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Properties of Cu_2ZnSnS_4 Films with Respect to Sulfurization Time Investigated using Cu-Zn-Sn Films Deposited by Co-sputtering

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Cu_2ZnSnS_4 (CZTS) thin films have been used as an absorber layer for solar cells because they have a large absorption coefficient and a direct band gap of suitable energy. We investigated the properties of CZTS thin films with respect to the sulfurization time by using Cu-Zn-Sn (CZT) metal precursor films. The CZT metal precursor films were deposited onto soda-lime glass by co-sputtering with single targets of copper (Cu), zinc (Zn), and tin (Sn). The sulfurization of the CZT films was performed in evacuated and sealed quartz ampoules using sulfur powder. The sealed samples were annealed at 550°C for times ranging from 1 to 60 min.

The crystallization of the CZTS films as a function of annealing time was investigated using X-ray diffraction (XRD). The XRD peaks of CZTS appeared in the XRD patterns of the samples that were annealed for at least 3 min. Furthermore, the intensity of the CZTS peaks increased with annealing time. The increase in peak intensity and decrease in the full width at half maximum (FWHM) indicate that crystallization increases with annealing time. The morphology and the atomic compositional ratios of the CZTS films were also analyzed by using field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDX), respectively. The band gap energy of the CZTS films was determined using a UV-Vis-NIR spectrophotometer. The estimated optical energy band gap of the CZTS films that were annealed for more than 10 min ranged from 1.4 to 1.5 eV, which is close to the previously reported value of 1.45 eV.

Keywords CZTS; Cu_2ZnSnS_4; Sulfurization; metal precursor; Solar cell; Photovoltaics

Introduction

Cu_2ZnSnS_4 (CZTS) film is receiving much attention as a photo-absorbing material for thin film solar cells [1–3]. CZTS film has a high absorption coefficient ($>10^4$ cm^{-1}), a direct band gap ($\sim$1.5 eV), and p-type semiconductors [1, 4]. The highest efficiency of a CZTS-based solar cell has been reported to be 12.6% using a $Cu_2ZnSnS_xSe_{4-x}$ (CZTSSe) thin film solar cell fabricated using a hydrazine pure-solution approach [5]. For the formation of the

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CZTS film, vacuum processes are advantageous compared to the solution process because they do not use toxic chemicals. Thus, various vacuum processes such as co-evaporation, sputter sulfurization, and rapid thermal annealing are being studied as methods to form the CZTS based absorbent layer [1–2, 6–7]. Especially, the sputter sulfurization method has been studied [1, 6] because this process is profitable for the fabrication of large area solar cells. Generally, with the sputter sulfurization method, the precursor layers have been various ordered metal or metal sulfide stacks that need many targets and sputtering processes to form. Therefore, a deposition method that uses a Cu-Zn-Sn (CZT) alloyed single sputter target for precursor layer formation may have a powerful effect on industrial productivity. However, the sulfurization condition that should be used for the single-layered CZT metal precursor film is unknown, causing difficulty in making CZT alloyed single sputter targets.

In this study, single-layered CZT metal precursor films were deposited using the co-sputtering method with a similar CZT alloyed single sputter target. Moreover, the CZTS photo-absorbing films were crystallized using the sulfurization method. The sulfurization of the CZT metal precursor films was performed by annealing the films in evacuated and sealed quartz ampoules with sulfur at 550°C for various times ranging from 1 to 60 min. We investigated the following properties of the CZTS films with respect to sulfurization time: crystallization, crystalline size, lattice parameters, morphology, atomic compositional ratio, and band gap energy.

Experimental

The CZTS thin films were crystallized through the sulfurization of CZT metal precursor films. The CZT metal precursor films were deposited onto soda-lime glass by co-sputtering with single targets of copper (Cu), zinc (Zn), and tin (Sn). The deposition of the metal precursor films was accomplished by RF-magnetron sputtering with a radio frequency (RF) power of 90, 135, and 100 W on the Cu, Zn, and Sn targets, respectively, for 5 min simultaneously. The thickness of the metal precursor films was measured to be about

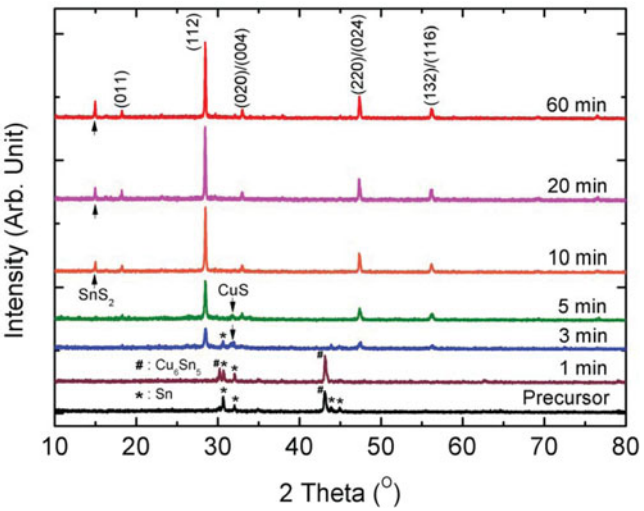

Figure 1. XRD patterns of the CZT metal precursor film and the CZTS films after annealing at 550°C for various times.

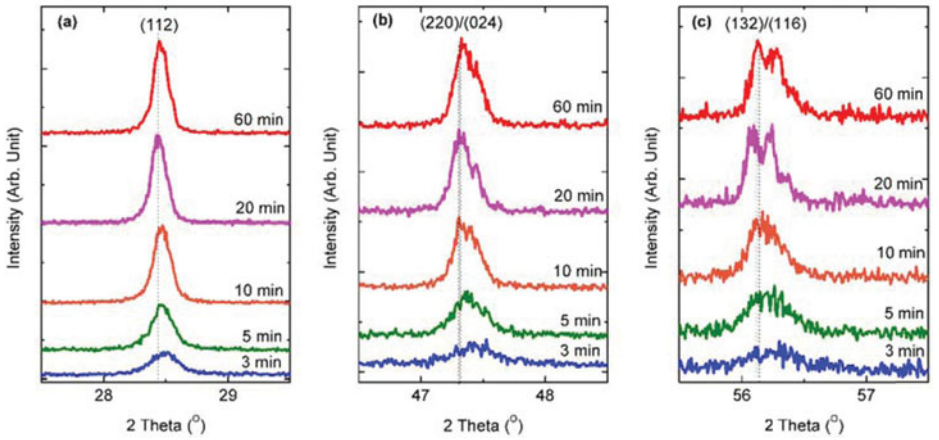

Figure 2. XRD main peaks of the CZTS films formed for various annealing times; (a) (112), (b) (220)/(024), and (c) (132)/(116) plane.

1 μm. The sulfurization was performed in evacuated and sealed quartz ampoules with 0.01 mmole of sulfur powder. The sealed samples were annealed in a tube furnace at 550°C for times ranging from 1 to 60 min with insertion and release times of 10 sec each. The released samples were allowed to cool naturally at room temperature. The crystalline properties of the CZTS films as a function of annealing time were investigated using X-ray diffraction (XRD, PANalytical, X'ert Pro-MPD) patterns. The morphology and the atomic composition of the films were analyzed by using field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800) and energy dispersive X-ray spectroscopy (EDX), respectively. The absorption coefficient and the optical energy band gap of the CZTS films were determined using a UV-Vis-NIR spectrophotometer (Varian, Carry 5000).

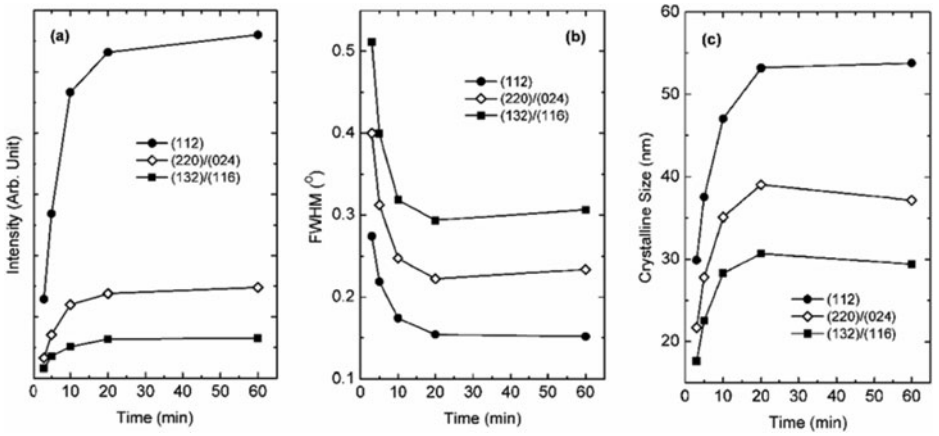

Figure 3. Changes in (a) intensity, (b) FWHM, and (c) crystalline size of the CZTS films annealed for various times.

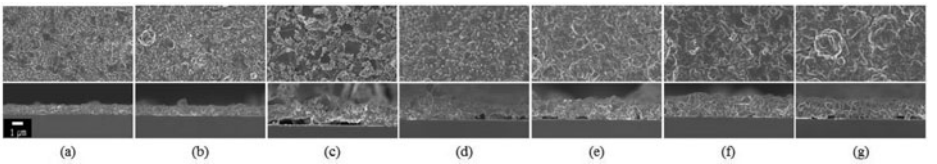

Figure 4. Surface and cross section SEM images of the CZT metal precursor film (a) and the CZTS films after annealing at 550°C for 1 min (b), 3 min (c), 5 min (d), 10 min (e), 20 min (f), and 60 min (g).

Results and Discussion

Figure 1 shows the XRD patterns of the CZT metal precursor film and the CZTS thin films after annealing at 550°C for various annealing time. The Cu_6Sn_5 and Sn peaks appear in the XRD patterns of the precursor film and the sample that was annealed for 1 min. The co-sputtering of the Cu, Zn, and Sn causes the Cu_6Sn_5 peaks. These results agree with the previous observation that a Cu-Sn thin film is deposited when the co-sputtering method is used [8–9]. The Cu_6Sn_5 peaks are clear, and the Sn peaks almost disappear in the XRD patterns of the sample annealed for 3 min. In addition, the XRD peaks of CZTS begin to appear in the XRD patterns of the sample annealed for 3 min [10]. As shown in Figs. 1 and 2, the intensity of the CZTS peaks increases with annealing time. Fig. 2 shows the XRD main peaks of the CZTS films that were annealed for more than 3 min. The (112) preferred orientation peak of the CZTS films clearly appears and increases with annealing time. The (220)/(024) and (132)/(116) peaks of the CZTS films, which have the second and the third highest relative intensities, also increase but widen slightly for the film annealed for 60 min, as shown in Figs. 2 and 3. The crystalline size also decreases for the film annealed for 60 min. The changes in the intensity, the full width at half maximum (FWHM), and the crystalline size of the CZTS films annealed for various times are shown in Fig. 3. The crystalline size was estimated from the XRD data using the Scherer formula [11] as follows:

$$\mathrm{D} = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ is the X-ray wavelength, β is the FWHM in radians, and θ is the Bragg angle.

The CZTS crystals have a tetragonal structure [12]. Therefore, the lattice parameters can be calculated using the following equation.

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

Table 1. Atomic compositional ratios of the CZT metal precursor film and CZTS films after annealing for various times

	Precursor	1 min.	3 min.	5 min.	10 min.	20 min.	60 min.
Cu/(Zn+Sn)	0.70	0.80	3.20	0.78	0.83	0.91	0.78
Zn/Sn	1.20	1.53	2.01	2.36	1.36	1.14	1.31
S/(Metals)	0.00	0.02	0.81	0.89	0.96	0.95	0.96

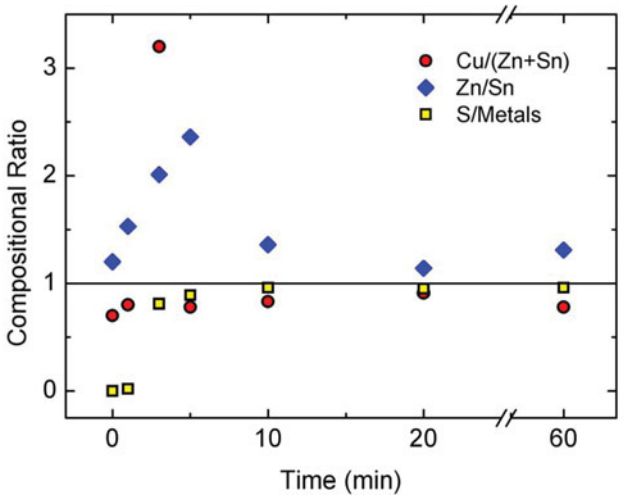

Figure 5. Atomic compositional ratios of Cu/(Zn+Sn), Zn/Sn, and S/metals of the CZTS films annealed for various times.

where h, k, and l are the Miller indices of the plane. The lattice constants, a and c, were calculated from the 2θ values of the (112) and (220)/(024) planes. The lattice constants of the CZTS films were determined to have average values of $a = 5.423$ Å and $c = 10.867$ Å with standard deviations of $a = 0.004$ Å and $c = 0.007$ Å, respectively. The lattice constants maintained similar values to those of a CZTS single crystal, which are, $a = 5.434$ Å and $c = 10.856$ Å [10].

Figure 4 shows surface and cross section SEM images of the CZT metal precursor film and the CZTS films after annealing for various times. As shown in Fig. 4 (a), the CZT metal precursor film was deposited uniformly with a thickness of about 1 μm. The CZTS films that were annealed for more than 10 min showed a large grain size and a thickness of

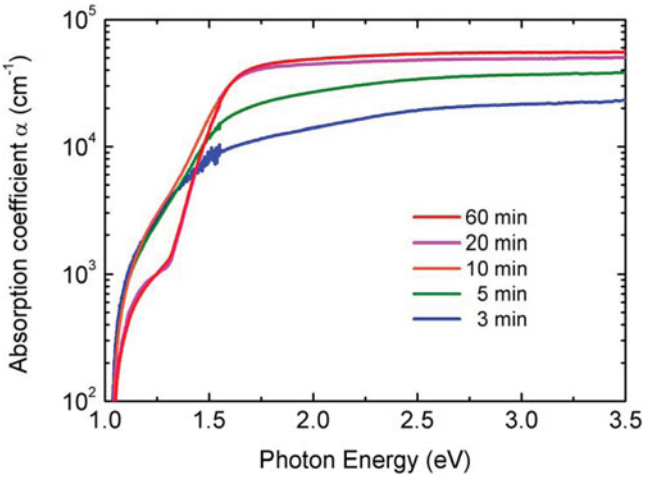

Figure 6. Absorption coefficient of the CZTS films formed by annealing at 550°C for various times.

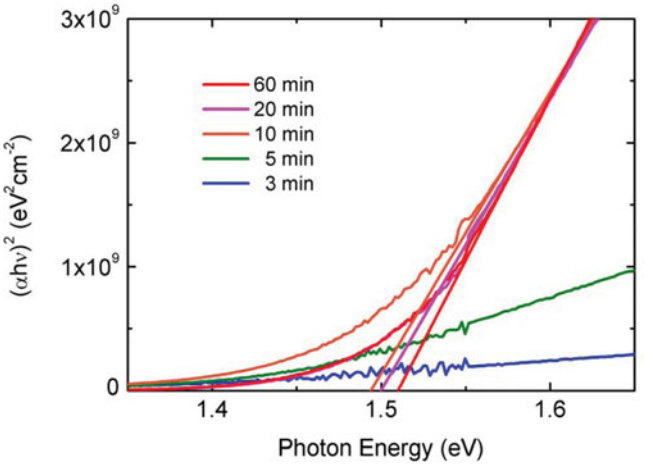

Figure 7. $(\alpha h\nu)^2$ versus the photon energy $(h\nu)$ for the CZTS films after annealing for various times.

about 2 μm in Figs. 4 (e-g). The atomic compositional ratios of the CZT metal precursor film and the CZTS films after annealing were determined by using EDX. As shown in Table 1 and Fig. 5, the atomic compositions of the CZTS films that were annealed for more than 10 min were similar to that of the CZTS absorber, which has shown the highest conversion efficiency to date [1]. The CZTS films that were annealed for 3 and 5 min show crystallization of the CZTS in the XRD pattern, as seen in Figs. 1 and 2, but also show a large deviation from the stoichiometry of CZTS.

Figure 6 shows the absorption coefficient α of the CZTS films, which was determined by using a UV-Vis-NIR spectrophotometer. Here, we can see the high absorption characteristics of the CZTS films formed by the sulfurization process in the near infrared and visible range. Fig. 7 shows the plot of $(\alpha h\nu)^2$ versus the photon energy $(h\nu)$ for the CZTS films. The optical band gap energy was obtained using the following equation [13]

$$\alpha h\nu = \mathrm{A}(h\nu - E_g)^{1/2}$$

where α is the optical absorption coefficient, h is the Planck's constant, ν is the frequency of the photon, A is a constant, and E_g is the optical band gap energy. The optical band gap energy of the CZTS films was estimated by extrapolating the linear region of the plot of $(\alpha h\nu)^2$ versus the photon energy $(h\nu)$ and ranges from 1.49 to 1.51 eV, which is close to the previously reported values of 1.48–1.51 eV [14, 15].

Conclusions

CZTS photo-absorbing thin films for CZTS solar cells were fabricated by annealing single-layered CZT metal precursor films with sulfur powder in evacuated and sealed quartz ampoules. The annealing process was carried out at 550°C for various times ranging from 1 to 60 min. The XRD peaks of the CZTS thin films began to appear in the XRD patterns of the sample that was annealed for 3 min. As the annealing time was increased, the intensity of the CZTS peaks increased and the FWHM of the CZTS peaks decreased. The lattice constants of the CZTS films were determined to be a = 5.423 Å and c = 10.867 Å. The CZTS films that were annealed for more than 10 min show large grain size and similar

atomic compositions to that of the CZTS absorber, which has shown the highest conversion efficiency. The optical energy band gap was estimated to range from 1.48 to 1.51 eV for the CZTS films that were annealed for more than 10 min. The main contribution of this study is a simple process that could be used in the fabrication of the CZTS solar cell, which has a better photovoltaic efficiency. From our observations, we found that the annealing time should be greater than 10 min in order to form the CZTS photo-absorber film by using CZT metal precursor films

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