

Compact $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ Thin Films Fabricated by a Simple Sol-Gel Technique

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Abstract: $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ (CZTSSe) thin films with a compact and crack-free morphology and large-grain are obtained *via* a green Sol-Gel process and post-selenization. The fabrication of CZTSSe films is simplified by predigesting preparation process of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) precursor solution and avoiding using sulfurization. Low-toxic ethylene glycol is selected as solvent, and $\text{Cu}(\text{CH}_3\text{COO})_2$, $\text{Zn}(\text{CH}_3\text{COO})_2$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and thiourea are used as raw materials. Energy dispersive X-ray analyzer (EDX), X-ray diffraction (XRD) and Raman spectra results indicate that all of CZTSSe thin films with the kesterite structure are of Cu-poor and Zn-rich states. Optical band gap (E_{opt}) of the CZTSSe thin films decreases from 1.51 to 1.14 eV with increasing Se content.

Key words: Sol-Gel; CZTSSe; thin film; selenization

Recently, much attention has been paid to CZTSSe semiconductor compound^[1-4], as a promising candidate of absorber layer materials in thin film solar cells. Furthermore, it has good photoelectric properties^[3], and the E_{opt} could be adjusted by varying the ratio of Se/(Se+S)^[2]. Currently, CZTSSe thin film solar cells have achieved power conversion efficiencies (PCE) as high as 12.6%^[4].

Solution-based deposition techniques are widely considered to be a route to low-cost, high throughput electronic and energy device fabrication^[5]. Advances in these techniques will open up new possible routes to address the challenges of fabricating cheap, scalable and efficient solar cells. Mitzi, *et al*^[4] fabricated the CZTSSe thin film by chemical solution-based method and they used hydrazine as solvent. Although that is a very exciting approach, hydrazine is toxic and explosive. Hydrazine-free and environment more friendly solution deposition methods are critically needed for developing CZTSSe. So far, there have been few reports about free-hydrazine solution processing methods for CZTSSe. In this experiment, to obtain CZTSSe films by a green or nontoxic routine, we selected $\text{Cu}(\text{CH}_3\text{COO})_2$, $\text{Zn}(\text{CH}_3\text{COO})_2$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and thiourea as raw materials, and ethylene glycol as non-toxic solvent.

Generally, CZTSSe films require a sulfurization process to form CZTS films *via* using hydrogen sulfide (H_2S) gas^[6], and then a selenization process to introduce Se element in films during the annealing process^[2]. H_2S is a

toxic and combustible gas and can pollute the environment. To resolve the problem, CZTS precursor films are prepared firstly and then post-annealed in selenium vapour ambient to form CZTSSe films in our experiment. It's noted that an excess amount of thiourea is added in the precursor solution. Finally, the results indicate that we have successfully fabricated compact CZTSSe films by a green and simple Sol-Gel process with selenization.

1 Materials and test

1.1 Material preparation

CZTS precursor solution was synthesized by dissolving $\text{Cu}(\text{CH}_3\text{COO})_2$, $\text{Zn}(\text{CH}_3\text{COO})_2$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and thiourea into ethylene glycol. The solvent was heated to 80°C to dissolve the raw materials and prepare CZTS precursor solution. All the solutes and solvent were analytical reagents. The initial concentration ratios were $\text{Cu}/(\text{Zn}+\text{Sn})=0.70$, $\text{Zn}/\text{Sn}=1$ and $\text{S}/\text{Cu}=4$, and the concentration of cation was around 0.8 mol/L. The CZTS precursor thin films were prepared by spin-coating the precursors onto soda lime glasses (SLG) at a rotation rate of 3500 r/min for 25 s. To obtain expected film thickness, the spinning process was repeated several times. Annealing of the films was carried out in a rapid thermal processor (RTP). The films were pre-annealed at 250°C for 5 min in air to remove organics, then selenized at 500°C for several minutes with different Se content under a N_2 environment to

Received date: 2014-02-11; **Modified date:** 2014-04-11; **Published online:** 2014-05-12

Foundation item: National Natural Science Foundation of China (61106064); Science and Technology Commission of Shanghai Municipality Project (11ZR1411400, 10JC1404600)

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form CZTSSe phase. The thickness of these CZTSSe thin films was about 1.0 μm measured by a field emission scanning electron microscope (FE-SEM).

1.2 Test procedure

XRD patterns were recorded on a Bruker D8 Discover diffractometer using Ni-filtered Cu K α radiation ($\lambda=0.15406$ nm) under the accelerating voltage of 40 kV at a scanning rate of 2θ at $6^\circ/\text{min}$. Raman scattering experiments were performed by a micro-Raman spectrometer (Jobin-Yvon LabRAM HR 800 UV) with a 488 nm Ar⁺ laser as the excited light. And the spot size and power are 20 μm and 8 mW, respectively. The surface micrographs and the composition of these thin films were determined by a microscope (FE-SEM: Philips XL30FEG) with an energy dispersive X-ray analyzer. The acceleration voltage was 20 kV. Optical transmission spectra was collected on an ultraviolet-visible-near-infrared spectrophotometer (cary500, USA Varian) equipped with integrating sphere.

2 Results and discussion

2.1 Composition analysis of CZTSSe thin films

Table 1 shows chemical compositions of CZTSSe thin films under different selenization conditions from EDX data. The chemical composition ratio Cu/(Zn+Sn) and Zn/Sn of the CZTSSe thin films is larger than that of the prepared solution, indicating that the elements of Zn and Sn in the films are lost partly during the annealing process, and that the lost amount of Sn is more than that of Zn in the films. This is because Zn is slightly evaporated from the CZTS thin films and Sn is more lost by evaporation of SnS phase during the annealing process^[7]. The molar ratio of (S+Se)/metal in the sample CZTSSe0 is around 1.0 and that in the others is slightly larger than 1.0. All the films are of Cu-poor and Zn-rich states which can improve the efficiency of CZTS-based solar cells^[6,8]. The molar ratio x of Se/(S+Se) becomes larger with increasing the post-annealing time and the added Se content during post-annealing.

2.2 XRD and Raman spectra of CZTSSe thin films

Figure 1 presents the XRD patterns and Raman spectra of the CZTSSe thin films at different $x=\text{Se}/(\text{S}+\text{Se})$ values. As shown in Fig. 1, all the specimens with different Se ratios show a single phase. For the sample $x=0$, several diffraction peaks at $\sim 18.2^\circ$, $\sim 28.5^\circ$, $\sim 33.0^\circ$, $\sim 47.5^\circ$ and $\sim 56.3^\circ$ can be observed, the peaks are attributed to the indices of (101), (112), (200), (220) and (312) planes of CZTS with a kesterite phase (JCPDS 26-0575). It is found that the positions of corresponding diffraction peaks of CZTSSe thin films are slightly shifted to low angles with the increase of x . The positions of (112), (220) and (312) diffraction peaks of CZTSSe thin films are slightly shifted to $\sim 27.1^\circ$, $\sim 45.1^\circ$ and $\sim 53.5^\circ$ as x increases to 0.91, respectively. It can be attributed to the fact that the S atoms in lattice are partially replaced by the Se where the ion radius of Se (0.198 nm) is slightly larger than that of S (0.184 nm)^[2]. All the thin films exhibit a major single diffraction peak (112), indicating a strongly preferred orientation in the [112] plane^[7]. All CZTSSe phases are polycrystalline and belong to the chalcopyrite crystal system. This result is in good agreement with the diffraction pattern of CZTSe crystals reported by He, *et al*^[7].

Generally, Raman spectroscopy is utilized to further detect the presence of secondary phases. The Raman spectra

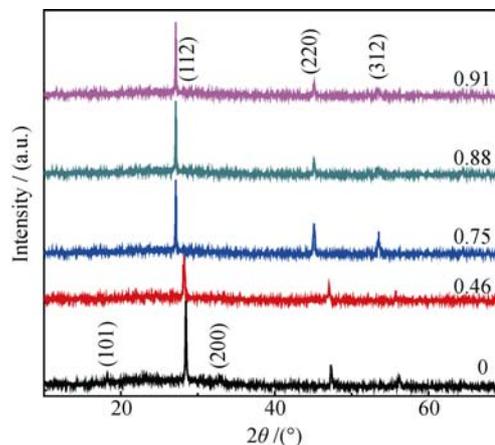


Fig. 1 XRD patterns of $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ thin films with different x

Table 1 Chemical compositions of CZTSSe thin films

Sample	Added Se content during post-annealing /g	Post-annealing time /min	Cu/(Zn+Sn)	Zn/Sn	(S+Se)/metal	x Se/(S+Se)
CZTSSe0	0	20	0.871	1.16	1.01	0
CZTSSe1	0.10	10	0.868	1.13	1.05	0.46
CZTSSe2	0.10	20	0.873	1.15	1.10	0.75
CZTSSe3	0.10	30	0.862	1.16	1.11	0.88
CZTSSe4	0.20	20	0.869	1.14	1.11	0.91

of the CZTSSe thin films are displayed in Fig. 2. For the sample CZTSSe0, the intense peak $\sim 334 \text{ cm}^{-1}$ is evidently observed, and it could be assigned to the A mode peak of CZTS thin films which is the strongest mode in the Raman spectra^[3]. A weak peak at 286 cm^{-1} and a shoulder peak at $\sim 368 \text{ cm}^{-1}$ are found, which are attributed to Raman peaks of CZTS^[3, 9]. As Se content increase, the intense peak around 334 cm^{-1} becomes smaller and broader, while the intense peak $\sim 196 \text{ cm}^{-1}$ appears and changes sharper, which is attributed to the A mode peak of CZTSe^[7]. The broadening of peaks is related to the structural disorder due to the random distribution of S and Se ions. A weak peak at $\sim 246 \text{ cm}^{-1}$ and a shoulder peak at $\sim 174 \text{ cm}^{-1}$ also appears, which is assigned to Raman peaks of CZTSe^[7]. For the CZTSSe1 film, $x = 0.46$, a peak at 233 cm^{-1} is observed, which is attributed to the CZTSe-like A mode peak^[7]. When x increases to 0.75, there is no obvious Raman peaks of CZTS. There is slight shift for the A mode peak of CZTSe thin films from $x = 0.75$ to 0.91, which is similar to our previous experiment results^[7].

2.3 Surface morphology of CZTSSe thin films

SEM images of CZTSSe thin films are presented in Fig. 3. There is obvious grain boundary in all samples except CZTSSe1. For sample CZTSSe1, the film is composed of small grains $\sim 200 \text{ nm}$ in size. The grain size of CZTSSe grows bigger as the selenization time increases. Noted that, when the selenization time reaches 30 min, which is for the sample CZTSSe3, the grain size of sample is slightly smaller than the sample CZTSSe2 and there exists some holes, which may be arisen by the part loss of metal elements. Moreover, the grain size of CZTSSe4 is $\sim 1.0 \mu\text{m}$ and larger than that of CZTSSe2. This result may be due to the agglomeration of small grains induced in high selenium vapour ambient. The CZTSSe film with a compact

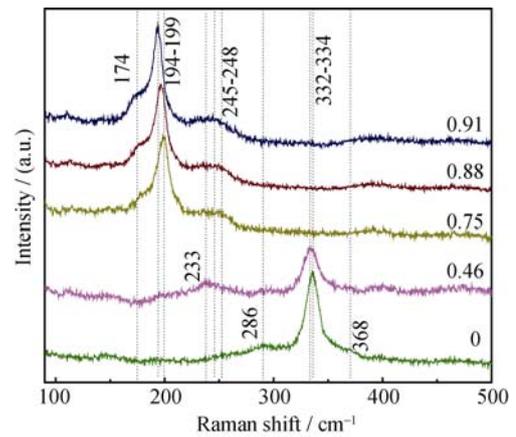


Fig. 2 Raman spectra of $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ thin films with different x

and crack-free morphology and larger grain has less recombination center, so the sample CZTSSe4 is more suitable for absorber layer material in solar cells than other samples.

2.4 Optical properties of CZTSSe films

Figure 4 displays the $(\alpha h\nu)^2$ plots and E_{opt} of CZTSSe thin films. The calculated absorption coefficient from transmittance data is larger than 10^4 cm^{-1} in the visible range. The value of E_{opt} is determined by extrapolation of the linear portion of the $(\alpha h\nu)^2$ curve versus the photon energy $h\nu$ to $(\alpha h\nu)^2 = 0$ ^[10]. The E_{opt} values of CZTSSe films ($x=0, 0.46, 0.75, 0.88$ and 0.91) are 1.51, 1.34, 1.22, 1.16 and 1.14 eV, respectively (in the inset of Fig. 4), which are near the reported values in the literatures^[2, 7].

3 Conclusions

Kesterite CZTSSe thin films are fabricated by a green and simple Sol-Gel process with selenization. The analysis of XRD patterns and Raman spectroscopy indicates that

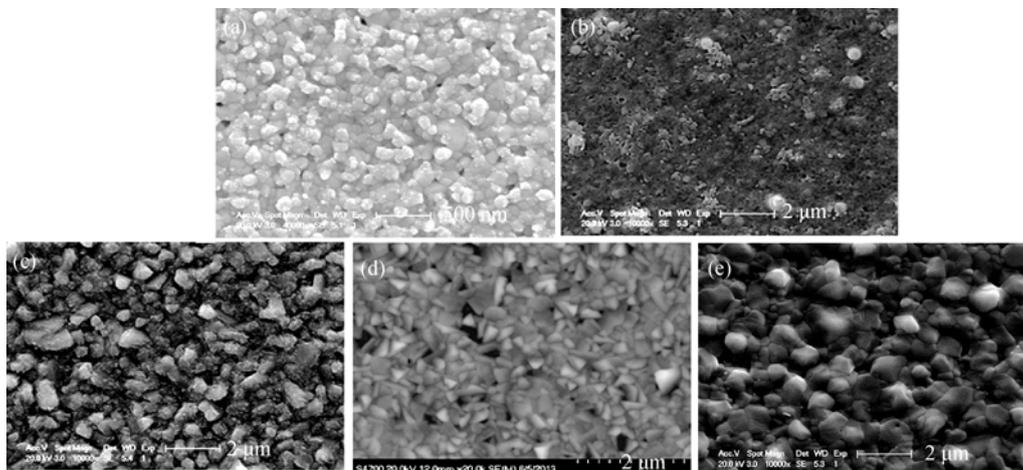


Fig. 3 SEM surface morphologies of CZTS thin films (a)-(e) represent the samples CZTSSe0-CZTSSe4, respectively

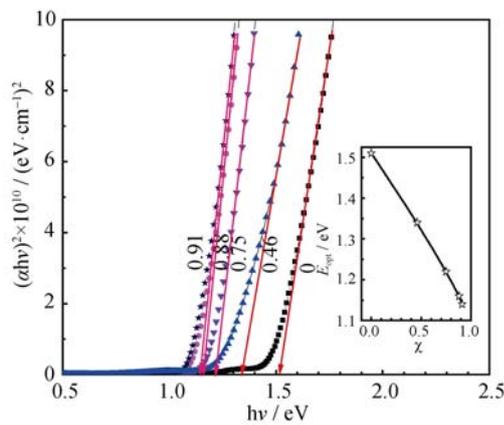


Fig. 4 The $(ah\nu)^2$ plots and optical band gap of Cu₂ZnSn(S_{1-x}Se_x)₄ thin films with different x

all of CZTSSe thin films have the kesterite structure. EDX suggests that all of CZTSSe thin films are of Cu-poor, Zn-rich states. SEM images show that CZTSSe thin film with $x=0.91$ has a compact and crack-free morphology and larger-grain. E_{opt} value of the CZTSSe thin films decreases from 1.51 to 1.14 eV with increasing of Se content.

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简单的溶胶-凝胶法制备致密的铜锌锡硫硒薄膜

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摘要: 采用溶胶-凝胶后硒化法制备了铜锌锡硫硒薄膜, 其薄膜表面平整、无裂纹。通过简化铜锌锡硫前驱体溶胶的制备以及后退火时避免使用硫化氢气体(H₂S)等方法使铜锌锡硫硒薄膜的制备工艺得到简化。选用低毒有机物乙二醇为溶剂, Cu(CH₃COO)₂、Zn(CH₃COO)₂、SnCl₂·2H₂O和硫脲为原料, 制备铜锌锡硫前驱体溶胶。XRD、Raman、EDX和SEM分析表明制备的铜锌锡硫硒薄膜为黄铜矿结构, 所有薄膜均贫铜富锌, 用0.2 g硒粉、硒化20 min得到的铜锌锡硫硒薄膜其结晶较好, 表面晶粒可达1.0 μm左右。透射光谱分析结果表明, 随硒含量的增加, 铜锌锡硫硒薄膜的光学带隙从1.51 eV减小到1.14 eV。

关键词: 溶胶-凝胶; 铜锌锡硫硒; 薄膜; 硒化

中图分类号: TQ174

文献标识码: A