Effect of H$_2$S annealing for CuInS$_2$ thin films prepared by a vacuum evaporation method

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Abstract. Evaporated CuInS$_2$ films using a single-source were annealed in H$_2$S atmosphere from 250 to 400 °C for 60 min. after the evaporation. X-ray diffraction spectra revealed that the films were successfully grown CuInS$_2$ single phase by annealing above 350 °C. We found that composition ratios of Cu, In and S atom were closed to stoichiometry with increasing the annealing temperature, and the ratios of the samples annealed in H$_2$S were closer to stoichiometry than those of the samples annealed in air. Furthermore, the carrier concentration and the resistivity of the films annealed above 375 °C were approximately 1×10$^{18}$ cm$^{-3}$ and 10 $\Omega$cm, respectively, at room temperature.

1. Introduction

Solar cell technologies using I-III-VI$_2$ chalcopyrite semiconductors have made rapid progress in recent years. In particular, CuInGaSe$_2$ (CIGS) based solar cells have been extensively reported in comparison with other chalcopyrite semiconductor based solar cells. Conversion efficiencies for polycrystalline CIGS based solar cells have been significantly improved over recent years and the best cell is now reported at 19.5 % [1]. However, among ternary chalcopyrite semiconductors, CuInS$_2$ may be the most promising material for photovoltaic applications due to the band gap energy of 1.53 eV [2] which perfectly matches the solar spectrum for energy conversion and to its large absorption coefficient above the band gap energy. Furthermore, since the material does not contain toxic Ga or Se atoms, this may have an advantage in comparison with the frequently studied CuInSe$_2$ and CIGS.

In our previous papers [3-5], non-doped and Sb and Bi-doped CuInS$_2$ films using the single-source thermal evaporation method had prepared on glass substrates, and the films were subsequently annealed from 100 to 500 °C in air. We reported that the polycrystalline CuInS$_2$ thin films with other phases were begun to grow by annealing at 200 °C by x-ray diffraction (XRD) measurement.
Furthermore, all samples indicated \( n \)-type conduction due to sulfur vacancy. However \( I - III - VI_2 \) chalcopyrite films, \( \text{CuInSe}_2 \) and \( \text{CIGS} \) films generally indicate \( p \)-type conduction when they use to solar cells [1]. Therefore, the prepared films are annealed in \( \text{H}_2\text{S} \) gas with carrier gas [6] or with sulfur powder in a furnace [7] due to sulfur vacancies in the films have to disappear. In this paper, we report on effect of \( \text{H}_2\text{S} \) annealing for the \( \text{CuInS}_2 \) thin films prepared by the single-source thermal evaporation method using \( \text{CuInS}_2 \) powder grown by a hot-press (HP) method.

2. Experimental procedure

Evaporated \( \text{CuInS}_2 \) thin films were deposited on glass substrates by the single-source thermal evaporation. The starting materials were used the polycrystalline \( \text{CuInS}_2 \) powder grown by the HP method at 700 °C for 1 hour under high pressure at 22.5 MPa from stoichiometric \( \text{Cu}_2\text{S} \) and \( \text{In}_2\text{S}_3 \) powders [8]. After the evaporation, the films were annealed in \( \text{H}_2\text{S} \) gas with \( \text{N}_2 \) carrier gas from 250 to 400 °C for 60 min. The thickness of the films was about 1.4–1.6 \( \mu \)m. The samples were examined by XRD, electron probe microanalysis (EPMA), scanning electron microscopy (SEM), optical transmission measurements and Hall effect measurement.

3. Results and discussion

Figure 1 shows XRD patterns of the samples annealed from 250 °C to 400 °C. By annealing above 250 °C, the samples are dominant one strong peak at 27.8 ° and two weak peaks at 46.6 and 55.1 °. They are well identified with (112) diffraction line for 27.8 °, (204)/(220) diffraction line for 46.6 ° and (116)/(312) diffraction lines for 55.1 ° in comparison with the Joint Committee of Powder Diffraction Standard (JCPDS) card of \( \text{CuInS}_2 \) crystal [9]. The films are strongly oriented to the (112) direction. However, the diffraction peaks for \( \text{CuS} \) phase with \( \text{CIS} \) phase are also appeared the films annealed below 325 °C. \( \text{CuS} \) phase disappears the \( \text{CuInS}_2 \) films annealed in air [3-5]. It is deduced that \( \text{Cu} \) atoms existed in the film surface are reacted to \( \text{S} \) atoms in \( \text{H}_2\text{S} \) gas.

The composition ratios of the \( \text{CuInS}_2 \) films examined by the EPMA are shown in figure 2. The composition ratios of \( \text{Cu}, \text{In} \) and \( \text{S} \) atoms become close to stoichiometry with increasing the annealing temperature, and the ratios of the samples annealed in \( \text{H}_2\text{S} \) are closer to stoichiometry than those of the samples annealed in air. In particularly, the samples annealed at 400 °C indicate slightly In-rich films, 24.5 atm.% for \( \text{Cu} \) atom, 25.2 atm.% for \( \text{In} \) atom and 50.3 atm.% for \( \text{S} \) atoms.

From SEM photographs, the grain size of the film annealed at 325 °C are approximately 0.5–2 \( \mu \)m,

![Figure 1. X-ray diffraction patterns of the evaporated CuInS2 thin films.](image)

![Figure 2. Electron probe microanalysis of the evaporated CuInS2 films. The circles, triangles and squares indicate Cu, In and S, respectively. The dot lines indicate stoichiometric values of each element.](image)
and that annealed at 400 °C is above 1.5 µm, the grain boundary of the sample annealed at 400 °C decreases in comparison with that of the sample annealed at 325 °C. The grain size and roughness of the CuInS$_2$ films annealed at 400 °C are larger than those annealed at 325 °C. The grain size of the films increases with increasing the annealing temperature. The observed grain sizes of the films prepared by this method are almost same as that of the films prepared by sulfurization for a metallic precursor, and the annealing temperature, at 400 °C, of this method is lower than that, at 500 °C, of the sulfurization method [7].

Optical transmittance is measured in the evaporated CuInS$_2$ films annealed above 250 °C. The transmittance of all the films annealed in H$_2$S is lower than that of all the film annealed in air [3-5]. In generally, copper sulfide crystals exist Cu-rich films that do not appear by XRD measurement, the crystals have removed by a cyanide solution [6,7,10]. We, however, did not carry out cyanide treatment due to the remove of the copper sulfide crystals. Therefore, the transmittance may be low due to the metallic copper sulfur crystals existed in these films. The transmittance of the films obtained by annealing above 350 °C drastically changed at approximately 830 nm. The wavelength is near the optical band gap energy of CuInS$_2$ crystal. The transmittance above 830 nm of the samples annealed below 325 °C is particularly lower than that of the samples annealed above 350 °C. It is deduced that the metallic copper sulfide crystals existed in these films.

Hall effect measurement using the Van der Pauw method is carried out in all the samples. The resistivity, mobility and carrier concentration at room temperature for the various annealing temperature are shown in figure 3. The carrier concentrations and the resistivities of the films annealed above 375 °C are approximately 1×10$^{18}$ cm$^{-3}$ and 10 Ω cm, respectively, at room temperature. The carrier concentration and the resistivity of the films decrease and increase, respectively, with increasing the annealing temperature below 350 °C. It is deduced that good crystallinity of the polycrystalline CuInS$_2$ films obtained by increasing the annealing temperature. The mobility of the films annealed above 375 °C is approximately 1 cm$^2$/Vs. The mobility of the films grown by this method is almost same as those of the films prepared by sulfurization method [11].

An absorption coefficient ($\alpha$) of the sample annealed at 400 °C is calculated from the transmission spectra in the wavelength range of 400-1100 nm and the reflectivity is calculated from a refractive index of n = 2.8 [12,13]. The $\alpha$ of the sample is approximately 10$^{4}$ cm$^{-1}$ above optical band gap region. Optical band gap of the sample annealed at 400 °C is evaluated from a plotting of ($\alpha$hv) versus photon energies. Optical band gap of the film annealed at 400 °C is evaluated to be 1.44 eV at room temperature. The value is smaller than those evaluated values of the films prepared by reactive annealing [14] or sulfurization of Cu-In alloys [15].

![Figure 3. Resistivity, mobility and carrier concentration at room temperature of the evaporated CuInS$_2$ films.](image)

![Figure 4. Relationship between ln $\sigma$ and 1/T for the evaporated CuInS$_2$ films annealed in H$_2$S at 400 °C.](image)
From Hall effect measurement using the Van der Pauw method, an activation energy is evaluated from the Arrhenius plot which is shown in figure 4. The activation energy for the film annealed at 400 °C is evaluated to be 24 meV at room temperature. The activation energy may be an acceptor level in CuInS₂ because the sample indicates p-type conduction by the Hall measurement. The acceptor level of 24 meV have already reported by Peza-Tapia et al [16], but they cannot identify the origin. The acceptor level, however, is smaller than that associated to the copper vacancy, other acceptor-like defect in p-CuInS₂, since the reported activation energy for this defect ranges in 100-150 meV interval [17].

4. Conclusion
Effect of H₂S annealing for the CuInS₂ films prepared by a single-source thermal evaporation method was studied. The films were annealed in H₂S atmosphere at from 250 to 400 °C for 60 min. after the evaporation. X-ray diffraction spectra indicated that the films were successfully obtained CuInS₂ single phase by annealing above 350 °C. We found that the composition ratios of Cu, In and S atom were closed to stoichiometry with increasing the annealing temperature. The grain size and roughness of the CuInS₂ films annealed at 400 °C were larger than those annealed at 325 °C. The carrier concentration and the resistivity of the films annealed above 375 °C were approximately 1×10¹⁸ cm⁻³ and 10 Ωcm, respectively, at room temperature. Optical band gap for the film annealed at 400 °C was evaluated to be 1.44 eV at room temperature. The activation energy for the film annealed at 400 °C was evaluated to be 24 meV at room temperature.

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