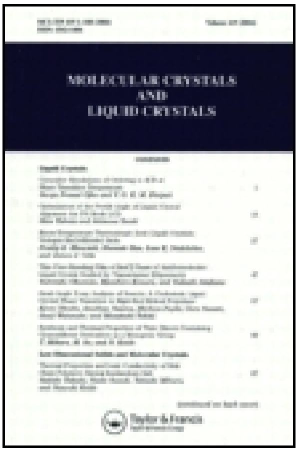

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Temperature Effects on Cu_2ZnSnS_4 (CZTS) Films Deposited by Spraying Method

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CZTS containing ink was prepared by a sonochemical method, and properties of CZTS thin films deposited by a spraying method were investigated. We used $CuCl_2$, ZnCl, $SnCl_2$ and thiourea as precursor materials, 2-methoxyethanol as a solvent, and monoethanolamine as a stabilizer. X-ray diffraction (XRD) patterns from the CZTS films mainly exhibited the (112), (200), (220), and (312) planes of a kesterite structure, and a phase transition was not observed in the range of annealing temperatures (maximum 500°C) investigated in this study. Full width at half maximum (FWHM) values of all the XRD peaks stay nearly constant up to the annealing temperature of 300°C, and suddenly decreases from 300°C to 450°C, and finally saturates above ∼450°C. The optical bandgap of CZTS films was ∼1.25 eV, and the atomic elemental ratio of Cu:Zn:Sn:S in CZTS films was approximately 2:1:0.9:3.5. These results demonstrate that the CZTS containing ink developed in this study has promising potential for the formation of high quality CZTS thin films for solar cell applications.

Keywords CZTS; sonochemical; spraying; non-vacuum Process; XRD

Introduction

$CuInGaSe_2$ (CIGS) materials are used as a light-aborption layer in thin films solar cells because of their suitable energy band-gap and a large absorption coefficient [1]. However, since indium and selenium are rare materials in the earth, large scale energy production using this material system can be restricted in the near future [1,2]. To solve this problem, it is necessary to develop alternative non-toxic materials from abundant resources. This issue has stimulated research to develop new absorption layers composed of earth-abundant elements. Presently, Cu_2ZnSnS_4 (CZTS) is considered to be a very promising light absorption material for low-cost photovoltaic devices, because CZTS is made of earth-abundant elements and contains environment-friendly stable compounds. Particularly, CZTS is suitable for photovoltaic devices due to its suitable optical band-gap (∼1.4 eV) and a large absorption coefficient ($\sim 10^4$ cm^{-1}) [2–5].

Deposition method of CZTS thin films can be classified into a vacuum process (evaporation, sputtering, chemical vapor deposition, etc.) and a non-vacuum process (sparying, spin coating, screen printing, electrochemical deposition, etc.). The vacuum-based deposition methods are advantageous, because the chemical composition of CZTS films is relatively

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easily controlable, and films with high reproductivity and good quality could be formed [1,2]. However, vacuum-based deposition methods have suffered from relatively slow deposition rate, high production cost, and limited availability of precursor materials. On the contrary, non-vacuum deposition methods have advantages in a relatively easy processing sequence, high growth rate, and low production cost [1–5]. In non-vacuum methods, precursor materials or solutions play an important role in determining the deposition technique and process condition.

In this study, CZTS containing ink is synthesized by a sonochemical method at room temperature, and the characteristics of CZTS thin films deposited by a spraying method is investigated. As-deposited CZTS films are annealed at different temperatures to study the effects of annealing temperature on the film properties.

Experimental Details

$CuCl_2$ (97%, Aldrich), ZnCl (98%, Aldrich), $SnCl_2$ (98%, Aldrich) and thiourea (99%, Aldrich) are used as precursor materials for preparing CZTS containing inks. The amount of Cu, Zn, Sn, and S precursors used in the synthesis are 0.2 mmol, 0.1 mmol, 0.1 mmol, and 0.4 mmol, repectively. 2-methoxyethanol (99.3%, Aldrich) is used as a solvent, and monoethanolamine (99%, TCI) is added to the solution to prevent premature formation of precipitates. $CuCl_2$, ZnCl and $SnCl_2$ are first dissolved into a mixture of 2-methoxyethanol and monoethanolamine (MEA), and subsequently, thiourea is added into the prepared solution. The solution is sonicated for 30 min. at room temperature to allow sonochemical reactions to occur. After the sonochemical reaction, prepared CZTS ink is sprayed onto Mo-coated glass substrates, keeping the substrate temperature at 170°C to remove the solvent and stabilizer during the spraying process. Spray coating is continued for 2 min at the spraying rate of 1 mL/min. As-deposited CZTS films are finally sintered in a vacuum oven at different temperatures for 1 h.

Structural properties of CZTS films such as the crystallinity and preferred orientation are investigated by X-ray diffractometer (XRD, Philips X'Pert-APD). Optoelectronic properties of CZTS films are analyzed by a photoluminescence (PL) spectrometer using an Ar-ion laser at the excitation wavelength of 488 nm. Morphologies of CZTS films are characterized by a scanning electron microscope (SEM, Hitachi S-4200) operated at 25 kV, and elemental analyses of the films are carried out using an energy dispersive X-ray spectroscopy (EDS & EMAX).

Results and Discussion

Figure 1 shows X-ray diffraction (XRD) patterns of annealed and non-annealed CZTS films spray-deposited on the Mo-coated glass substrates. Both CZTS films show clear diffraction peaks from the (112), (220), and (312) crystal planes. The XRD patterns are well matched to kesterite structure (JCPDS card 26-0575) that has a tetragonal unit cell including sulfur atoms positioned in a face centered cubic (fcc) sublattice and other atoms (Cu, Zn, and Sn) occupying half the tetrahedral interstitial sites within the S sublattice [4,6,7]. The CZTS compounds typically have two major structures known as stannite structure and kesterite structure. Difference between the two stuctures is the arrangement of Cu and Zn atoms in the lattice, and the kesterite structure is thermodynamically more stable than the stannite structure [6,7].

Figure 2 shows the contour diagram of XRD patterns of CZTS films along the annealing temperature axis. This diagram clearly shows the peak's evolution as a function of annealing

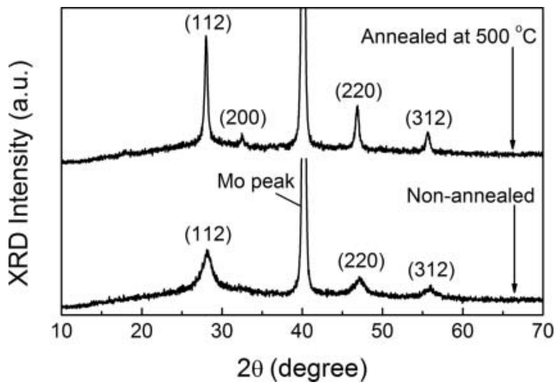

Figure 1. The XRD patterns of CZTS films: Non-annealed and annealed at 500°C.

temperature and reveal that there is no phase transition with annealing temperature increase up to 500°C. As-deposited CZTS films (non-annealed) also exhibit clear but broad XRD patterns of kesterite CZTS phase, indicating that the synthesized CZTS ink has already contained crystallites of nanometer scale which were formed during the sonochemical synthesis. The sonochemical synthesis at room temperature seems very useful, efficient and convenient in preparing the CZTS containing ink to apply the technique to various non-vacuum processes for thin film solar cell fabrication.

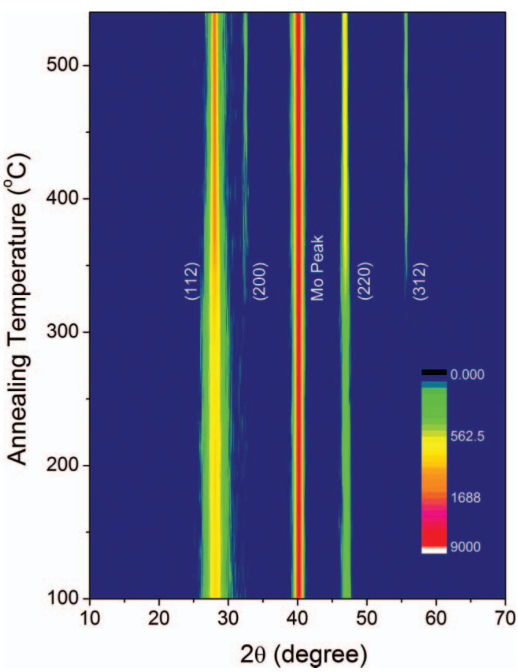

Figure 2. The contour map of XRD pattern evolution of CZTS thin films as a function of annealing temperature.

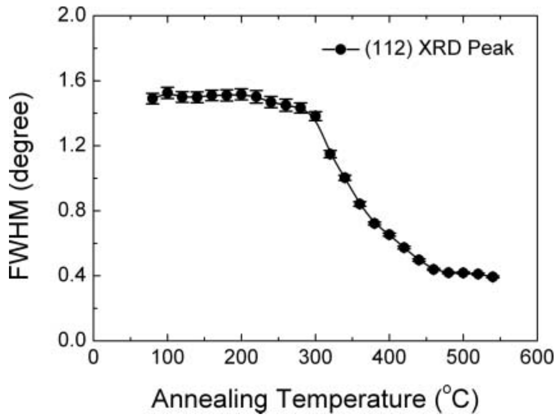

Figure 3. The FWHM value of (112) XRD peak as a function of annealing temperature.

Figure 3 shows the variation of a full-width at half-maximum (FWHM) of (112) peak of CZTS films as a function of annealing temperature. The FWHM of (112) peak of CZTS film dramaticlly changes as the annealing temperature changes. The FWHM stays at a nearly constant value up to the annealing temperature of 300°C, then suddenly decreases from 300°C to 450°C, and finally saturates above ~450°C. The Scherrer's equation describes the relationship between the grain size and the FWHM value of the peaks [8]:

$$D = \frac{0.9\lambda}{(B - b)\cos\theta} \tag{1}$$

where D is the grain size or particle size, λ is the wavelength of CuKα X-ray source, B is the FWHM value of a diffraction peak, b is the instrument line broadening, and θ is the diffraction angle. This equation represents an inverse linear relationship between the FWHM value and the grain size, and thus the result shown in Fig. 3 means that the grain size of CZTS films suddenly grows at the temperatures above ~300°C, and the crystallinity also improves in this temperature regime.

This grain growth tendency is also comfirmed from the SEM images of CZTS films annealed at different temperatures. Figure 4 shows the cross-sectional images of CZTS films, (a) non-annealed and (b) annealed at 500°C. In non-annealed CZTS films, small size CZTS particles are physically aggregated together. In annealed CZTS films, however, the

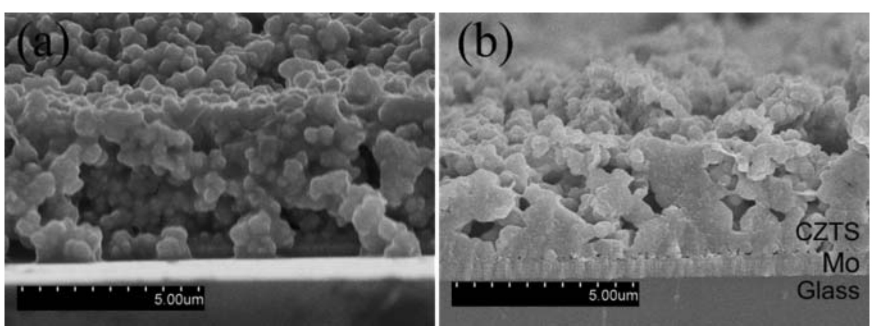

Figure 4. The cross-sectional SEM images of CZTS films: (a) non-annealed; (b) annealed at 500°C.

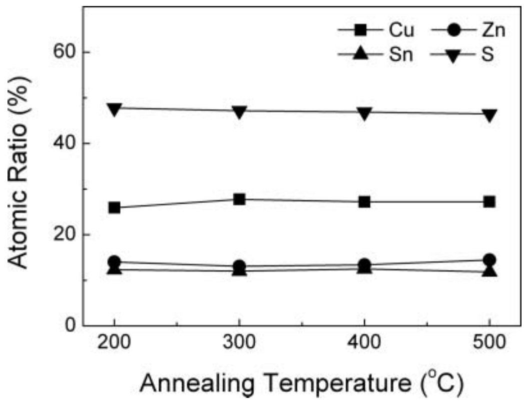

Figure 5. The atomic elemental ratio of CZTS films as a function of annealing temperature.

size of masses gradually grows due to a necking process between adjacent masses, and the grain size of CZTS crystals increases with the increase of annealing temperature. The dramatic change in CZTS morphology corresponds well to the XRD results discussed above.

The atomic elemental ratio of CZTS films at different annealing temperatures is shown in Fig. 5. The elemental ratio changes very little with annealing temperature, and the ratio of Cu:Zn:Sn:S in CZTS films is approximately 2:1:0.9:3.5. Interestingly, the elemental ratio of Cu, Zn, and Sn in CZTS films replicates closely the ratio of Cu, Zn, Sn in precursor state. This result implies that the precursors of (Cu, Zn, Sn) were unpreferentially reacted with S element via S-redox process, and CZTS inks with near stoichiometric ratio in (Cu, Zn, Sn) elements were successfully synthesized. The atomic elemental ratio in CZTS films plays a crucial role in determining the properties of light absorption layer for photovoltaic devices. Many previous reports indicated that the CZTS thin film solar cells with high power conversion efficiency were produced from Cu-poor and Zn-rich growth conditions in the elemental ratio [2,9]. Thus, controlling the atomic elemental composition of CZTS absorption layer is important to fabricate high-efficiency photovoltaic devices.

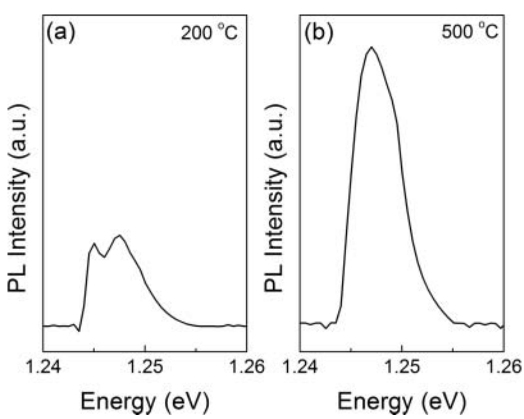

Figure 6. The photoluminescence (PL) spectra of CZTS films annealed at: (a) 200°C and (b) 500°C.

Figure 6 shows the PL spectra of CZTS films annealed at the temperature of 200°C and 500°C, respectively. The optical energy bandgap at room temperature is about 1.25 eV in both cases, and the PL intensity of CZTS films annealed at 500°C is much higher than that of CZTS films annealed at 200°C. This result is in good accordance with the change of FWHM values of XRD peaks upon annealing, and means that the optical property of CZTS films is enhanced with the improvement of crystallinity of the films. In addition, since the kesterite structure is very similar to the chalcopyrite structure, CZTS films are expected to have similar electronic properties to CIGS films.

Conclusions

In this study, CZTS ink was prepared by a sonochemical synthesis method, and the prepared ink was deposited on Mo-coated glass by a spray-coating method. Characteristics of as-deposited CZTS films were investigated, and especially the effects of annealing temperature on the film properties were studied in detail. XRD peaks from the CZTS films corresponded to the (112), (200), (220), and (312) planes, indicating that the kesterite structure is formed. Phase transitions did not occur with increased annealing temperature, which implied that CZTS inks already had crystallites formed during the sonochemical synthesis. In the grain growth process, the size of CZTS grains began to increase suddenly above 300°C, kept growing until 450°C, and then saturated above ~450°C. Optimum annealing temperature was chosen to be 450°C for fabricating the light absorption layers with high optical quality. The optical band-gap, measured by PL spectroscopy, was approximately 1.25 eV, and the PL intensity of CZTS films increased by nearly a factor of four after annealing at 500°C. The change in optical properties is closely related to the crystallinity of CZTS films, and the PL results correspond well with those from the XRD measurements. From all these results, we confirm that the sonochemically derived CZTS ink is suitable for depositing CZTS thin films for solar cell applications, because the ink can be easily spray-coated and reproduced as thin films on substrates, with good crystallinity and optical properties, in a fairly controllable way.

Acknowledgments

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