using cadmium sulfate (CdSO<sub>4</sub>·8/3H<sub>2</sub>O) as cadmium precursor sources (Neuschitzer et al., 2015), followed by the radio frequency magnetron sputtering deposition of i-ZnO (50 nm) and ITO (260 nm). Finally, Al grid electrode ( $\sim$ 1.0 µm) was made though thermal evaporation.

The crystal structures of the films were characterized by an X-ray diffractometer (XRD) with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). The morphologies of surface are measured by scanning electron microscope (SEM) (Hitachi S-4800) equipped with an energy-dispersive X-ray spectroscopy (EDS) system (EDAX Genesis 2000). The structure of the surface layer is detected by Raman scattering spectroscope excited with 633 nm wavelength (T64000 Horiba Jobin-Yvon spectrometer at backscattering configuration). The composition of film is measured by EDS. Composition of the surface and valence state of elements of the film are detected by X-ray photoelectron spectra (XPS) with Mg Ka radiation ( $h\nu = 1253.6 \text{ eV}$ ) and a resolution of 1.0 eV (VG ESCALAB Mark II XPS). For the power conversion efficiency measurements of CZTSSe based solar cells, the current density-voltage curves were measured with a Keithley 2400 source meter and a solar simulator (Abet Sun 2000; AM 1.5). The light intensity was calibrated to 100 mW/cm<sup>2</sup> using a Newport optical power meter (model 842-PE) certified by Newport.

#### 3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of CZTSSe thin film and etched-CZTSSe thin film, indicating that both films consist of CZTSSe with kesterite structure (Amal et al., 2014; Li et al., 2016a,b; Xiao et al., 2015, 2016), metal Mo (JCPDS Card No. 42-1120) (Yang et al., 2016) and MoSe<sub>2</sub> (Li et al., 2015; Würz et al., 2003). The existence of Mo is ascribed to the Mo layer coated on the glass substrate, while the MoSe<sub>2</sub> is formed due to the reaction of Mo and Se at the CZTSSe/Mo interface during the selenization process. The XRD results reveal that both the CZTSSe and etched-CZTSSe films are composed by a single kesterite CZTSSe phase. The sharp diffraction peaks imply that they have a good crystalline quality.

Fig. 2a and c show the SEM images of the surface morphology of CZTSSe and etched-CZTSSe films, respectively. It is found that the surface of CZTSSe film appears fish scale residual after etching with KMnO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> + Na<sub>2</sub>S, which is due to that the chemical reaction residual cannot be washed out completely. In addition, the small grains on the surface of the CZTSSe film (marked by red circles) disappeared after etching. This implies that the small grains may be secondary phases and can be removed by etching.



Fig. 1. XRD patterns for the CZTSSe (lower curve) and etched-CZTSSe (upper curve).



Fig. 2. SEM images of surface and cross-sectional morphology of the CZTSSe (a, b) and etched-CZTSSe (c, d).

## Table 1 Compositions and atom ratios of metal elements for surface layer and bulk of the CZTSSe and etched-CZTSSe films measured by XPS and EDS.

	Sample	Cu (at%)	Zn (at%)	Sn (at%)	Se (at%)	S (at%)	Cu/metal elements	Zn/metal elements	Sn/metal elements
Surface	CZTSSe Etched-CZTSSe	16 18	14 25	18 13	52 44	-	0.33 0.32	0.29 0.44	0.37 0.23
Bulk	CZTSSe etched-CZTSSe	21 21	11 12	10 12	54 47	4 8	0.5 0.46	0.26 0.26	0.23 0.26

Both first principle calculations and experiments demonstrate that the phase composition of CZTSSe film is closely related to its chemical composition. In order to figure out secondary phases in the surface layer of the CZTSSe film, the chemical compositions of surface layer and bulk of the CZTSSe films before and after etching were measured by XPS and EDS, respectively, as shown in the Supporting information. The results are listed in Table 1, which shows a great difference between the bulk and the surface layer.

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Fig. 3 shows ternary phase diagram of composition-structures calculated by Altamura and Vidal (2016). The red dot around the center of phase diagram shows the composition range to form a single-phase Cu<sub>2</sub>ZnSnSe<sub>4</sub>, indicating that single phase Cu<sub>2</sub>ZnSnSe<sub>4</sub> can be form when the composition is near stoichiometric ratio of Cu<sub>2</sub>ZnSnSe<sub>4</sub>. According to the results listed in Table 1, the compositions of bulk CZTSSe and etched-CZTSSe are both close to the stoichiometric ratio of CZTSSe. So, it is deduced from the phase diagram that the bulk of both samples are composed of single kesterite CZTSSe, which is in agreement with the results of Fig. 1. However, the surface compositions of CZTSSe and etched-CZTSSe films deviate far from the stoichiometric ratio, implying that their surface layer should be composed of multi-phases. Based on Table 1, the surface composition of CZTSSe film locates at the position marked by a black star in Fig. 3, which indicates that the secondary



Fig. 3. Cu-Zn-Sn-X diagram calculated by G. Altamura et al using first principle calculation (Altamura and Vidal, 2016).

phases of  $Cu_2ZnSn_3Se_8$  and ZnSe exist on the surface besides kesterite CZTSSe phase. The surface composition of etched-CZTSSe locates at the position marked by a blue square in Fig. 3, indicating that the secondary phase is ZnSe. It can be inferred from above analysis that the etching treatment can remove  $Cu_2ZnSn_3Se_8$  and lead to the exposure of ZnSe, which is exactly supported by the higher concentration of Zn in



Fig. 4. Raman scattering spectra of the CZTSSe and etched-CZTSSe films (a) and their  $A_1$  vibration mode (b) using excitation wavelength of 633 nm.

etched-CZTSSe than that of CZTSSe for the proportion of Zn in ZnSe is higher than that of  $Cu_2ZnSn_3Se_8$ .

In order to confirm the secondary phases, Raman scattering spectra of the CZTSSe and etched-CZTSSe films were measured. Fig. 4 shows the Raman spectra of the CZTSSe and etched-CZTSSe films measured with excitation wavelength of 633 nm. As shown in Fig. 4a, there are five Raman peaks at 175, 197, 233, 247 and  $328 \text{ cm}^{-1}$  for both films, corresponding to the Raman vibrational modes of CZTSSe (Chalapathy et al., 2018; Grossberg et al., 2011; Lai et al., 2016; Li et al., 2016a,b). The strongest peak at  $197 \text{ cm}^{-1}$  is ascribed to the vibration of Se, while the weak peak at  $328 \text{ cm}^{-1}$  originates from the vibration of S. These results indicate that two types of anions coexist in the CZTSSe films but the content of Se is dominant. It is noted that a shoulder (labeled by an orange club) appears beside high Raman shift of the 197 cm<sup>-1</sup> peak for the CZTSSe film but disappears after etching, as shown in Fig. 4b. This result implies that the shoulder is caused by the Raman scattering of a surface secondary phase. From the analysis about surface composition mentioned above, it is known that the surface secondary phases are Cu<sub>2</sub>ZnSn<sub>3</sub>Se<sub>8</sub> and ZnSe. Since the Raman peaks of ZnSe is far from the region around 197  $\rm cm^{-1}$ , it can be inferred that the shoulder should originate from Cu<sub>2</sub>ZnSn<sub>3</sub>Se<sub>8</sub>. Disappearance of the shoulder implies that the Cu<sub>2</sub>ZnSn<sub>3</sub>Se<sub>8</sub> is completely removed from the surface after etching (Altamura, 2014). In addition, the intensity of the  $247 \text{ cm}^{-1}$  peak is stronger than that of 233 cm<sup>-1</sup> peak before etching but drops down to the same level after etching, which implies that the  $247 \text{ cm}^{-1}$  peak is related to the secondary phases. It is reported that ZnSe has a Raman peak at 249 cm<sup>-1</sup> which is very close to the value of 247 cm<sup>-1</sup> as obtained in our present work (Fairbrother et al., 2014; Hegedus and Shafarman, 2004; Li et al., 2016a,b). Therefore, the peak at 247 cm<sup>-1</sup> should be ascribed to ZnSe. The decline in the intensity of  $247 \text{ cm}^{-1}$ 

peak indicates that the ZnSe on the surface of CZTSSe is partially removed after etching.

In order to investigate effect of the etching on performance of CZTSSe-based solar cell, two types of solar cells were fabricated with the CZTSSe and etched-CZTSSe films as the absorbers, respectively. The J-V curves of the two types of solar cells with best PCE are shown in Fig. 5a, which indicates that the PCE of the etched-CZTSSe-based solar cell is larger than that of the CZTSSe-based solar cell and the improvement of the PCE is due to enhancement of Voc, short-circuit current density (Jsc) and fill factor (FF) after etching. It is found from Fig. 5b that the EOE of etched-CZTSSe-based solar cell is higher than that of CZTSSe-based solar cell at the wavelength larger than 600 nm. which is mainly due to that the electricity loss of the etched-CZTSSebased solar cell is smaller than that of the CZTSSe-based solar cell (Hegedus and Shafarman, 2004; Hsu et al., 2013). The Jsc is calculated by integration of the EQE are 28.8 and 31.1 mA/cm<sup>2</sup> for the CZTSSe and etched-CZTSSe-based solar cell, respectively, which agrees with the value measured from the J-V curves, indicating that our measurement is reliable. The band gaps (Eg) derived from the EQE indicates that the bandgap of CZTSe-based solar cell is somewhat larger than that of the etched-CZTSSe-based solar cell, as shown in the inset of Fig. 5b. The decreased bandgap of the etched-CZTSSe-based solar cell may result from formation of surface state due to its rough surface.

The J<sub>sc</sub>, V<sub>oc</sub>, FF and PCE of all of etched-CZTSSe- and CZTSSe-based solar cells were listed in Table 2, where the performance parameters with a prefix "etch" are for the etched-CTZSSe-based solar cells. To elucidate the influencing mechanism of etching on the PCE, the electrical parameters including shunt resistance ( $R_{sh}$ ), series resistance ( $R_s$ ), diode ideality factor (A) and reverse saturation current density (J<sub>0</sub>) for each solar cell are calculated by using site's method (Yang et al., 2017), and are listed in Table 3. Similarly, a prefix "etch" was used for electrical parameters of etched-CTZSSe-based solar cells.

In order to reveal the effect of etching clearly, the performance and electrical parameter ratios (R(x)) of each pair of etched-CZTSSe- and CZTSSe-based solar cells are introduced and defined as:

$$R(x) = \frac{\text{etch}-x}{x} \quad (x = J_{sc}, V_{OC}, FF, PCE, R_{sh}, R_s, A \text{ and } J_0)$$
(1)

Obviously, R > 1 (or R < 1) presents that the etching makes the performance and electrical parameters increase (or decrease). Using the data in Table 2, we plot R of Jsc,  $V_{oc}$ , FF and PCE for the six pairs of solar cells, as shown in Fig. 6. It can be seen from Fig. 6 that the R(PCE) is always larger than 1 for the six pairs of cells, indicating that etching is beneficial to the improvement of PCE. The R( $V_{oc}$ ) of the each pairs of cells is larger than 1 and the change of the R( $V_{oc}$ ) is very similar to that of R(PCE), which indicate that the improvement of PCE should be mainly attributed to the increase of  $V_{oc}$ . It is known that the



Fig. 5. J-V curves of typical CZTSSe and etched-CZTSSe solar cells (a) and the EQE curves and (b). Inset in (b) indicates the band gap estimation of CZTSSe and etched-CZTSSe absorber layer.

 Table 2

 Performance of CZTSSe- and etched-CZTSSe-based solar cells.

Group	Etch-J <sub>sc</sub> (mA/ cm <sup>2</sup> )	J <sub>sc</sub> (mA/ cm <sup>2</sup> )	Etch- V <sub>oc</sub> (V)	V <sub>oc</sub> (V)	Etch- PCE (%)	PCE (%)	Etch- FF (%)	FF (%)
1	31.32	29.30	0.35	0.31	5.33	4.23	48.6	47.2
2	29.00	26.04	0.34	0.30	4.45	3.63	45.4	45.9
3	27.11	28.60	0.33	0.28	4.24	3.41	47.1	42.4
4	28.60	28.28	0.32	0.31	4.20	4.17	45.9	47.6
5	28.52	26.13	0.34	0.30	4.39	3.85	45.3	49.1
6	28.86	28.18	0.34	0.30	4.45	3.96	45.2	46.8

However, it is also found from Table 3 that  $R_{\rm sh}$  increases after etching, which enhances improvement of  $V_{\rm oc}$ . The increased  $R_{\rm sh}$  is due to that the  $Cu_2ZnSn_3Se_8$  and partial ZnSe secondary phases are removed from the surface by etching and suppresses shunt effect. Based on above discussion, it is concluded that the enhancement of  $V_{\rm oc}$  comes from the increased  $R_{\rm sh}$  induced by removing of the secondary phases with etching. It may be a pathway to further improve the  $V_{\rm oc}$  and decrease  $J_0$  through the rough surface of etched CZTSSe.

#### 4. Conclusion

Table 3

Electrical parameters of CZTSSe- and etched-CZTSSe-based solar cells.

Group	Etch- $R_{sh}$ ( $\Omega^* cm^2$ )	$R_{sh} (\Omega^* cm^2)$	etch- $R_s$ ( $\Omega^*$ cm <sup>2</sup> )	$R_s (\Omega^* cm^2)$	etch-A	А	Etch-J <sub>0</sub> (mA/cm <sup>2</sup> )	$J_0 (mA/cm^2)$
1	248	158	1.49	1.80	2.40	1.96	0.11	0.07
2	303	227.8	1.59	2.14	2.65	2.00	0.23	0.07
3	327	219.3	1.89	2.21	2.24	2.00	0.08	0.12
4	182	112.4	1.81	1.91	2.24	1.85	0.10	0.04
5	292	233.1	1.69	1.48	2.62	1.91	0.19	0.06
6	299	135	1.70	1.86	2.60	1.78	0.19	0.04



Fig. 6. Photovoltaic parameter ratio (R) of etched CZTSSe-based and CZTSSe-based solar cells.

relationships of Voc with J0, A, and Rsh can be expressed as:

$$\frac{1}{R_{sh}}V_{oc} = J_{ph} - J_0 \left(\exp\frac{qV_{oc}}{AkT} - 1\right)$$
(2)

where J<sub>ph</sub> is photogenerated current density, q, k and T are electron charge, Boltzmann constant and kelvin temperature, respectively. It is known from the EQE of Fig. 5b that the bandgaps of CZTSSe-based solar cell is larger than that of etched-CZTSSe-based solar cell and change of the EQE is due to electrical loss. So it is deduced from Eq. (2) that the effects of etching on Voc come from electrical parameters. It can be seen from Table 3 that both J<sub>0</sub> and A increase after etching and A values are all larger than 2, which implies that the increased  $J_0$  is due to the enhancement of recombination at CdS/CZTSSe interface (Kassis and Saad, 2003; Saad and Kassis, 2003a; Scheer and Schock, 2011). It can be seen from Fig. 2 that the surface of CZTSSe becomes rough. Since the rough surface can increase the density of charged interface states (Nir) and thus lead to the enhancement of surface recombination (Saad and Kassis, 2003b). The increased recombination may be ascribed to that the surface of CZTSSe becomes rough after etching. Based on Eq. (2) and the discussion mentioned above, it is concluded that etching is not helpful to increase V<sub>oc</sub> from the point of view of interface recombination.

Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> (CZTSSe) films with kesterite structure and smooth surface were prepared by solution approach. It is found that the composition of the bulk CZTSSe is closed to its stoichiometry but the composition of the surface of the CZTSSe deviates far from the stoichiometry, leading to the formation of Cu<sub>2</sub>ZnSn<sub>3</sub>Se<sub>8</sub> and ZnSe secondary phases at the surface. After etching, the Cu<sub>2</sub>ZnSn<sub>3</sub>Se<sub>8</sub> is completely but the ZnSe partially removed from the surface, and the surface becomes rough. The R<sub>sh</sub> is increased by the elimination of secondary phases, and the J<sub>0</sub> is also increased due to the enhancement of interface recombination induced by the rough surface of CZTSSe. The promotion of etching to the performance of solar cell is mainly attributed to the increase of R<sub>sh</sub> which improves the V<sub>oc</sub> of CZTSSe-based solar cell and thus leads to the increase of PCE.

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