

THE STUDY OF ANNEALING PROCESS FOR CZTSSe UNDER EXTRA CHALCOGEN VAPOR PRESSURE

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$\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) is one of the most promising candidates for photovoltaic devices as it abstains from expensive elements while preserving the virtues of high absorption coefficient and appropriate band gap. Among other methods, the liquid-process involving hydrazine manifests the best performance hitherto and the quaternary semiconducting materials are grown at relatively low cost. Based on this hybrid slurry approach, a “closed annealing” process was developed for sulfurization or selenization of CZTSSe films, and a short annealing period (no more than 15 min) was applied. It was found that the formation conditions for Se-dominant CZTSSe films were much more tolerant than those for S-dominant layers when annealing under a “closed” Se and S ambient respectively. Assisted with extra vapor pressure, S-dominant CZTSSe films could be obtained at 450°C while Se-dominant ones could form at even 400°C. Impurities distinguished with the help of Raman scattering were identified as ternary chalcogenides.

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1. Introduction

Since direct band gap materials are applied in thin film photovoltaic devices, continuous progress has been made. Comparing to the traditional silicon-based technology, solar cells made of $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ (CIGS) are very promising as the devices grown on flexible polymer substrates demonstrate a conversion efficiency of 18.7% [1], let alone other cells on soda-lime glass [2]. But the deployment of rare elements, such as In, Ga, is likely to limit its application below the terawatt level. $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) with kesterite structure not only maintains the advantages of CIGS including high absorption coefficient of over 10^4 cm^{-1} and tunable band gap with different S:Se ratio [3, 4], but also involves materials which are more earth abundant. In addition, numerous vacuum and non-vacuum techniques have been successfully used in growing CZTSSe layers with outstanding material qualities. Solar cells with 9.15% power conversion efficiency by co-evaporation is reported by Repins et al [5], and RF co-sputtering is also used to achieve 6.8% efficiency [6]. For non-vacuum approaches, a synthetic way of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) nanocrystals is developed and the corresponding solar cells turn out to be 7.2% efficiency [7]. Electrodeposition, chemical vapor deposition and sol-gel processes are also adopted, resulting in 7.3%, 6% and 4.1% efficiency, respectively [8-10]. Comparing within the $\text{I}_2\text{-II-IV-VI}_4$ semiconductors, pure $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) devices show an efficiency as high as 9.15% while pure CZTS produces solar cells of 8.4% efficiency [5, 11]. The record in efficiency comes from the hydrazine system which is firstly applied to CIGS [12,13], and then swiftly transfers to the less expensive material CZTSSe [14-17] with an optimum efficiency of 11.1% [18]. The liquid-process has some unique characteristics including exclusion of high-vacuum equipment and possible contamination (e.g., C,

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O, Cl) during precursor preparation. Furthermore, the hybrid slurry is favorable for forming thicker absorbers as dispersed particles serve as stress-relieving centers [14]. In order to form the absorber, the spin-coated layers are subjected to a final annealing step, during which sulfur-rich atmosphere leads to CZTSSe films with a S/(S+Se) ratio of 0.4 ± 0.1 while with no extra sulfurization, S evaporates and is replaced by excess Se [16,17]. Yang's team also develops hydrazinocarboxylic acid saturated hydrazine to fully react with zinc powder in order to obtain a clear precursor solution [19]. An intermediate heat treatment is performed and pure CZTS layer forms at high annealing temperature as precursor contains only sulfides and sulfur element.

In this paper, we provided more details concerning the formation of CZTSSe via hydrazine-process as a function of annealing times and temperatures. The results indicated that the extra sulfur or selenium vapor pressure during annealing might help reducing the treating temperatures, thus providing a way to fabricate CZTSSe films on less refractory, but more flexible substrate materials like polyimide.

2. Experimental

The CZTSSe deposition process was performed in a nitrogen-filled glove box to keep H_2O and O_2 at a very low level. Two solutions labeled A and B were prepared separately: solution A contained Cu_2S (0.6 M) and S (1.2 M) dissolving in hydrazine; solution B contained $SnSe$ (0.57 M) and Se (1.8 M) in hydrazine, and zinc powder (0.69 M) was subsequently added to form the slurry. The additional chalcogen was added to both solutions in order to increase the solubility of the corresponding chalcogenides. Then the two solutions were totally mixed and sufficiently agitated to make the precursor. Soda-lime glass (SLG) substrates for deposition were cleaned ultrasonically in the sequence of acetone, alcohol and de-ionized water. By dipping the slurry onto the substrate, several successive layers were spin coated at 1200 rpm, and after each coating, a pre-annealing was carried out on a hot plate of $250^\circ C$ for 2 min.

The final annealing process was conducted by a "closed" annealing process in which a film sample was sealed into a nitrogen-filled stainless steel bomb (volume of ~ 0.004 L), which has been reported in our previous works [20], containing only enough sulfur or selenium powder to provide a saturated vapor pressure at the set temperature studied. The bomb was divided into two parts by a baffle with vents to produce S or Se atmosphere after the chalcogen was vaporized. One of the most important things for this closed annealing process is it could provide a controlled high vapor pressure (HVP) for S or Se to compensate for excessive loss of S or Se which may occur at the annealing temperature. The HVP of Se within the bomb is also beneficial to CZTSSe formation as it may promote crystallization and suppress poor adhesion when the size of grains increases. A typically procedure was to push the bomb immediately into the tube furnace already heated to $530^\circ C$ with the help of a matching support. The bomb was kept there for the next 5 to 15 min. After annealing, the bomb was then pulled out promptly to let it cool down in the air condition.

The crystalline structure of the deposited films was determined by D8 Focus x-ray diffraction (XRD) equipped with a $Cu K_\alpha$ source (wavelength $\lambda = 1.5418 \text{ \AA}$). Raman scattering (Super Laser Raman, LabRam II) with an incident laser wavelength of 532 nm was also used to distinguish between impurities and primary phases. Hitachi S-4000 field emission scanning electron microscopy (FESEM) equipped with energy dispersive spectrometers (EDS) was applied to obtain the morphologies and chemical composition of the CZTSSe layer. The optical transmittance of the CZTSSe thin films was measured using an optical spectrometer (Aquila NKD-8000).

3. Results and discussion

Herein, the samples annealed under extra chalcogen vapor pressure (evp) were abbreviated as S-evp or Se-evp, respectively. The closed annealing makes the formation of CZTSSe start as early as 5 minutes under selenium atmosphere as shown in Fig. 1 (a). Among all Se-evp, the

strength of preferred (112) orientation was profoundly enhanced when the treatment was prolonged, indicating an improvement in crystallization and film quality. In addition, all the diffraction peaks remained at approximately the same position (marked by the dot line). Annealing time seemed to be more sensitive for S-evp (Fig. 1 (b)). Similar to the sample only pre-annealed at 250°C (Fig. 1 (c)), a 5-minute sulfurization was far less sufficient for CZTSSe to form, and this could be attributed to the volatility of sulfur and its much higher saturated vapor pressure (comparing to Se) which was not reached inside the bomb within such a short annealing. Correspondingly, the diffraction peak for (112) plane moved to lower degree (comparing between the two dot lines) indicating a relatively higher content of Se in the compounds. With the elongation of annealing time, the film exhibited better crystallization as the peak intensities for (112), (220) and (312) planes enhanced dramatically and other characteristic peaks belonging to CZTS became distinguishable. But a 15-minute treatment consequentially led to some impurities such as Cu_2SnS_3 , Cu_2S , and SnS , implying decomposition of the film due to loss of S, i.e. insufficient S pressure during longer annealing.

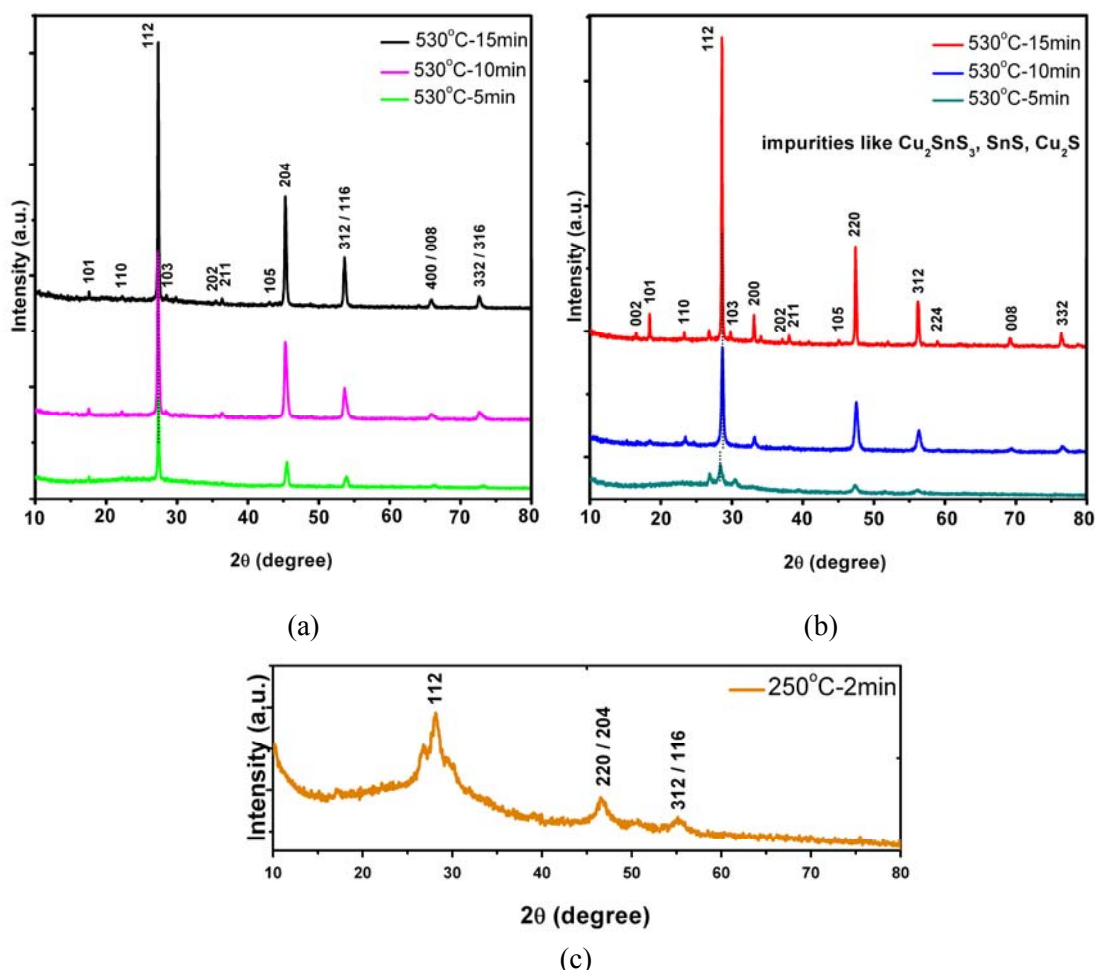


Fig. 1 XRD patterns for (a) Se-evp annealed for 5, 10 and 15 min respectively, (b) S-evp annealed for 5, 10 and 15 min respectively, and (c) sample pre-annealed at 250°C for 2 min.

However, as main XRD peaks and orientations of tetragonal and cubic phases of Cu_2SnS_3 and cubic-ZnS are identical with those of $\text{Cu}_2\text{ZnSnS}_4$ [21] and that's also true for $\text{Cu}_2\text{ZnSnSe}_4$, it is

essential to use Raman scattering to distinguish some possible impurities. Fig. 2 (a) revealed that a selenization lasting for 15 min resulted in three Raman peaks at 172, 194 and 234 cm^{-1} , close to the values reported for pure CZTSe [4, 22]. As no other noticeable peaks from impurities can be observed, the as-synthesized film could be confirmed as single phase. But when annealing time was reduced, the Raman peaks gradually declined and the main peak slightly blue-shifted as S was not sufficiently expelled from the film treated for only 5 minutes (comparing between the two dot lines). Furthermore, the sample also illustrated a shoulder between the peaks at 172 and 194 cm^{-1} , suggesting the existence of Cu_2SnSe_3 (Raman shift at 180 cm^{-1}) [23] which was marked by a circle. From Fig. 2 (b), an intense Raman shift at 333 cm^{-1} and a weaker one at 287 cm^{-1} were found for S-evp treated for 15 min. The broader, red-shifted and more asymmetric main peak was supposed to be caused by residual Se content. The Raman shift for Cu_2SnS_3 located at 303 cm^{-1} was more pronounce for the sample withstood shorter sulfurization (10 min), indicating Cu_2SnS_3 might be the intermediate product during the formation of CZTS as was discussed elsewhere [24].

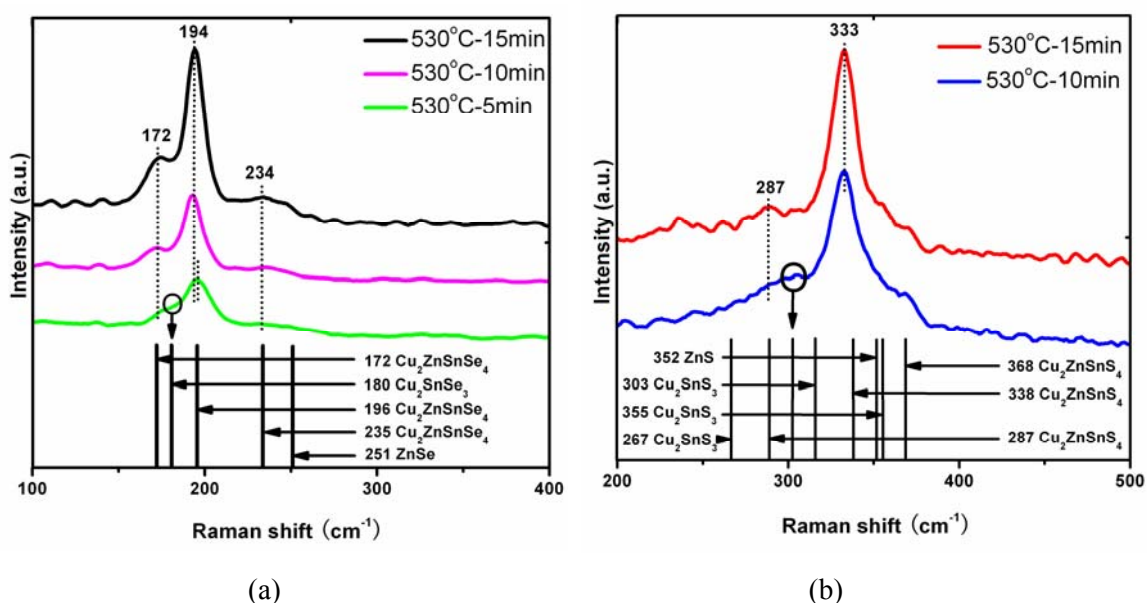


Fig. 2 Raman spectra for (a) Se-evp annealed for 5, 10 and 15 min respectively, and (b) S-evp annealed for 10 and 15 min. Raman peaks for (a) $\text{Cu}_2\text{ZnSnSe}_4$, Cu_2SnSe_3 , ZnSe, and (b) $\text{Cu}_2\text{ZnSnS}_4$, Cu_2SnS_3 , ZnS were shown below for reference.^{4, 20-24} For Se-evp annealed for 5 min and S-evp annealed for 10 min, circles were marked to clarify the possible existence of Cu_2SnSe_3 or Cu_2SnS_3 respectively.

The SEM images of the films treated under extra sulfur or selenium vapor pressure for 15 min were shown in Fig. 3. Fig. 3 (a) illustrated a better crystallization for Se-evp. Larger crystal size is always associated with better film quality as crystal boundaries are reduced. On the other side, S-evp (Fig. 3 (b)) presented numerous holes. The compositions of the same samples were obtained by EDS (Fig. 4 (a), (b)). S-evp was Cu-rich and Zn-poor due to some impurities, while Se-evp had a final composition of $\text{Cu}/(\text{Zn}+\text{Sn}) = 0.95$ and $\text{Zn}/\text{Sn} = 1.08$ which was more satisfactory for solar cell application.¹⁴⁻¹⁹ The estimated S or Se left in the CZTSSe films ($\text{S}/(\text{S}+\text{Se})$ or $\text{Se}/(\text{S}+\text{Se})$) was 0.04 and 0.05, respectively.

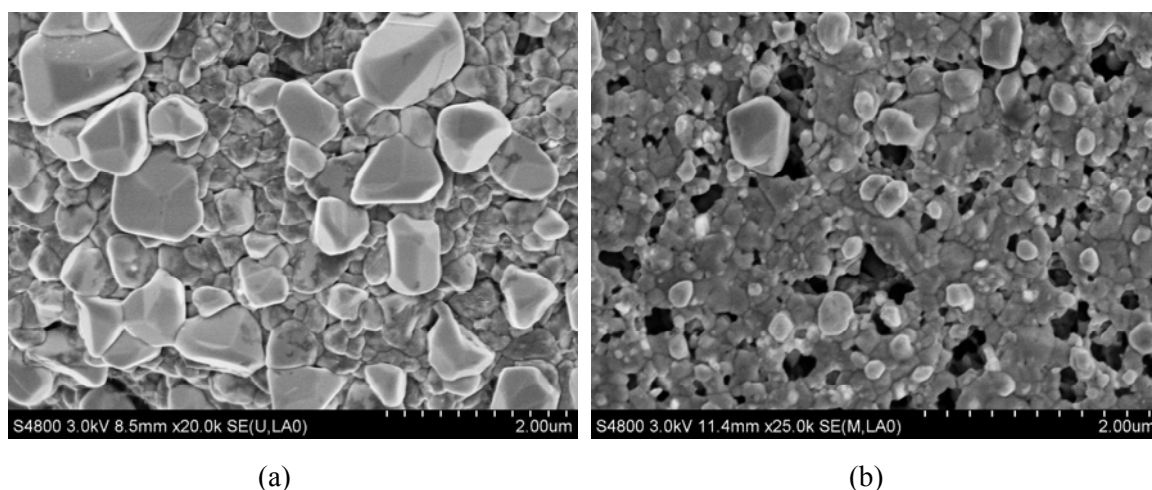


Fig. 3 SEM images for (a) Se-evp annealed for 15 min, and (b) S-evp annealed for 15 min.

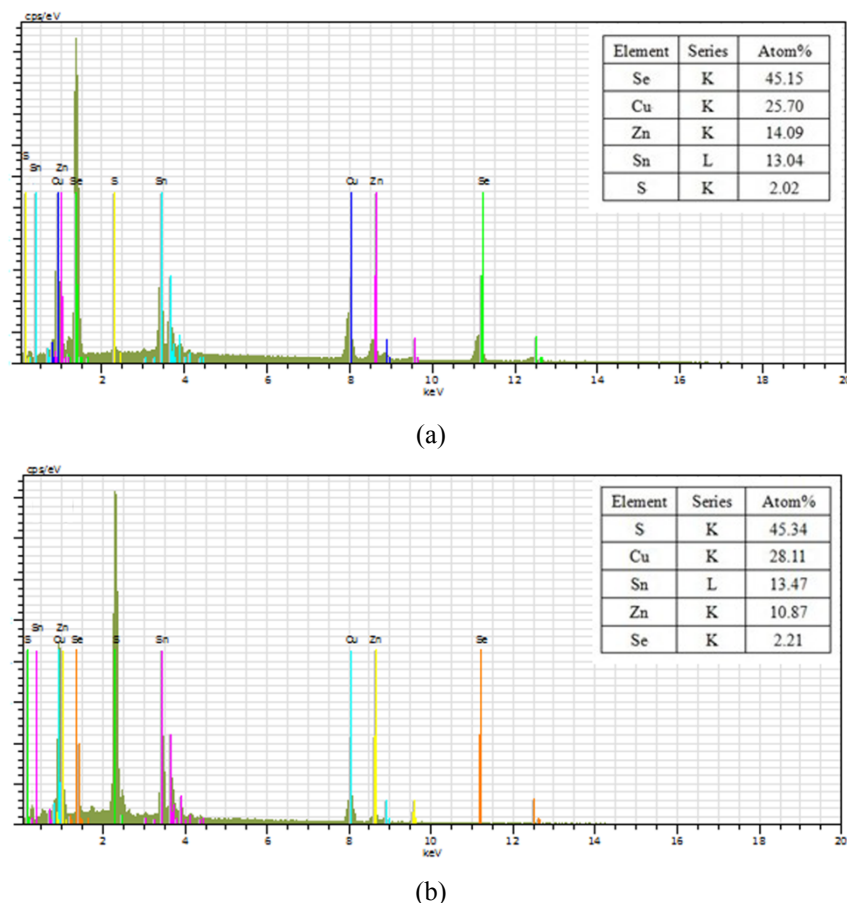


Fig. 4 EDS results for (a) Se-evp annealed for 15 min, and (b) S-evp annealed for 15 min.

Fig. 5 showed the optical absorption coefficient spectra of Se-evp and S-evp. The values for optical band gap (E_g) were derived from a plot of $(\alpha h\nu)^2$ versus $h\nu$ where α is the absorption coefficient and $h\nu$ is the photon energy. The band gap was estimated by extrapolating the linear part of the curve to intercept the photon energy axis. The E_g for S-evp turned out to be ~ 1.38 eV, which was lower than the bulk value for pure CZTS at around 1.5 eV [3, 25]. One explanation was concerned with residue Se corresponded to Raman and EDS analyses and the co-existence of secondary phase Cu_2SnS_3 with a band gap ranging from 0.96 to 1.35 eV might also have some

influence [26-28]. For the sample selenized in extra selenium vapor pressure, Se-evp had a E_g of ~ 1.06 eV which was consistent with other works [3, 17, 25].

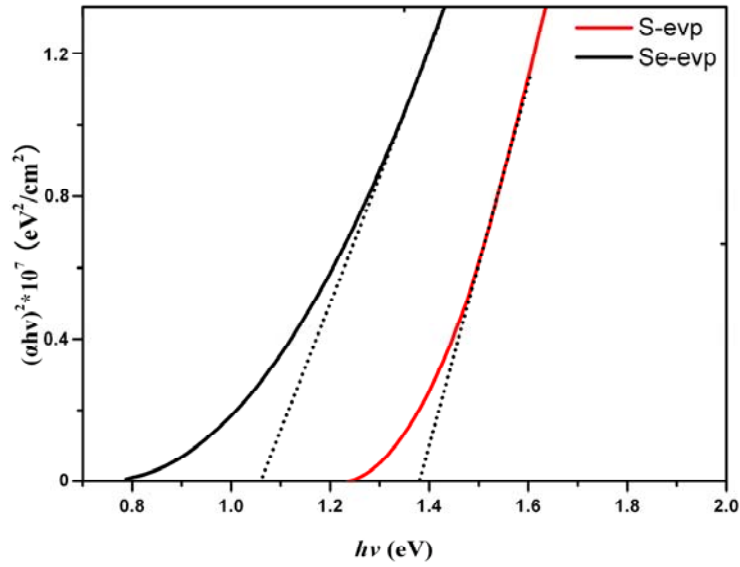


Fig. 5 Function between $(ahv)^2$ and $h\nu$ for S-evp and Se-evp treated by closed annealing process for 15 min.

The closed annealing process was further used to investigate the low-temperature annealing for CZTSSe films. In Fig. 6 (a), the XRD patterns for Se-evp showed no significant impurities, but the diffraction peaks slightly shifted to a higher position (comparing to CZTSe (JCPDS no. 70-8930)), suggesting a small amount of Se atoms were supplanted by S in the lattice. The sample annealed at 400°C also had a relatively high (112) preference. It was proved in Fig. 6 (b) that annealing at 400°C was definitely not enough for crystallization, but the resident amount of Se was very low after a 15-minute sulfurization (comparing to CZTS (JCPDS no. 26-0575)). Only 50°C higher facilitated crystal growing although the two peaks at 26.7° and 30.2° were still present.

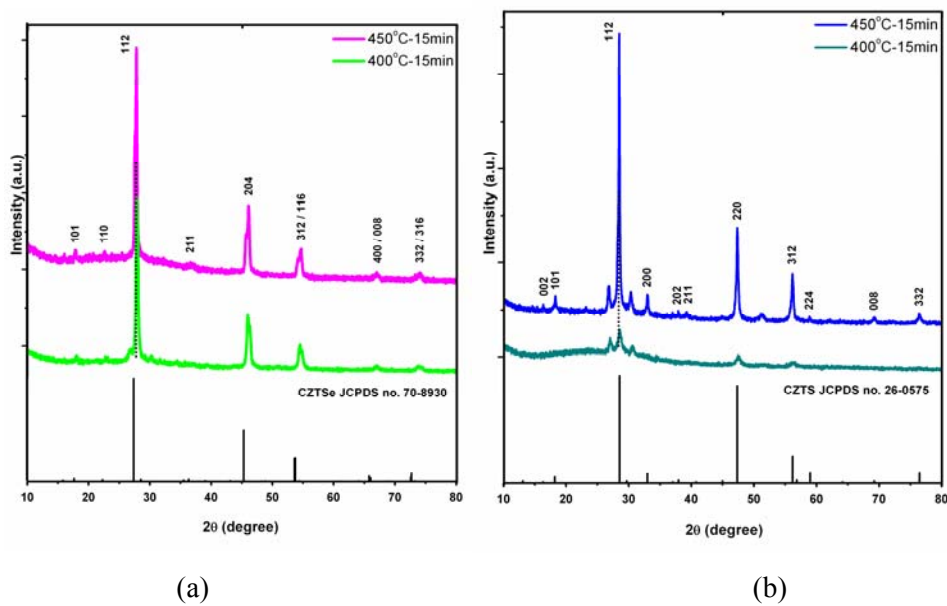


Fig. 6 XRD patterns for (a) Se-evp annealed at 450°C or 400°C, and (b) S-evp annealed at 450°C or 400°C.

We once again referred to Raman spectra in determining the composition of the films. Higher ratio of S in the CZTSSe film was confirmed in Fig. 7 (a) as the major Raman peak for the sample annealed at 450°C blue-shifted to 200 cm^{-1} and a bimodal behavior (203 and 328 cm^{-1}) appeared in the sample of 400°C which was similar to previous report [4, 19, 25]. But the broader peaks might have covered the information from secondary phases such as ZnSe (251 cm^{-1}) and Cu_2SnSe_3 (180 cm^{-1}) for lower temperature samples. Despite of the deficiency, Se-dominant CZTSSe films were deemed to be achieved at lower temperature under Se atmosphere. Like the sample annealed at 530°C for 10 min, S-evp withstood a sulfurization at 450°C (Fig. 7 (b)) also demonstrated Raman peaks for Cu_2SnS_3 .

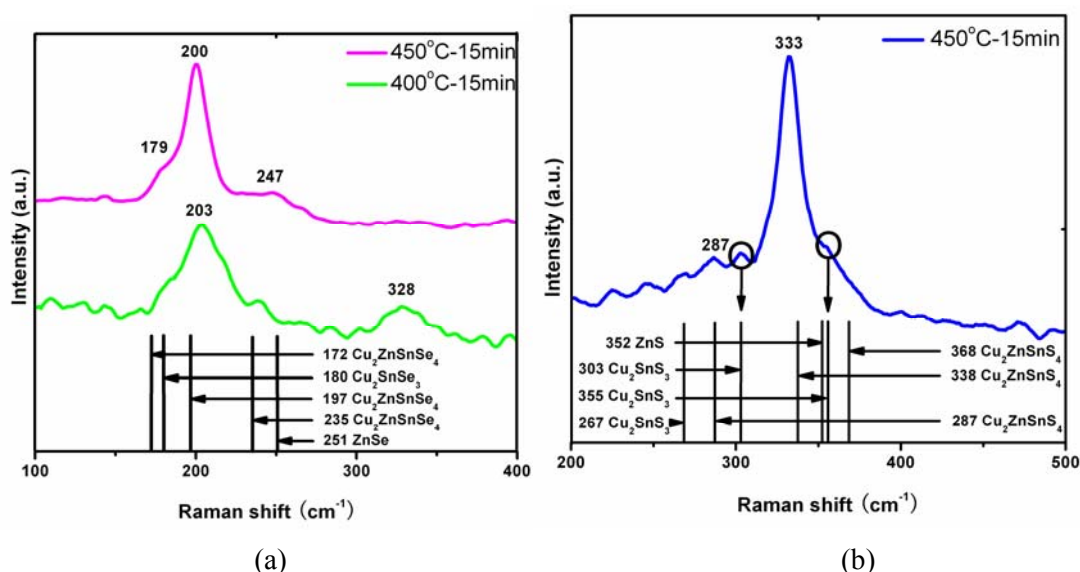


Fig. 7 Raman spectra for (a) Se-evp annealed at 450°C or 400°C, and (b) S-evp annealed at 450°C. Raman peaks for (a) $\text{Cu}_2\text{ZnSnSe}_4$, Cu_2SnSe_3 , ZnSe, and (b) $\text{Cu}_2\text{ZnSnS}_4$, Cu_2SnS_3 , ZnS were shown below for reference [4, 21-25]. For S-evp annealed at 450°C, two circles were marked to clarify the possible existence of Cu_2SnS_3 .

4. Conclusions

In summary, some specifics of the sulfurization or selenization processes for CZTSSe layers were discussed. A closed annealing method with extra selenium vapor pressure could facilitate the formation of Se-dominant CZTSSe films within a shorter annealing period (5 to 10 min) or at lower temperature (400 to 450°C). And it was proved that Se-dominant CZTSSe films required less strict deposition conditions comparing to S-dominant CZTSSe layers which demanded precise control over annealing time and temperature. The most possible secondary phases co-existed in Se-evp or S-evp were ternary compounds, i.e. Cu_2SnS_3 or Cu_2SnSe_3 , which could be detected by Raman scattering.

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