Temperature induced phase transformation in coevaporated Cu_2SnSe_3 thin films

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Abstract

Cu_2SnSe_3 (CTSe) thin films were prepared by coevaporation at different substrate temperatures (325–400°C). The dependence of the phase transformation of CTSe thin films on the substrate temperature was investigated by X-ray diffraction and transmission electron microscopy analyses. The CTSe films grown at low temperatures ($\leq 350^\circ\text{C}$) crystallized in the monoclinic phase and showed a strong preferential orientation of the (002) plane. The films grown at higher substrate temperatures ($\geq 375^\circ\text{C}$) were randomly oriented with a cubic structure. A slight increase in the optical band gap from 0.84 eV to 0.91 eV was observed as substrate temperature was increased from 325°C to 400°C.

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1. Introduction

Cu-based ternary chalcogenide semiconductors have been investigated owing to their various applications in acousto-optics [1], thermoelectrics [2], and solar cells [3, 4]. In particular, Cu_2SnSe_3 (CTSe) can be used as an absorber in solar cells because of its direct band gap of 0.7-1.7 eV and high absorption coefficient of $\sim 10^4$ - 10^5 cm^{-1} [1, 4, 5]. Also, CTSe is considered to be a precursor material for the growth of $\text{Cu}_2\text{ZnSnSe}_4$ solar cells by a solid-state reaction between CTSe and ZnSe [6]. CTSe compounds have been reported to crystallize in both the cubic (space group $F\bar{4}3m$) [7, 8] and monoclinic (space group Cc) [1, 9] crystal structures. Recently, Skoug et al. [10] reported that a slowly cooled CTSe bulk single crystal had a monoclinic structure, while a water-quenched sample crystallized in the cubic phase. This indicates that the crystal phase of CTSe depends on the growth conditions. However, for CTSe thin films, no detailed investigations have yet been published on the dependence of the phase transformation on the growth temperature. Additionally, band gaps of CTSe nanoparticles with different crystal structures have been investigated. The optical band gaps of monoclinic, cubic, and wurtzite CTSe nanoparticles were estimated to be 1.3 eV, 1.5 eV, and 1.7 eV, respectively [11, 12]. Therefore, the band gap of CTSe may be affected by its crystal structure. Hence, a detailed understanding of the effects of growth conditions on the structural and optical properties of CTSe thin films is essential for the optimization of the thin films for photovoltaic applications.

In this study, we report the effect of the substrate temperature on the phase transformation in CTSe thin films and the dependence of their optical properties on the crystal structure.

2. Experiments

Cu₂SnSe₃ films were grown on soda-lime glass substrates by coevaporation. The beam equivalent pressures of Cu and Sn cells were adjusted to obtain stoichiometric samples grown at different temperatures, whereas the selenium flux was kept constant. During the growth, the sample holder was rotated to retain the uniformity of the samples. The growth temperature of the CTSe films was varied in the range of 325-400°C. The thicknesses of the grown samples were approximately 1 µm. The composition of the CTSe films was estimated by electron probe microanalysis (EPMA) using an acceleration voltage of 15 kV. The EPMA results were reported elsewhere [4]. The crystal structure was studied by X-ray diffraction (XRD) analysis with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) at 45 kV and 300 mA. Bright-field (BF) transmission electron microscopy (TEM) images, their corresponding selected-area electron diffraction (SAED) patterns, and high-resolution TEM (HR-TEM) images of the samples were obtained using a Hitachi H-9000NAR transmission electron microscope with an operating voltage of 300 kV. The optical transmittance and reflectance of the samples were measured at room temperature in the wavelength range of 340-2000 nm using a UV-VIS spectrophotometer (U4000, Hitachi).

3. Results and discussion

Figure 1(a) shows XRD patterns of CTSe thin films grown in the temperature range of 325-400°C. Considerable changes in the crystal structure and texture of CTSe thin films were observed by XRD measurement when the substrate temperature was raised from 325°C to 400°C. At a substrate temperature of 325°C, the peaks at $2\theta = 26.85^\circ$ and 29.55° could be indexed to the (002) and (22 $\bar{1}$) planes of the monoclinic CTSe phase (ICCD no. 00-056-1111), respectively. The diffraction patterns of the thin

films grown at substrate temperatures of 325°C and 350°C show a strong (002) preferential orientation and peaks of secondary phases such as SnSe and/or SnSe₂. The same tendency was observed by Chandra et al. [13]. This oriented films growth is related to the minimization of the surface energy at low growth temperatures [14]. At 375°C and above, the relative intensities of the diffraction peaks are similar to those of the cubic CTSe powder diffraction peaks (ICCD no. 01-089-2879), indicating that there is no preferential orientation of the crystallites. Furthermore, the diffraction peaks of the films grown at higher substrate temperatures (i.e., 375°C and 400°C) can be assigned to the cubic CTSe phase. However, at present, it is not possible to confirm the dependence of the CTSe phase on the substrate temperature owing to the similarity between the major diffraction peaks of cubic and monoclinic CTSe and the existence of secondary phases in the CTSe films. This point will be examined further on the basis of the TEM results in Fig. 2.

The crystalline structure of the CTSe thin films grown at difference substrate temperatures was further confirmed by TEM, HR-TEM, and SAED analysis, as shown in Fig. 2. Figures 2(a) and (d) show cross-sectional TEM images of the thin films grown at 325°C and 400°C, respectively. The film deposited at 325°C showed columnar grain structures, which resulted from the lower energy required for transverse diffusion at the lower substrate temperature during the growth [15]. For the substrate temperature of 400°C, the columnar grains of the thin film change to equiaxial grains. An increase in the grain size was also observed. HR-TEM images obtained in circles in Figs. 2(a) and (d) and their corresponding SAED patterns are presented in Figs. 2(b) and (e) and Figs. 2(c) and (f), respectively. The HR-TEM image (Fig. 2(b)) of the film grown at 325°C reveals a lattice fringe with an interplanar spacing of 3.25 Å, which can be assigned to the ($\bar{1}$ 31) plane of monoclinic

CTSe. The corresponding SAED pattern shows diffraction spots corresponding to the $(1\bar{2}1)$, (012) , and $(\bar{1}31)$ planes of monoclinic CTSe. When the substrate temperature is increased, the HR-TEM image and SAED pattern of the CTSe film indicate changes in the crystal phase from monoclinic to cubic CTSe. The lattice fringe of (111) planes, which can be ascribed to cubic CTSe, can be clearly observed in Fig. 2(e). The SAED pattern of the film grown at 400°C shows sharp diffraction spots corresponding to the $(11\bar{1})$, (200) , and $(1\bar{1}1)$ planes of cubic CTSe. The TEM results are consistent with the XRD measurements and indicate that the monoclinic-to-cubic polymorphic transformation of CTSe thin films is dependent on the substrate temperature. The cubic CTSe phase without any secondary phases was formed at high temperature of 400°C , whereas the monoclinic CTSe phase and secondary phases such as SnSe and SnSe₂ appear below 350°C .

The band gaps of the monoclinic and cubic CTSe thin films were estimated to be 0.84 eV and 0.91 eV, respectively, by extrapolating the linear region of the plot of $(ah\nu)^2$ versus photon energy $(h\nu)$, as shown in Fig. 3. It has been reported that CTSe thin films have a wide range of band gap energies (0.7-1.1 eV) [5, 8, 13]. The band gap of a monoclinic CTSe thin film prepared at 300°C by flash evaporation and then annealed at 400°C was found to be 0.84 eV [13]. On the other hand, the band gap of a cubic CTSe thin film grown at 300°C by coevaporation and then annealed at 450°C was reported to be 0.9 eV [5]. Our experimental values are in good agreement with these reported values. Very recently, it has also been reported that the band gap of CTSe nanocrystals depends on their crystal structure [11]. Hence, the difference in the optical band gap for CTSe thin films is related to changes in the crystal phase.

4. Conclusion

We synthesized CTSe thin films by coevaporation at various substrate temperatures in the range of 325-400°C. XRD and TEM results revealed that CTSe thin films grown at low substrate temperatures have a strong (002) texture with a monoclinic crystal structure, whereas, at high substrate temperatures, CTSe thin films crystallized in the cubic phase without a preferential orientation. The monoclinic-to-cubic polymorphic phase transformation is affected by the substrate temperature during the growth. Optical characterization showed that the optical band gaps of monoclinic (low temperature) and cubic (high temperature) CTSe were 0.84 eV and 0.91 eV, respectively.

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Figure Captions

Figure 1. (a) XRD patterns of CTSe thin films grown at different temperatures and (b) and (c) simulated XRD patterns of cubic (red) and monoclinic (blue) CTSe

Figure 2. Low-resolution TEM images of CTSe thin films grown at (a) 325°C and (d) 400 °C. (b), (e) HR-TEM images and (c), (f) SAED patterns of the region marked with circles in (a) and (d), respectively.

Figure 3. $(\alpha h\nu)^2$ versus $h\nu$ curve for (a) monoclinic and (b) cubic CTSe thin films.