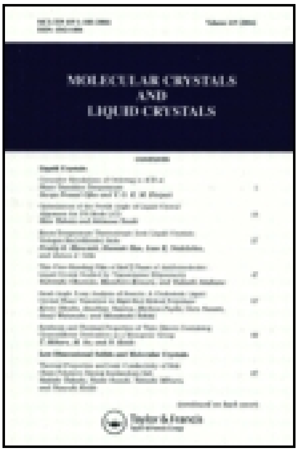

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Characteristics of $Cu_2ZnSnSe_4$ Film Formed by Using Co-sputtered Precursors and Selenization

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A $Cu_2ZnSnSe_4$ (CZTSe) film was formed by the selenization of Cu(Zn, Sn) (CZT) alloy precursors. The CZT precursor was prepared by depositing zinc onto a layer of Cu-Sn co-sputtered on molybdenum-coated soda-lime glass. Selenium was evaporated on the CZT precursor. The CZTSe film was then annealed for a minute at various substrate temperatures ranging from 350°C to 650°C in steps of 50°C in a rapid thermal process using tungsten halogen lamps. The lattice parameters of the CZTSe annealed at temperatures over 500°C were found to be $a = 5.709$ Å and $c = 11.351$ Å. We also found that the energy gap of the CZTSe was 1.137 eV, which was independent of the annealing temperature.

Keywords CZTSe; solar cell; band gap energy

Introduction

Quaternary Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) thin films are new interesting p-type semiconductor materials for solar cell applications. Both CZTS and CZTSe semiconductors have a direct band gap, high absorption coefficient (10^4 cm^{-1}), and p-type electrical conductivity [1–3]. In addition to these beneficial qualities, their constituent elements, Zn and Sn, are relatively abundant and cheap. CZT-based optical absorbers can be derived from the $CuInSe_2$ chalcopyrite structure by replacing half of the indium content with zinc and the other half with tin [4]. The band gaps of these materials have been calculated theoretically to be 0.96 eV for CZTSe and 1.50 eV for CZTS [5]. The corresponding experimental values of these band gaps were 0.98 eV for selenide and 1.5 eV for sulfide [6–7]. The highest efficiencies for CZTS- and CZTSe-based solar cells formed using a vacuum process have been reported to be 6.7% and 3.2%, respectively [8–9]. However, the efficiency of a CZTSe-based solar cell was recently reported to increase to 9.3% when a hydrazine-based solution process was used [10]. This result demonstrated the potential application of a CZTSe-based thin film to a high-efficiency solar cell.

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In this study, CZTSe thin films were fabricated using a co-sputtering deposition method, in which elemental targets of Cu, Zn, and Sn were used to fabricate a metal precursor. Selenium (Se) was deposited on the metal precursor using thermal evaporation. The CZTSe film was then annealed at various temperatures using an RTP (rapid thermal process). During this annealing process, the CZTSe film was crystallized. The crystallization of CZTSe as a function of the annealing temperature was observed using X-ray diffraction (XRD) patterns. The XRD patterns of the films annealed at temperature over 500°C matched well with those of the CZTSe crystal. The lattice parameters of the CZTSe annealed at temperature over 500°C were found to be $a = 5.709$ Å and $c = 11.351$ Å. These values are close to the lattice parameters for a single crystal sample of $Cu_2ZnSnSe_4$, which are $a = 5.693$ Å and $c = 11.333$ Å. The band gap energy of the CZTSe samples was determined to be 1.137 eV using photoluminescence spectroscopy.

Experimental

The $Cu_2ZnSnSe_4$ thin film was fabricated using a two-step process, which included the formation of the metal precursor followed by its selenization. First, the metal precursor was grown on a molybdenum-coated soda-lime glass substrate by sputtering copper (Cu), zinc (Zn), and tin (Sn). Cu and Sn were co-sputtered for 15 min using 80 W and 90 W of RF power, respectively. Then, Zn was sputtered onto the film for 15 min using 130 W of RF power. The stoichiometry of this metal precursor was estimated based on the deposition time and RF power. The background pressure of the chamber was less than 1.6×10^{-6} torr. The metal precursor was deposited under an argon gas pressure of 5.5×10^{-3} torr and an argon flow rate of 10 sccm. Next, selenium was deposited onto the metal precursor film without heating the substrate in the thermal evaporator, by using a pyrolytic boron nitride (PBN) crucible to evaporate high-purity selenium shots (99.999%, CERAC). The deposition rate of the selenium was 10 Å/s. The initial pressure in the chamber of the thermal evaporator was less than 3×10^{-6} torr as established by a cryopump. The selenization was carried out by the RTP, in which the CuZnSnSe thin film was annealed for a minute at various substrate temperatures ranging from 350°C to 650°C, in steps of 50°C. The increasing rate of the temperature was 20°C/s, with an argon flow rate of 10 sccm. The surface morphology, chemical composition, and crystalline properties of the CZTSe film were analyzed using a scanning electron microscope (SEM, Hitachi S-4200), energy dispersive X-ray spectroscopy (EDS, Burker XFlash Detector 5030), and X-ray diffraction (XRD, PANalytical X'pert Pro-MPD goniometer), respectively. The band gap of the CZTSe film was determined using a photoluminescence spectrometer (PL, Coherent Innova 90), which had a 488-nm Ar-ion laser.

Results and Discussion

Figure 1 shows the XRD patterns of the CZTSe thin films at various annealing temperatures. The Zn peak and $Cu_{5.6}Sn$ phase (# symbol) appeared in the XRD patterns (letter M) of the metal precursor. The $Cu_{5.6}Sn$ peak was caused by the co-sputtered layer of Cu and Sn. In the inset of Fig. 1, the Se phase (‡ symbol) can be seen in the XRD patterns (letter S) of the CuZnSnSe thin film because Se was deposited on the metal precursor. The $Cu_{5.6}Sn$ phase in the patterns(letter S) was changed to the $Cu_{6.25}Sn_5$ phase (* symbol) in the XRD patterns of the sample annealed at 350°C. The planes (112), (204), and (312) of the $Cu_2ZnSnSe_4$ crystalline and SnSe phase (□ symbol) began to appear in the XRD patterns of the sample

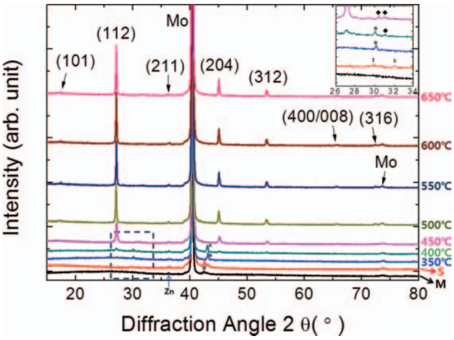

Figure 1. XRD patterns of metal precursor (letter M), CZTSe thin film before annealing (by letter S), and CZTSe thin film after annealing at various temperatures ranging from 350°C to 650°C, in steps of 50°C.

annealed at 400°C. The SnSe peak was the largest at 450°C, and then disappeared at 500°C. This result showed that selenium began to diffuse into the CZT metal precursor at 400°C and was bonded to the CZT metal precursor before 500°C. The $Cu_{6.25}Sn_5$ phase disappeared, and the CZTSe peak appeared more clearly over 450°C. At annealing temperatures higher than 500°C, the peaks of the CZTSe phases became larger. Table 1 indicates that the film annealed at 650°C had only small amounts of Cu ($Cu/(Zn+Sn) = 0.85$) and Sn ($Zn/Sn = 1.15$).

Figure 2 shows the SEM images of the metal precursor (Fig. 2-a), CuZnSnSe thin film before the annealing process (Fig. 2-b), and the CuZnSnSe thin film after annealing at temperatures ranging from 350°C to 650°C, in steps of 50°C (Figs. 2-c to -i). The SEM images of the crystallized Mo layer, the Cu-Sn layer on the Mo layer, and the Zn layer on the Cu-Sn layer are shown in Fig. 2-a. The thickness of the metal precursor was about 450 nm. A SEM image of the Se layer on the metal precursor before annealing is shown in Fig. 2-b. The thicknesses of the Se layers in the CZTSe films annealed at 350°C (Fig. 2-c) and 400°C (Fig. 2-d) were smaller than that in the film before annealing (Fig. 2-b). We can also see from these SEM images that there was no change in the metal precursors. However, as shown in Fig. 2-e, at the annealing temperature of 450°C selenium was diffused into the metal precursor. This result was also confirmed in the analysis of the XRD patterns. Figure 2-f shows that, at 500°C, the metal layer of the CZTSe film was crystallized, bound with Se, and began to disappear from the Mo substrate. The SEM images of the CZTSe thin films annealed at 550°C, 600°C and 650°C are shown in Figs. 2-g, -h, and -i, respectively. From these figures, we can see that the CZTSe grain size increases with the annealing temperature.

Table 1. Elemental compositions of CZT metal precursor and selenized film at 650°C.

	CZT Precursor	CZTSe absorber
Cu/(Zn+Sn)	0.80	0.85
Zn/Sn	1.32	1.15
Se/metal	–	1.14

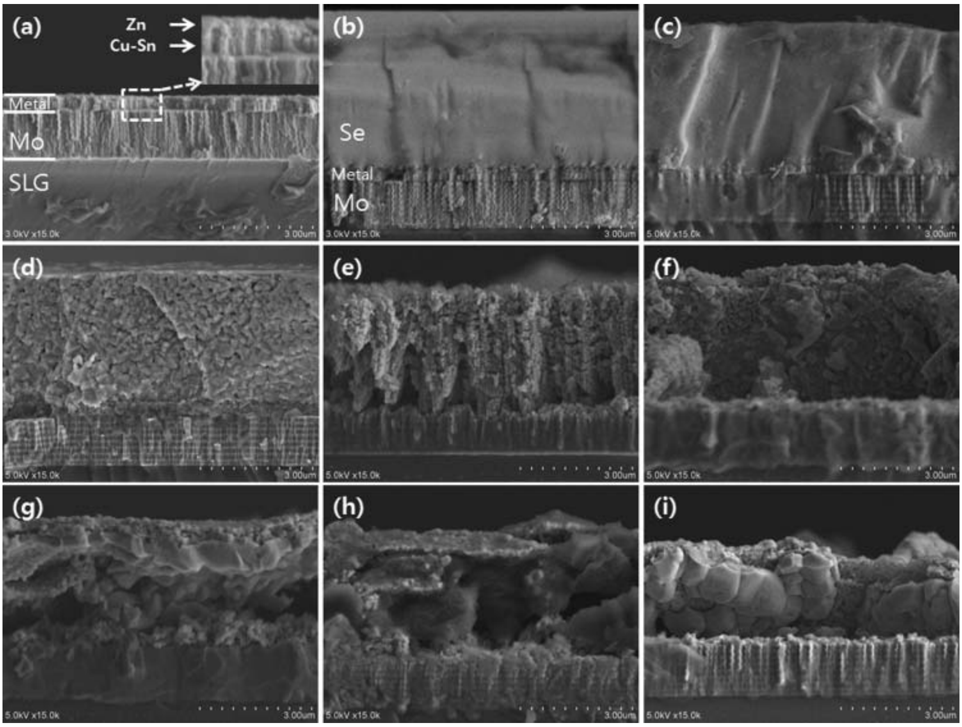

Figure 2. SEM images of metal precursor (a), CuZnSnSe thin film before annealing (b), and CuZnSnSe thin film after annealing at temperatures ranging from 350°C to 650°C, in steps of 50°C (c∼i).

Figure 3 shows the change in the crystalline size as a function of the annealing temperature for three different crystalline directions. From the data of the XRD patterns, the crystalline size can be determined using the Scherrer formula [2], which is given as

$$D = \left(\frac{0.9\lambda}{\beta \cos\theta}\right), \tag{1}$$

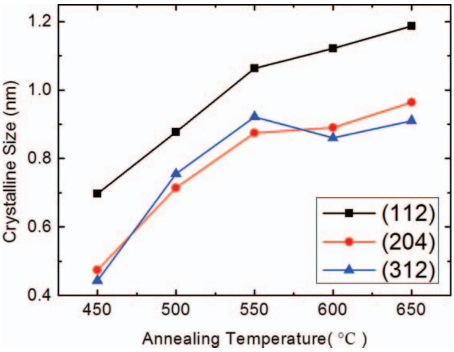

Figure 3. Change in the crystalline size of CZTSe film as a function of annealing temperature.

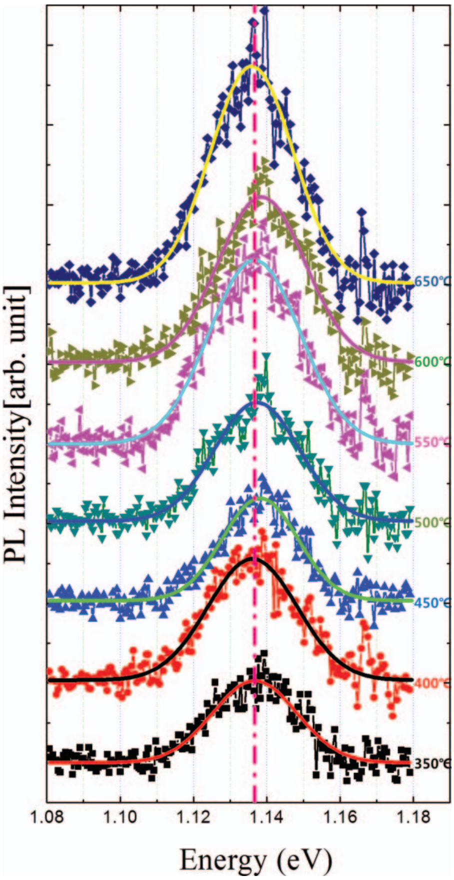

Figure 4. Photoluminescence spectra of CZTSe films at various annealing temperatures.

where λ is the X-ray wavelength, β is the FWHM in radians, and θ is the Bragg angle. Crystallized CZTSe has a tetragonal structure. Thus, the lattice parameters can be calculated by

$$\frac{4\sin^2\theta}{\lambda^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}, \tag{2}$$

where h, k, and l are the Miller indices of the plane. The lattice parameters of CZTSe annealed at temperature over 500°C were found to be a = 5.709 Å and c = 11.351 Å. These values are close to the lattice parameters for a single crystal sample of $Cu_2ZnSnSe_4$, which are a = 5.693 Å and c = 11.333 Å [3, 11].

Figure 4 shows photoluminescence peaks of the CZTSe absorbers as a function of the annealing temperature. We found that the direct band gap of the CZTSe film (1.137 eV) was independent of the annealing temperature.

Conclusions

A metal precursor was formed by co-sputtering Cu and Sn onto a Zn/Mo layer. Then, selenium was deposited onto the metal precursor by thermal evaporation, and the film was subsequently selenized using an RTP process at various annealing temperatures. We found that selenium began to diffuse into the metal precursor at 400°C. The crystallized CZTSe had lattice parameters of a = 5.709 Å and c = 11.351 Å. We also found that the energy gap of CZTSe was 1.137 eV, which was independent of the annealing temperature.

Acknowledgment

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References

[1] Ito, K., & Nakazawa, T. (1998). *Jpn. J. Appl. Phys.*, *27*, 2094.
[2] Rajeshmon, V. G., Kartha, C. S., Vijayakumar, K. P., Sanjeeviraja, C., Abe, T., & Kashiwaba, Y. (2011). *Solar Energy*, *85*, 249.
[3] Matsushita, H., Maeda, T., Katsui, A., Rakizawa, T. (2000). *J. Cryst. Growth*, *208*, 416.
[4] Wibowo, R. A., Kim, W. S., Lee, E. S., Munir, B., & Kim, K. H. (2007). *J. Phys. Chem. Solids*, *68*, 1908.
[5] Chen, S., Gong, X. G., Walsh, A., & Wei, S. (2009). *Appl. Phys. Lett.*, *94*, 041903.
[6] Friedlmeier, T. M., Wieser, N., Walter, T., Dittrich, H., & Schock, H. W. (1997). *Proceedings of the 14th European Photovoltaic Specialists Conference*, Barcelona, 1242.
[7] Katagiri, H. (2005). *Thin Solid Films*, *480–481*, 426.
[8] Katagiri, H., Jimbo, K., Maw, W. S., Oishi, K., Yamazaki, M., Araki, H., & Takeuchi, A. (2009). *Thin Solid Films*, *517*, 2455.
[9] Zoppi, G., Forbes, I., Miles, R. W., Dale, P. J., Scragg, J. J., & Peter, L. M. (2009). *Prog. Photovoltaics*, *17*, 315.
[10] Todorov, T. K., Reuter, K. B., & Mitzi, D. B. (2010). *Adv. Mater.*, *22*, 1.
[11] Babu, G. S., Kumar, Y. K., Bhaskar, P. U., & Raja, V. S. (2008). *Semicond. Sci. Technol.*, *23*, 085023.