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Research

IMPACT OF SELENIZATION TEMPERATURE AND PRE-ANNEALING TREATMENT ON THE MICROSTRUCTURAL PROPERTIES OF $Cu_2ZnSnSe_4$ THIN FILMS GROWN BY RAPID THERMAL PROCESS

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ABSTRACT

The impact of selenization temperature and pre-annealing treatment on the microstructural characteristics of CZTSe thin films were studied. CZTSe thin films were obtained by two-stage process. This processes includes deposition of metallic layers and Se cap layer employing physical vapor deposition systems followed by selenization process performed at elevated temperatures using RTP system with a heating rate of 8°C/s. The compositional properties of CZTSe thin films changed after the heat treatment, but performing pre-annealing treatment before high reaction temperature (550°C) partially prevented element loss in CZTSe compound. Both Raman and XRD measurements confirmed the formation of the kesterite CZTSe phase. However, according to Raman results, CZTSe phase started to decompose into secondary phases such as CTS regardless of temperature. According to the top view images of the samples, the grain structure completely changed with employing heat treatment. Zn-rich phase detected in reacted sample at 550 °C, which indicates decomposition of CZTSe that is confirmed in Raman spectra.

Keywords: CZTSe thin film, RTP, XRD, Microstructure

1. INTRODUCTION

$Cu_2ZnSn(S,Se)_4$ (CZTSSe) semiconductor compound can be used as an active absorber layer in thin film solar cells due to its optical and electrical properties such as 1.5 eV forbidden energy gap, high absorption coefficient ($\geq 10^4$ cm^{-1}) and p type conductivity. CZTSSe compound is seen to be as an alternative to the $CuInGaSe_2$ (CIGSe) in thin film solar cells, since it contains inexpensive and abundant raw materials. However, there is a huge difference between experimental and theoretical efficiency values of CZTSSe-based solar cells compared to CIGSe. Studies have been conducted to reveal the possible causes of this difference. The main reasons for such difference are the crystallization of the kesterite CZTSSe structure in a very narrow range in the phase diagram [1], requiring partial pressure for S and/or Se during annealing [2], and the decomposition of the CZTSSe compound at high temperatures [3].

There are several reported work in the literature to find out the optimum growth parameters of CZTSSe absorber material for understanding the efficiency limitations [4-8]. For example, Márquez-Prieto et al. examined the effect of the annealing treatment on the optical and structural properties of CZTSe thin films and they reported that the $SnSe_2$ phase was formed at low temperatures (450°), while the $MoSe_2$ phase was started to form as a result of the reaction of Mo back contact layer with Se at higher temperature (550°) [9]. On the other hand, Kumar et al. produced CZTSe thin films by thermal deposition of Cu, Zn, Sn, and Se on Mo-coated SLG substrates followed by selenization process using various temperature and time. According to this study, with increasing temperature, CuSe phase was formed in the film, grain size and conductivity of the film increased [10]. Several groups have included the pre-annealing step as a process strategy for CZTSe production [11, 12]. This pre-annealing treatment is applied to promote the diffusion and mixing of metals. In this way, the compositional and morphological homogeneity of the CZTSe film are promoted. In another study carried out by our group, the effect of mild annealing on the film features was studied. In that study, the metallic precursors were exposed to a pre-annealing treatment for 30 min at a temperature range of 200–350 °C and then selenized at 550 °C for 15 min in tubular furnace. We demonstrate that the CZTSe thin film produced by employing metallic stacks annealed at 250 °C was provided proper composition and crystalline quality [13].

In this study, we report the effect of selenization temperature and pre-annealing process on the microstructural properties of CZTSe thin films grown by rapid thermal processing (RTP).

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2. MATERIAL AND METHOD

The $Cu_2ZnSnSe_4$ thin films were produced by two-stage process consisting of i) sequential deposition of Cu (Kurt J. Lesker, 5N), Zn (Kurt J. Lesker, 4N), Sn (Beijing Goodwill Metal, 5N) layers by sputtering system, ii) deposition of Se cap layer using Se shots (Alfa Aesar, 5N) by vacuum evaporation, and iii) subsequent selenization (pre/post annealing) in graphite box using RTP method. The SLG/Mo/Cu/Sn/Zn/Cu stacked layer was covered onto Molibdenyum coated substrate. 500 nm thick Mo (Beijing Goodwill Metal, 4N) layer was deposited by DC sputtering system. While Cu layer was deposited using by DC source, Zn and Sn layers were deposited by RF power supply. The total thickness of stack is about 650 nm for the metallic layer with Cu / (Sn + Zn) = 0.80 and Zn / Sn=1.20 atomic ratio [14]. The thickness of the layers were measured using profilometre. The Se cap layer was coated onto metallic layers by vacuum evaporation with a thickness of 400 nm and the film thickness was monitored using a crystal controller. For formation of CZTSe, SLG/Mo/Cu/Sn/Zn/Cu/Se stacked precursor layers were placed in graphite box within a selenium powder (15 mg) and then annealing treatment was performed using 8 °C/s heating rate in RTP system. Selenization procedure was performed at 500°C and 550°C for 3 min. In addition, one CZTSe sample was prepared with pre-annealing at 250 °C for 3 min followed by post annealing at 550 °C for 1 min.

The atomic percentages of CZTSe samples were measured (point and map) by energy dispersive X-ray spectroscopy (EDS, FEI Quanta 250 equipped with EDX detector and Oxford Aztec software). The structural properties of the samples were characterized by X-ray diffraction method (XRD, Panalytical, Empyrean) and Raman spectroscopy (633 nm) (Renishaw, Invia). The surface structure of the CZTSe samples were monitored by scanning electron microscopy (SEM, FEI Quanta 250).

3. RESULTS AND DISCUSSION

The atomic percentage and some atomic ratios of metallic stack and the reacted CZTSe samples were given in Table 1. Cu / (Sn+Zn) and Zn / Sn ratio of the metallic layers are 0.86 and 1.19, respectively. The sample reacted at 500 °C continued to have a copper poor and zinc rich composition, but Zn / Sn value of the film increased to 1.53. This indicates that element loss (Sn) took place in the structure. On the other hand, it was determined that the Sn loss increased with the increment of reaction temperature, but the amount of Sn loss decreased partially by employing pre-treatment. Due to high vapor pressure, Sn(Se) is a volatile compound, that can evaporate easily [15, 16]. Under these experimental conditions, it has been determined that high heating rate was not sufficient to prevent Sn loss, but pre-annealing treatment inhibited the elemental loss partially by formation of metallic alloying.

Table 1. EDX results of CZTSe thin films

Sample	Cu (%)	Sn (%)	Zn (%)	Se (%)	$\frac{Cu}{(Sn+Zn)}$	$\frac{Zn}{Sn}$	$\frac{Se}{(Cu+Sn+Zn)}$
Metallic stack	46.16	24.56	29.28	-	0.86	1.19	-
CZTSe-(500)	23.20	9.51	14.60	52.69	0.96	1.53	1.11
CZTSe-(550)	19.59	10.00	16.95	53.46	0.73	1.69	1.14
CZTSe-(250/550)	20.26	10.02	16.34	53.38	0.77	1.63	1.14

The XRD pattern of CZTSe-(500), CZTSe-(550) and CZTSe-(250/550) samples measured in the range of 2θ=20-60° shown in Figure 1. Regardless of the reaction temperature, there are three main peaks located at 2θ= 27.1°, 45.1°and 53.4° which were respectively refered to (112), (220 / 204) and (312 / 116) diffraction planes of the kesterite CZTSe structure (JCPDS card no: 01-070-8930) [17]. Apart from the characteristic CZTSe peaks, the peak of the Mo phase was observed at an angle of about 2θ = 40.5 (JCPDS card no: 01-089-5023). In addition, the peaks of the $MoSe_2$ phase formed as a result of the Mo-Se reaction at high reaction temperature (>500°) that were detected at 2θ = 31.5° and 55.8° (JCPDS card no: 09-0312)

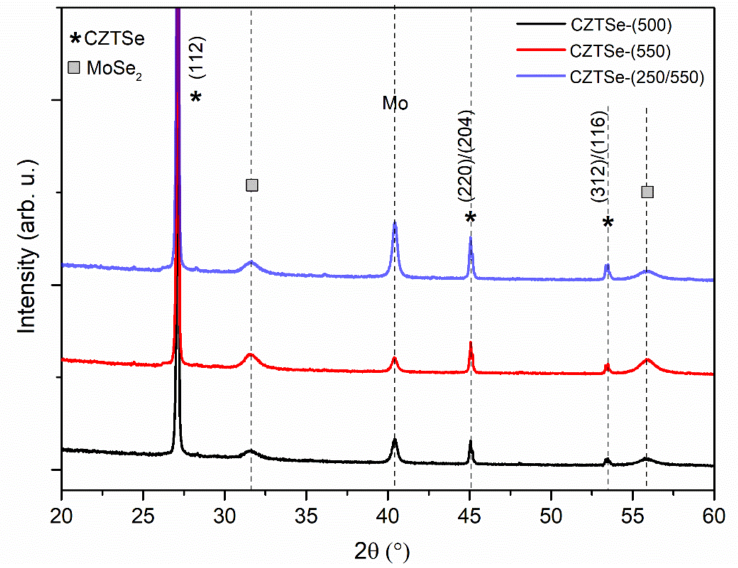

Figure 1. XRD spectra of CZTSe thin films

The crystallite size (D) and micro strain (Ɛ) values of the reacted samples were calculated using Equations 1 and 2, respectively [18, 19]. K is the shape factor (K=0.9), β_{hkl} is the full width at half maximum (FWHM) of (112) diffraction plane of the CZTSe samples and λ is the wavelength of the X-ray (λ=1.5406 Å). The calculated values were given in Table 2. The FWHM value, which is an indicator of crystal quality, expresses the formation of sharper peak due to the contribution of identically oriented planes to the diffraction peak. While this value was 0.125 for the sample reacted at 500°C, it reached the lowest value (best crystal quality) with increasing temperature to 550 °C, but it was increased partially with pre-annealing treatment. It was seen that the dependence of crystallite size and micro-strain values with annealing treatment is similar to the behavior of the FWHM value. As a result, it can be said that CZTSe-(550) has the highest crystal size and lowest strain, that is, it is low-defective and high-crystal-quality compound.

$$D = \frac{K\,\lambda}{\beta_{hkl}\cos\theta} \tag{1}$$

$$\varepsilon = \frac{\beta_{hkl}\cos\theta}{4} \tag{2}$$

The CZT(S,Se) structure has similar XRD patterns with the $Cu_2Sn(S,Se)_3$ and/or Zn(S,Se) phases. Therefore, Raman measurements of the samples were taken and given in Figure 2, for both confirmations the occurrence of the kesterite CZTSe phase and detection whether the crystallized phases with similar structures were formed. As seen in figure, the Raman peaks related to CZTSe kesterite phase were detected at 172, 195 and 235 cm^{-1} regardless of the temperature. In addition, relatively less intense peak was detected at 251 cm^{-1} which was attributed to CTSe phase in annealed samples. This shows that decomposition has started in the samples produced at ≥500°C temperature with high heating rate.

Table 2. Some structural parameters of the samples calculated by XRD datas

Sample	FWHM(°)	Crystallite size (nm)	ϵ (strain) (x10^{-4})
CZTSe-(500)	0.125	65.4	5.5
CZTSe-(550)	0.084	97.3	3.7
CZTSe-(250/550)	0.093	87.9	4.1

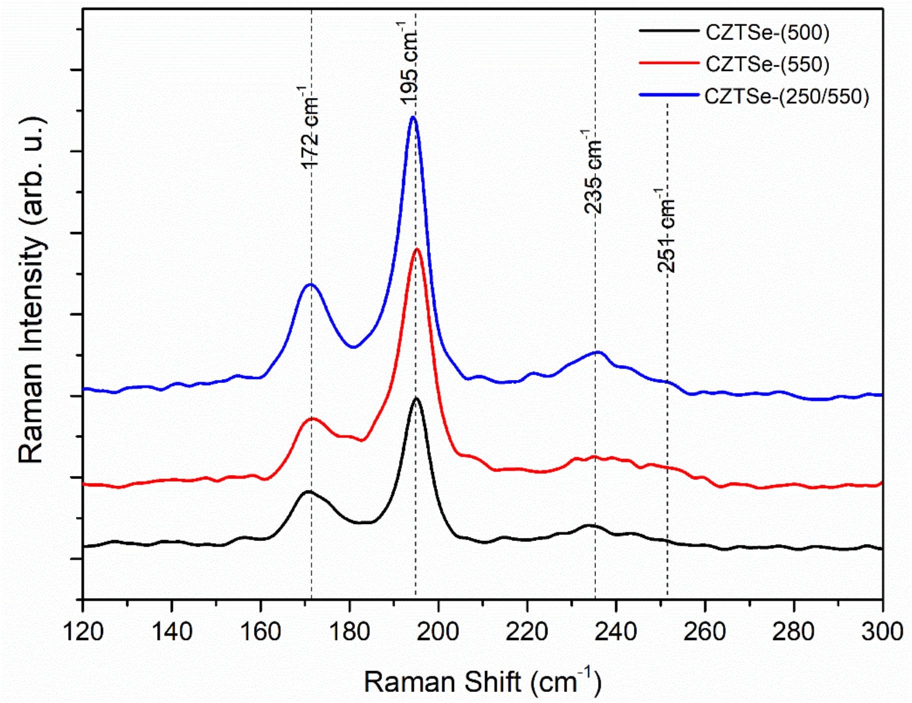

Figure 2. Raman spectra of CZTSe samples

Top view SEM images of CZTSe samples are demonstrated in Figure 3. According to images, CZTSe-(500) has a rounded-shape grain-structure which is dense and homogeneous but, some voids and/or cracks are also seen in the surface structure. It was observed that the grain size increased from 1-3 micrometers to 2-5 micrometers by increasing the temperature to 550°C. However, as the enlarged image of the sample was examined in detail (figure 3d), it was seen that submicron grains were formed both between and on the large grains. According to the atomic composition results given in Table 3, large grains have the targeted composition of CZTSe (point B), while small grains correspond to a Zn rich phase (point A). In addition to this, the phase of the small grain structure may be in the form of $Cu_{1.7}Zn_{2.2}Sn_1Se_{5.3}$. Employing with pre-annealing treatment to the same sample, it was observed that the grain size decreased, while a more compact structure was formed.

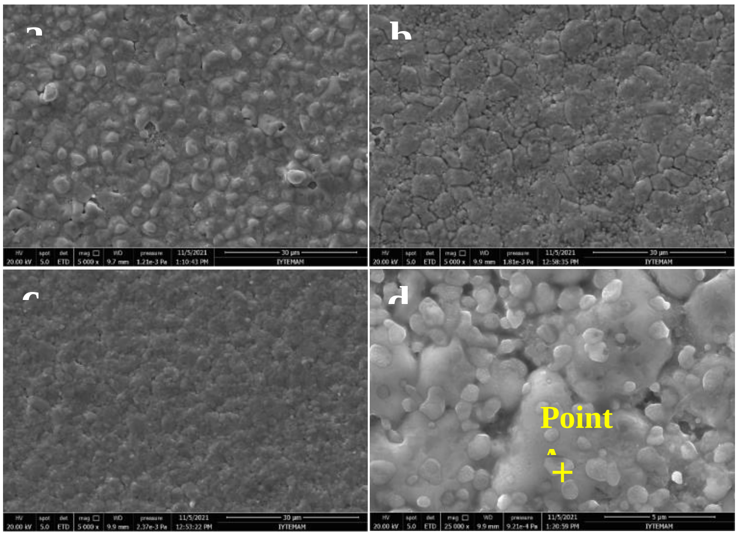

Figure 3. The SEM images of the surface morphology of CZTSe thin films; a) CZTSe-(500), b) CZTSe-(550), c) CZTSe-(250/550), d) Enlarged view of CZTSe-(550)

Table 3. EDX results from different points of the surface of the CZTSe-(550) sample

Sample	Cu (%)	Sn (%)	Zn (%)	Se (%)	$\frac{Cu}{(Sn+Zn)}$	$\frac{Zn}{Sn}$	$\frac{Se}{(Cu+Sn+Zn)}$
CZTSe-(550-point A)	15.84	9.35	20.88	53.93	0.52	2.23	1.17
CZTSe-(550-point B)	23.61	12.30	13.05	51.04	0.93	1.06	1.04

4. CONCLUSION

In this study, the effect of selenization temperature and pre-annealing treatment on the microstructural features and atomic composition of CZTSe thin film were investigated. The precursor stacks formed by deposition of Cu, Sn, Zn layers via sputtering system and thermally evaporated Se cap layer, then were annealed at different temperatures with a heating rate of 8°C/s using RTP system. The EDX measurements showed that after annealing treatments, the CZTSe thin film had a copper poor and zinc rich composition, but elemental Sn loss was determined. The XRD and Raman results of the samples demonstrated evolution of kesterite CZTSe structure. However, CTSe and Zn-rich undesired phases in the structure were detected in Raman spectra and SEM images, respectively. Overall, in a two-step process employed for the formation of CZTSe layer, it is recommended that pre-annealing reaction step can be used where the reaction temperature is raised rapidly to > 500°C in presence of Se atmosphere. In addition, further investigation is needed to obtain purer and higher quality of CZTSe thin film using various heating rates in the RTP system.

SIMILARTY RATE: 18%

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