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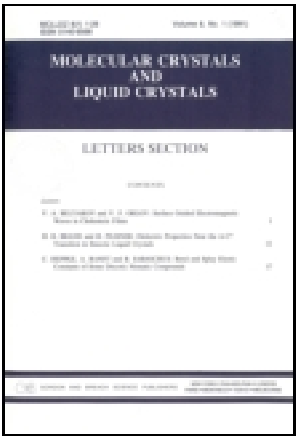

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Annealing Time Dependence of Crystallization in $Cu_2ZnSnSe_4$ Films

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Annealing Time Dependence of Crystallization in $Cu_2ZnSnSe_4$ Films

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$Cu_2ZnSnSe_4$ (CZTSe) films were formulated by the selenization of Cu(Zn, Sn) (CZT) metal precursors. The CZT precursor was prepared by depositing zinc onto a Cu-Sn layer co-sputtered on molybdenum-coated soda-lime glass substrates. Selenium was evaporated thermally onto the CZT precursor. The resulting CZTSe film was then annealed at 450 °C for various annealing times (1, 3, 5, 10 and 15 min) using a rapid thermal process (RTP). Crystallization of the CZTSe film as a function of the annealing time was observed by X-ray diffraction (XRD). The XRD patterns of the films annealed over 3 min were well matched to those of a CZTSe single crystal. The lattice parameters of the CZTSe films annealed over 5 min were $a = 5.639$ Å *and* $c = 11.356$ Å*. These values were reasonably close to the lattice parameters of a single crystal of $Cu_2ZnSnSe_4$* ($a = 5.693$ Å *and* $c = 11.333$ Å*). The energy gap of the CZTSe films was 1.14 eV.*

Keywords Band gap energy; crystallization; CZTSe; RTP; selenization; solar cell

Introduction

Copper-zinc-tin-chalcogenide compounds are earth-abundant and less toxic, and are considered promising candidates to replace Cu(In, Ga)Se_2 in thin film solar cell applications. Compounds, such as Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSn(S,Se)_4$ (CZTSSe) and $Cu_2ZnSnSe_4$ (CZTSe), have a direct band gap, high absorption coefficient (10^4 cm^{-1}), and p-type electrical conductivity [1–3]. The band gaps of these materials were calculated theoretically to be 0.96 eV for CZTSe and 1.50 eV for CZTS [4]. The corresponding experimentally determined band gaps were 0.98 eV for selenide and 1.5 eV for sulfide [5,6].

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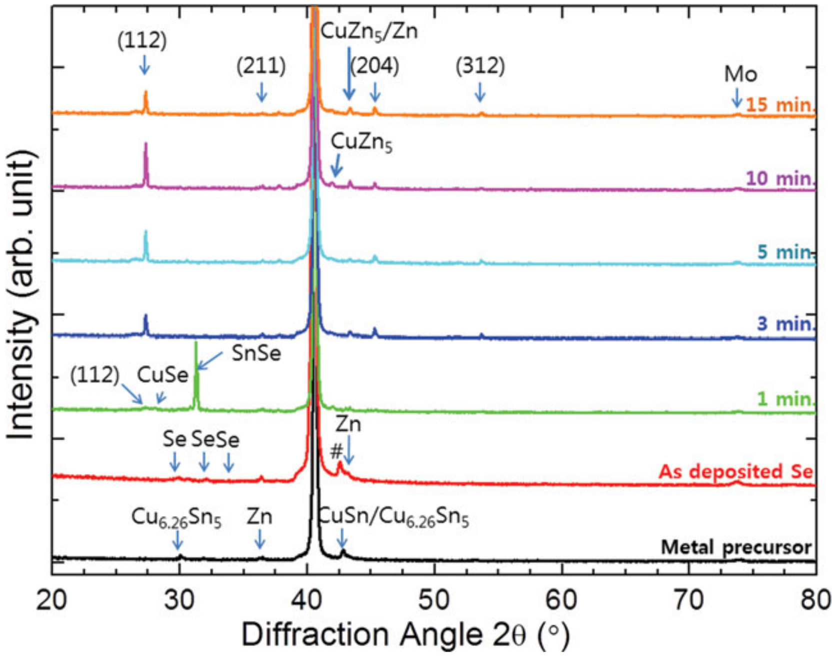

Figure 1. XRD patterns of the metal precursor, CZTSe film before annealing, and CZTSe thin film after annealing for various times.

Recently, CZTSe-based thin film solar cells constructed from a hydrazine-based solution processing showed a photovoltaic efficiency of up to 10.1% [7]. On the other hand, a photovoltaic efficiency of 7.2% was reported for CZTSSe-based solar cell devices using a colloidal nanocrystal-based process. The highest efficiency for CZTS- and CZTSe-based solar cells constructed by a vacuum process was reported to be 8.4% and 6.0%, respectively [8,9]. These results showed that a CZTSe-based vacuum process is a possible way of producing high efficiency solar cell devices.

In the vacuum process, the CZTSe absorbers were crystallized by annealing the selenium deposited on the Cu-Zn-Sn metal precursor in a furnace at temperatures $\geq$320 °C for 90 min [10]. On the other hand, in the liquid process, CZTSe absorbers are crystallized by annealing a spin coated-CZTSe solution on a hot plate at temperatures $\geq$500 °C for a short time [7,11]. In the rapid thermal process (RTP), the selenium deposited on the metal precursor reaches a certain set temperature within a very short time [12]. In a previous paper [12], the characteristics of the crystallization of CZTSe absorbers were determined as a function of the annealing temperature [12]. On the other hand, this study examined the effect of the annealing time on the crystallization of CZTSe absorbers.

Experimental

Metal precursors of the $Cu_2ZnSnSe_4$ absorber were deposited on a molybdenum-coated soda-lime glass substrate by RF magnetron sputtering. The zinc (Zn) layer was deposited on the copper (Cu)-tin (Sn) co-sputtered layer. This order of layer formation showed a good

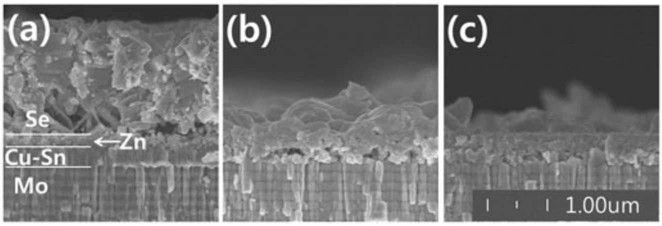

Figure 2. SEM images of the CuZnSnSe film before annealing (a), and CuZnSnSe thin film after annealing at 450 °C for 1 min (b) and 5 min (c).

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surface morphology [13]. The surface morphology is an important parameter for improving the conversion efficiency of thin film solar cells [6]. Cu and Sn were co-sputtered for 15 min with RF power of 80 W and 90 W, respectively. Subsequently, Zn was sputtered onto the film for 15 min with RF power of 130W. These RF powers and deposition times were used to estimate the stoichiometry of the metal precursor. 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 with a flow rate of 10 sccm. Selenium was evaporated thermally onto the metal precursor. Selenization was performed using the RTP process, in which the CuZnSnSe thin film was annealed at 450 °C for various times (1, 3, 5, 10 and 15 min). The temperature was increased at a rate of 20 °C/sec with an argon flow rate of 10 sccm. The surface morphology, chemical composition and crystalline properties of the CZTSe film were analyzed by scanning electron microscopy (SEM, Hitachi S-4200), inductively coupled plasma spectrometry (ICP, Optima 7300DV), and X-ray diffraction (XRD, PANalytical X'pert Pro-MPD goniometer). The band gap energy of the CZTSe films was determined by photoluminescence (PL, Coherent Innova 90) spectrometry with a 488 nm Ar-ion laser.

Results and Discussion

The crystallization of the CZTSe film as a function of the annealing time was observed by XRD, as shown in Fig. 1. The XRD patterns of the films annealed for more than 3 min were well matched to those of the CZTSe crystal [3]. The peaks of $Cu_{6.26}Sn_5$ and CuSn in the metal precursor suggested that they were crystallized during the co-sputtering of Cu and Sn.

As selenium was evaporated on the metal precursor, the $Cu_{6.26}Sn_5$ and CuSn phases transformed to a $Cu_{5.6}Sn$ phase (marked by the symbol # in the XRD pattern of the CZTSe film), which showed a change in the bonding structure of Cu and Sn in the film due to the evaporation heat.

Table 1. Chemical compositions of the CZT metal precursor and selenized film

Annealing Time	1 min.	3 min.	5 min.	10 min.	15 min.
Cu/(Zn+Sn)	0.83	0.82	0.83	0.85	0.90
Zn/Sn	1.23	1.21	1.25	1.35	1.45

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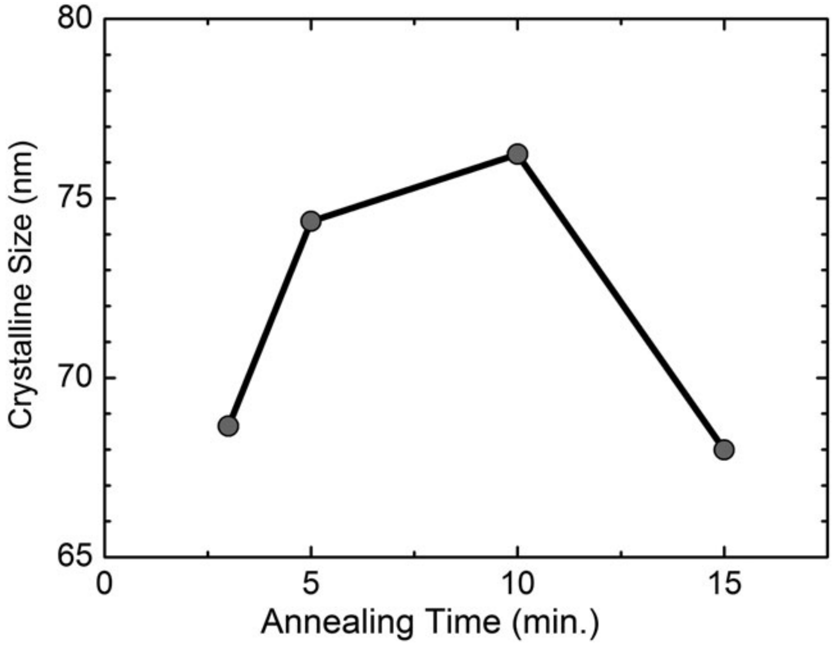

Figure 3. Change in the crystalline size in the CZTSe film as a function of the annealing time.

After 1-min annealing, the $Cu_{5.6}Sn$ and Se phases in the CZTSe film disappeared and the SnSe and CuSe phases appeared. These peaks disappeared after 3-min annealing, and the (112), (204) and (312) peaks of CZTSe appeared. These results show that the selenium began to diffuse into the metal precursor after 1-min annealing, and was bonded to the CZT during the 3-min annealing process.

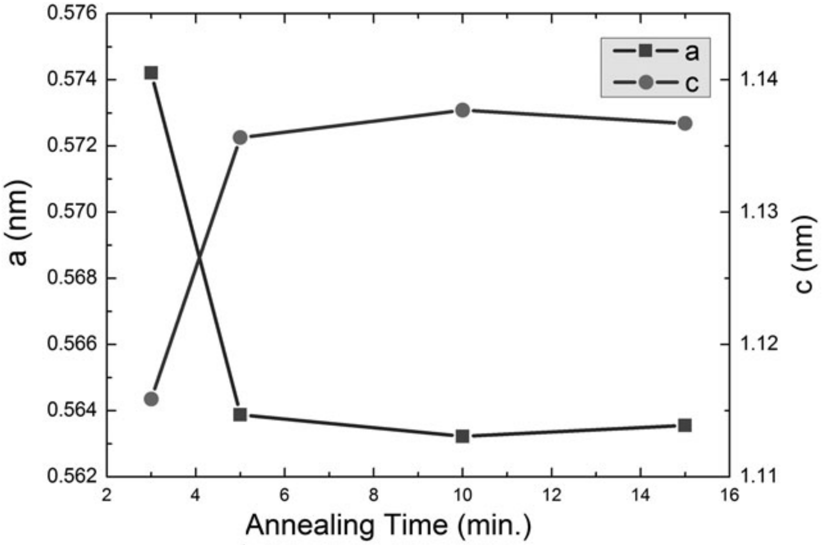

Figure 4. Change in the lattice constants of the CZTSe film as a function of the annealing time.

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The intensity of the (112) XRD peak increased with increasing annealing time. On the other hand, this peak began to decrease after 15-min annealing. The $CuZn_5$ phase appeared after 10-min annealing. This was attributed to Sn loss in the CZTSe film with increasing annealing time. The above XRD analyses confirmed that the optimal annealing time for the CZTSe film is between 3 and 5 min for an annealing temperature of 450 °C with the RTP method.

Figure 2 shows SEM images of the intersections of the CZTSe films. Figure 2(a) shows the Se, Zn and co-sputtered Cu-Sn layers on the Mo layer. More selenium was deposited than needed for the stoichiometry of CZTSe, but this excessive selenium was extracted with the argon flow during the annealing process. On the other hand, if the film was annealed for more than 10 min, Sn can be extracted along with selenium in the form of SnSe, resulting in a loss of Sn [10,14].

Figures 2(b) and (c) show voids between the Mo and CZTSe layer. These voids were caused by the higher mobility of Cu than Zn and Sn [15]. Figure 2(c) shows an image of the CZTSe absorber annealed for 5 min. The thickness of the CZTSe absorbers was approximately 500 nm. The chemical compositions of the annealed CZTSe absorbers were determined by ICP analysis, as shown in Table 1. The composition of the samples after 1-, 3- and 5-min annealing was similar to that of the CZTSe absorber, which has shown the highest conversion efficiency to date [7]. On the other hand, Sn loss was observed in the samples annealed for 10 and 15 min.

The crystalline size was estimated from the XRD data using Scherrer formula [2] as follows:

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

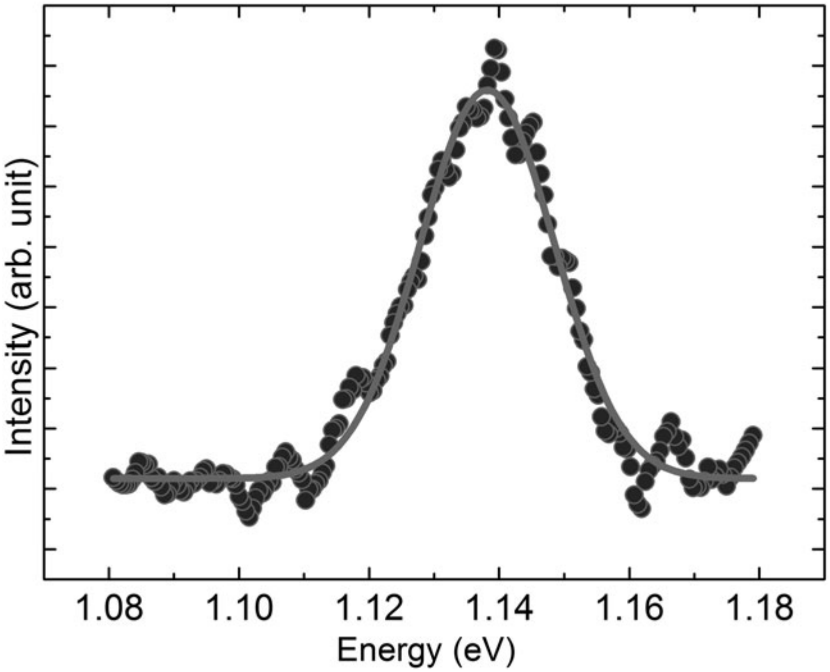

Figure 5. Photoluminance spectra of CZTSe films annealed at 450 °C for 5 min.

where λ is the X-ray wavelength, β is the full width at half maximum (FWHM) in radians, and θ is the Bragg angle. Figure 3 shows the change in the crystalline size as a function of the annealing time for the crystalline direction of (112), which is the main peak in the CZTSe crystal. The crystalline size increased with increasing annealing time to 10 min. On the other hand, it decreased rapidly after an annealing for 15 min. This was attributed to Sn loss in the CZTSe absorber.

Figure 4 shows the change in the lattice parameters in the CZTSe crystal. The crystallized CZTSe has a tetragonal structure. Therefore, the lattice parameters can be calculated by the following equation

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

where h, k and l are Miller indices of the plane. The lattice constants, a and c, were calculated from the 2θ values of the (112) and (204) planes. The lattice constants of the CZTSe crystal after 3- and 5-min annealing were $a = 0.574$ nm, $c = 1.1159$ nm and $a = 0.5639$ nm, $c = 1.1356$ nm, respectively. For the samples annealed for more than 5min, the lattice constants maintained similar values to those of a CZTSe single crystal [3,16]. This shows that the optimum annealing time in the RTP process is 5 min at 450 °C.

Figure 5 shows the PL peaks of the CZTSe absorbers in the CZTSe film annealed for 5 min. The direct band gap of the CZTSe films was 1.14 eV.

Conclusions

The metal precursor was formulated by depositing Zn on a Cu-Sn co-sputtered layer. Selenium was evaporated thermally onto this metal precursor, and the film was subsequently selenized using the RTP process at 450 °C for various annealing times. Selenium was diffused into the metal precursor starting from 1-min annealing. The crystallized CZTSe annealed for more than 5 min had lattice parameters of $a = 0.5639$ nm and $c = 1.1356$ nm. From XRD and ICP analyses, the CZTSe film annealed for 10 and 15 min was crystallized with the loss of Sn. The energy gap of the CZTSe was 1.14 eV and was independent of the annealing time.

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] Chen, S., Gong, X. G., Walsh, A., & Wei, S. (2009). *Appl. Phys. Lett.*, *94*, 041903.

[5] Friedlmeier, T. M., Wieser, N., Walter, T., Dittrich, H., & Schock, H. W. (1997). *Proceedings of the 14th European Photovoltaic Specialists Conference, Barcelona*, 1242.

[6] Katagiri, H. (2005). *Thin Solid Films*, *480–481*, 426.

[7] Bag, S., Gunawan, O., Gokmen, T., Zbu, Y., Todorov, T. K., & Mitzi, D. B. (2012). *Energy Environ. Sci.*, *5*, 7060.

[8] Shin, B., Gunawan, O., Zhu, Y., Bojarczuk, N. A., Chey, S. J., & Guha, S. (2011). *Prog. Photovolt: Res. Appl.*, *DOI10.1002/pip* 1174.

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[9] Grenet, L., Bernardi, S., Kohen, D., Lepoittevin, C., Noel, S., Karst, N., Brioude, A., Perraud, S., & Mariette, H. (2012). *Sol. Energy Mater. Sol. Cells*, *101*, 11.

[10] Redinger, A., & Siebentritt, S. (2012). *Appl. Phys. Lett.*, *97*, 092111.

[11] Todorov, T. K., Reuter, K. B., & Mitzi, D. B. (2010). *Adv. Mater.*, *22*, E156.

[12] Hong, S., Kim, C., Park, S. C., Rhee, I., Kim, D. H., & Kang, J. K. (2012). *Mol. Cryst. Liq. Cryst.*, *565*, 147.

[13] Hong, S. (2012). *Mol. Cryst. Liq. Cryst.*, *565*, 153.

[14] Redinger, A., Berg, D. M., Dale, P. J., & Siebentritt, S. (2011). *J. Am. Chem. Soc.*, *133*, 3320.

[15] Fernandes, P. A., Salome P. M. P., & Cunha, A. F. (2009). *Semicond. Sci. Technol.*, *24*, 105013.

[16] Babu, G. S., Kumar, Y. K., Bhaskar, P. U., & Raja, V. S. (2008). *Semicond. Sci. Technol.*, *23*, 085023.

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