Structural and Optical Properties of $CuInS_2$ Thin Films Fabricated by Electron-beam Evaporation

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Single phase $CuInS_2$ thin film with the strongest diffraction peak (112) at diffraction angle (2θ) of 27.7° and the second strongest diffraction peak (220) at diffraction angle (2θ) of 46.25° was well made with chalcopyrite structure at substrate temperature of 70℃, annealing temperature of 250℃, annealing time of 60 min. The $CuInS_2$ thin film had the greatest grain size of 1.2 ㎛ when the Cu/In composition ratio of 1.03, where the lattice constant of *a* and *c* were 5.60Å and 11.12Å, respectively. The Cu/In stoichiometry of the single-phase $CuInS_2$ thin films was from 0.84 to 1.3. The film was p-type when the Cu/In ratio was above 0.99 and was n-type when the Cu/In was below 0.96. The fundamental absorption wavelength, absorption coefficient and optical band gap of p-type $CuInS_2$ thin film with Cu/In =1.3 were 837nm, 3.0×10^4 cm^{-1} and 1.48 eV, respectively. The fundamental absorption wavelength, absorption coefficient and optical energy band gap of n-type $CuInS_2$ thin film with Cu/In=0.84 were 821 nm, 6.0×10^4 cm^{-1} and 1.51 eV, respectively.

Keywords: $CuInS_2$, Chalcopyrite structure, Single-phase, Solar cell, Ternary compound

1. INTRODUCTION

The ternary compound $CuInS_2$ has the potential to accept high conversion efficiencies of 27~32 % due to its direct energy band gap of about 1.5 eV lies in the optimum solar energy conversion range[1-3]. But there is a distinct discrepancy between theoretical and actual efficiency of around 12 %. So, it's necessary to develop the fabrication technology of $CuInS_2$ thin film solar cell with higher crystalline quality and conversion efficiency. In particular, the binary Cu-S (Cu_2S, CuS) and In-S (In_2S_3, InS) compound must not be occurred during formation of $CuInS_2$ [4-7].

In this work, we present the successful growth of single phase $CuInS_2$ thin film by EBE (Electron Beam Evaporation) method. $CuInS_2$ thin films were fabricated by annealing in vacuum the stacked layers (Cu/In/S/TCO) deposited by sequence on TCO glass substrate that was well matched with $CuInS_2$ more than soda lime glass. And the structural or optical properties of $CuInS_2$ thin films were analyzed.

2. EXPERIMENTAL

At first, S/In/Cu stacked layers were prepared by sequential EBE of S, In and Cu. For the stoichiometric composition of $CuInS_2$, the thickness of S/In/Cu were 7,500Å, 5,500Å and 2,400Å, respectively. The substrate was SnO_2 coated glass because that was well matched with $CuInS_2$ than ITO glass. The sulfur was well deposited at the substrate temperature of 70℃, and $CuInS_2$ thin films were made by annealing temperature of 50℃~300℃ with annealing time of 30 min~120 min at pressure of 10^{-3} Torr. Table 1 showed sample of $CuInS_2$ thin films by deposition and composition conditions.

Table 1. Samples of $CuInS_2$ thin films by deposition and composition conditions. (all samples annealed at 250℃, 60min)

Sample number	Deposition ratio	Composition ratio
	Cu : In : S	Cu : In : S
C25-60	28 : 22 : 50	27.93 : 22.15 : 49.92
C25-60(s)	28 : 22 : 50	26.49 : 23.47 : 50.04
D25-60	25 : 25 : 50	24.62 : 25.43 : 49.95
D25-60(s)	25 : 25 : 50	25.39 : 24.58 : 50.03
E25-60	22 : 28 : 50	22.93 : 27.11 : 49.96
E25-60(s)	22 : 28 : 50	24.84 : 25.12 : 50.04
H25-60	20 : 20 : 60	26.16 : 23.90 : 49.94
I25-60	18 : 18 : 64	25.08 : 24.90 : 50.02
J25-60	16 : 16 : 68	25.37 : 24.57 : 50.06

In addition to, $CuInS_2$ thin films were fabricated at various composition ratios in order to determine the dependence of absorption coefficient and optical energy band gap on the Cu/In composition condition in room temperature. For the most time, excess S has to be supplied as the several S layers to compensate the compositional shift due to desorption of S during the annealing. The thicker S films were required in the sulfurization of the S/In/Cu stacked layer for the stoichiometric composition. The thickness of $CuInS_2$ thin film was about 1.5㎛ which was enough to obtain absorption coefficient of 1×10^4 cm^{-1}. We analyzed the structural and optical characteristics by XRD (X-Ray Diffraction), SEM (Scanning Electron Microscope), ESCA (Electron Spectroscopy for Chemical Analysis) and UV-Visible Spectro-photometer for energy band gap calculation.

3. RESULTS AND DISCUSSION

3.1 Structural properties

From XRD results, it was found that annealing temperature had considerable effects on the growth of $CuInS_2$ thin films. The multiphase of $CuInS_2$, In_2S_3, Cu_2S, CuS, InS and In were appeared until annealing temperature of 200℃ at all annealing times. The (112) peak of single phase $CuInS_2$ thin film was showed at annealing temperature of 250℃ and annealing time 30 min. Single phase $CuInS_2$ with the highest diffraction peak (112) at diffraction angle (2θ) of 27.7°and the second highest diffraction peak (220) at diffraction angle (2θ) of 46.25°was made well at substrate temperature of 70℃, annealing temperature of 250℃ and annealing time of 60 min. It can be seen that single phase $CuInS_2$ thin film with chalcopyrite structure was well formed at 250℃ and 60 min.

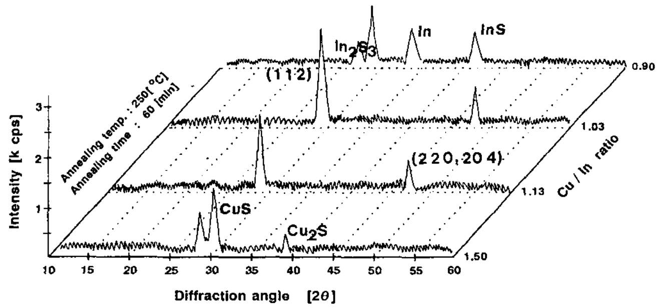
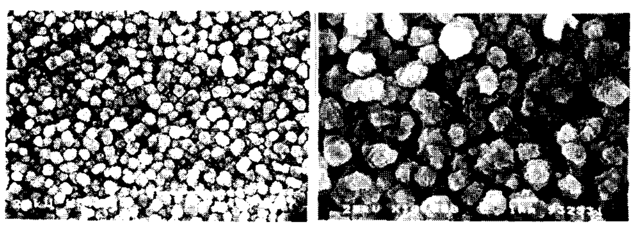


Fig. 1. XRD patterns of $CuInS_2$ thin films by composition ratios.

On the contrary, annealing temperature of 300℃ decreased the (112) intensity of XRD compared with that of 250℃. The peaks of multiphase of $CuInS_2$, In_2S_3, InS, Cu_2S and CuS also appeared under the excess S supply. The (112) peak of single phase of $CuInS_2$ thin film with excess S supply at annealing temperature of 250℃ appeared a little(about 11%) higher than no excess S supply. While, XRD patterns of $CuInS_2$ thin films at various Cu/In composition ratios were shown at Figure 1. Cu/In composition ratios were analyzed by ESCA. When Cu/In composition ratio of 1.03, $CuInS_2$ thin film had the highest peak (112). And Photo 1 showed the surface morphology of the $CuInS_2$ thin film. Its greatest grain size was 1.2 ㎛.



(a) ×5,000 (b) ×10,000

Photo. 1. SEM photograph of $CuInS_2$ thin film at Cu/In composition ratio of 1.03.

In particular, ESCA spectrum of the $CuInS_2$ thin film with Cu/In composition ratio of 1.03 was shown at Figure 2. From the results of XRD and ESCA, we knew that the (112) peaks of single phase $CuInS_2$ thin films were appeared from 0.84 to 1.3 of Cu/In ratio. The conduction types of $CuInS_2$ thin films were measured by hot probe method. We knew that p-type $CuInS_2$ thin films were appeared when the Cu/In ratio was above 0.99. When the Cu/In composition ratio was below 0.99, conduction types of $CuInS_2$ thin films were n-type. From extrapolation with Miller index, Bragg condition equation and Nelson-Riley correction equation, lattice constant of $CuInS_2$ thin film was a=5.6 Å and c=11.12 Å, respectively.

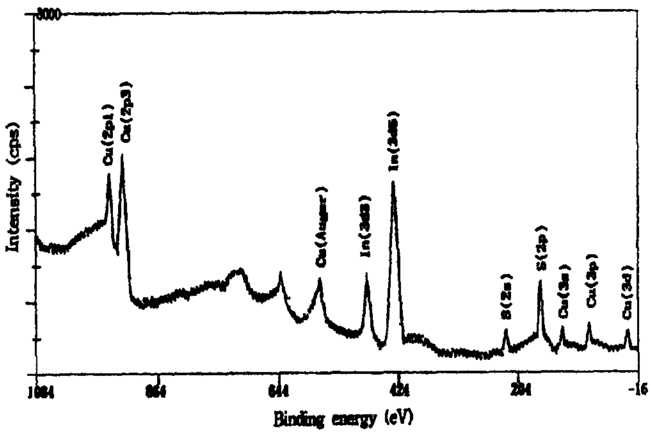


Fig. 2. ESCA spectrum of $CuInS_2$ thin film at annealing temperature of 250℃.

3.2 Optical properties

The optical absorption spectra of $CuInS_2$ thin films with chalcopyrite structure by Cu/In composition ratios were shown at Fig. 3 at room temperature. The fundamental absorption wavelength and the absorption coefficient of p-type $CuInS_2$ thin film with Cu/In composition ratio of 1.3 was 837 nm and 3.0×10^4 cm^{-1}, respectively. When Cu/In composition ratio was 0.99, the fundamental absorption wavelength and the absorption coefficient of p-type $CuInS_2$ thin film was 810 nm and 9.6×10^4 cm^{-1}, respectively.

We know that the fundamental absorption band moved onto the short wavelength and the absorption coefficient increased at lower Cu/In ratio. In this case, we concluded that decrease of relative defect density made grain size smaller and at last energy band gap larger.

While, when the Cu/In composition ratio of below 0.96, the fundamental absorption of n-type $CuInS_2$ thin film moved onto the longer wavelength and the absorption coefficient decreased than that of 0.99. The fundamental absorption wavelength and the absorption coefficient of n-type $CuInS_2$ thin film with Cu/In composition ratio of 0.96 was 832 nm and 7.2×10^4 cm^{-1}, respectively.

When Cu/In composition ratio was 0.84, the fundamental absorption wavelength and the absorption coefficient of n-type $CuInS_2$ thin film was 821 nm and 3.2×10^4 cm^{-1}, respectively. Fig. 4 showed plots of $(\alpha h\nu)^2$ versus the incident photon $h\nu$ for $CuInS_2$ thin

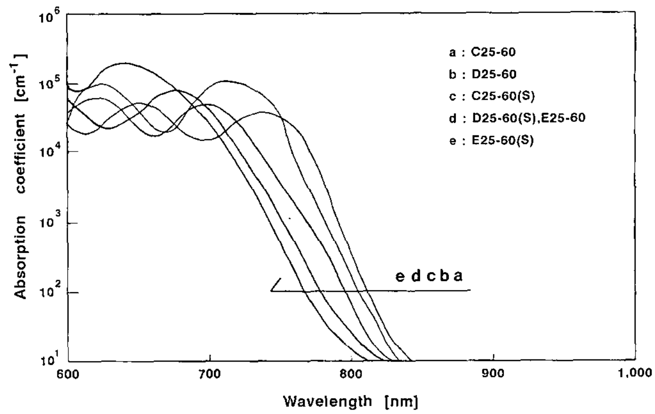


Fig. 3. Optical absorbance spectra of $CuInS_2$ thin films by Cu/In ratios.

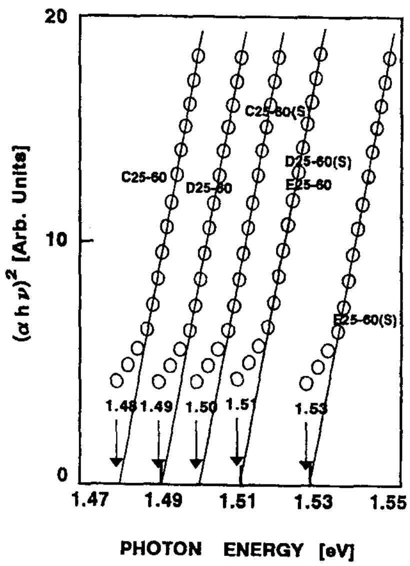


Fig. 4. Plots of $(\alpha h\nu)^2$ versus the incident photon $h\nu$ for $CuInS_2$ thin films by Cu/In ratios.

films at various Cu/In ratios by extrapolation mdhods for getting energy band gap.

Figure 5 showed optical energy band gaps of $CuInS_2$ thin film by Cu/In ratio. Energy band gap of p-type $CuInS_2$ was 1.48 eV ~ 1.53 eV under the Cu/In ratio of 1.3 ~ 0.99. We knew that the lower Cu/In ratio was, the higher absorption coefficient and optical energy band gap were. We can explain this situation from screening length effect by free carrier and ionized dopant. On the contrary, energy band gap of n-type $CuInS_2$ was 1.49 eV and 1.51 eV at Cu/In ratio of 0.96 and 0.84, respectively. We knew that the lower Cu/In ratio was, the lower absorption coefficient of n-type $CuInS_2$ were. And we knew that the band gap of n-type $CuInS_2$ increased owing to the increase of electron density.

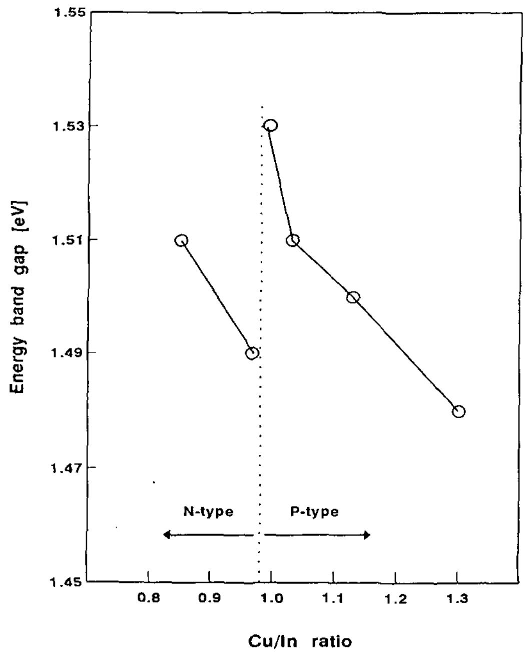


Fig. 5. Optical energy band gap of $CuInS_2$ thin films by Cu/In composition ratio.

4. CONCLUSION

Single phase $CuInS_2$ with the highest peak (112) at diffraction angle (2θ) of 27.7° and the second peak (220) at diffraction angle (2θ) of 46.25° was well fabricated at substrate temperature of 70℃, annealing temperature of 250℃ and annealing time of 60 min. Single-phase $CuInS_2$ thin films were realized from Cu/In composition ratio of 0.84~1.3. P-type $CuInS_2$ thin films were appeared at only over Cu/In composition ratio of 0.99. When Cu/In composition ratio was below 0.96, conduction types of $CuInS_2$ thin films were n-type. And the optical energy band gap of p-type $CuInS_2$ thin film was 1.48 eV~1.53 eV under the Cu/In ratio of 1.3~0.99. Also energy band gap of n-type $CuInS_2$ was 1.49 eV and 1.51 eV at Cu/In ratio of 0.96 and 0.84, respectively.

We found that the polycrystalline p-type $CuInS_2$ thin films were well made at these conditions were appropriate for absorber layer of solar cell from structural and optical properties.

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