전자빔 증착으로 제조한 $CuInS_2$ 박막의 구조적 및 광학적 특성

Structural and optical properties of $CuInS_2$ thin films fabricated by electron-beam evaporation

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Abstract

Single phase $CuInS_2$ thin film 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 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 ㎛ and Cu/In composition ratio of 1.03. Lattice constant of a and c of that $CuInS_2$ thin film was 5.60 Å and 11.12 Å respectively. Single phase $CuInS_2$ thin films were accepted from Cu/In composition ratio of 0.84 to 1.3. P-type $CuInS_2$ thin films were appeared at over Cu/In composition ratio of 0.99. Under Cu/In composition ratio of 0.96, conduction types of $CuInS_2$ thin films were n-type. Also, fundamental absorption wavelength, the absorption coefficient and optical energy band gap of p-type $CuInS_2$ thin film with Cu/In composition ratio of 1.3 was 837 nm, 3.0×104 cm^{-1} and 1.48 eV respectively. When Cu/In composition ratio was 0.84, fundamental absorption wavelength, the absorption coefficient and optical energy band gap of n-type $CuInS_2$ thin film was 821 nm, 6.0×10^4 cm^{-1} and 1.51 eV respectively.

Key Words : $CuInS_2$, 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 range solar energy conversion. But there is a distinct discrepancy between theoretical and actual efficiency of around 12 %. So, it's necessary to grow the thin film technology of $CuInS_2$ with high crystalline quality for solar cell with higher 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 $CuInS_2$.

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 which was well matched with $CuInS_2$ more than sodalime glass. And the structural and optical properties of $CuInS_2$ thin films were analyzed.

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2. Experiment

At first, S/In/Cu stacked layers were prepared by sequential EBE of S, In and Cu with thickness of 7,50C Å, 5,500 Å and 2,400 Å respectively for stoichiometric composition of $CuInS_2$ *on TCO (TCO was* SnO_2 glass well matched with $CuInS_2$ than ITO glass) substrate at 10^{-6} Torr. At this time, the sulfur was well deposited at the substrate temperature of 70 ℃, And $CuInS_2$ thin films were made by annealing temperature of 50 ℃ ~300 ℃ and annealing time 30 min~120 min at vacuum 10^{-3} Torr of the stacked layers. Table 1 showed sample numbers of $CuInS_2$ thin films by annealing, deposition and composition conditions.

Table 1. Sample number 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 dependance of the room temperature absorption coefficient and optical energy band gap on the Cu/In composition condition. At some time, in the sulfurization of the S/In/Cu stacked layer, to compensate the compositional shift due to desorption of S during the annealing, excess S has to be supplied as the S layer several times thicker than required for the stoichiometric composition. The thickness of $CuInS_2$ thin film was about 1.5㎛ which was enough to obtain 1×10^4 cm^{-1} of absorption coefficient. Structural and optical characteristics were analyzed by X-Ray Diffraction(XRD), Scanning Electron Microscope(SEM), Electron Spectroscopy for Chemical Analysis(ESCA), UV-Visible Spectrometer and computer system for energy band gap calculation.

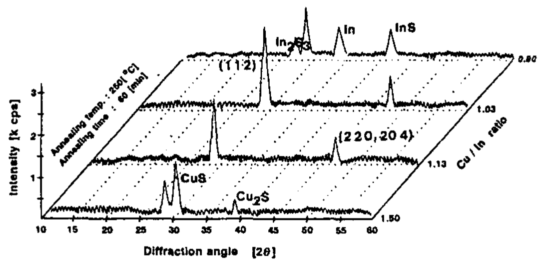

Fig. 1. XRD patterns of $CuInS_2$ thin films by composition ratios.

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. On the contrary, annealing temperature of 300 ℃ decreased the (112) intensity of XRD compared with of 250 ℃. And the peaks of multiphases of $CuInS_2$, In_2S_3, InS, Cu_2S and CuS also appeared until 200 ℃ with excess S supply. The (112) peak of single phase of $CuInS_2$ thin film at annealing temperature of 250 ℃ with excess S supply 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, the highest peak (112) of $CuInS_2$ thin film was accepted. And at that time, SEM photograph of Photo. 1 showed the surface morphology of the thin film. Its greatest grain size was 1.2 μm.

In particular, ESCA spectrum of the fabricated $CuInS_2$ thin film by 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 of $CuInS_2$ thin films were appeared from 0.84 to 1.3 of Cu/In ratio. And conductive types of $CuInS_2$ thin films were accepted by hot probe method. We knew that p-type $CuInS_2$ thin films were appeared over Cu/In of 0.99. Under Cu/In composition ratio of 0.96, 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 a and c of that $CuInS_2$ thin film was accepted as 5.6 Å and 11.12 Å respectively.

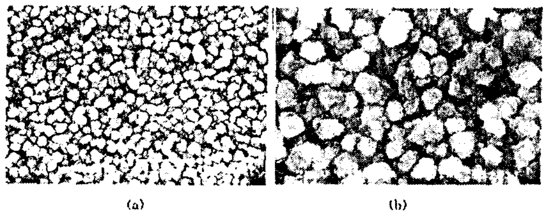

Photo. 1. SEM photograph of $CuInS_2$ thin film at Cu/In composition ratio of 1.03.

3.2 Optical properties

The optical absorption spectra of $CuInS_2$ thin films with chalcopyrite structure at room temperature by Cu/In composition ratios were shown at Figure 3. 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.

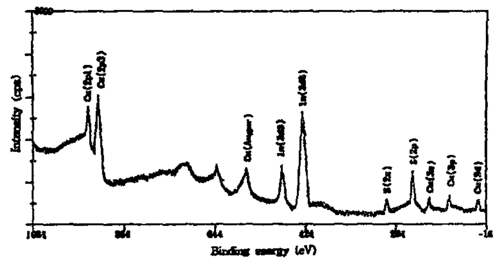

Fig. 2. ESCA spectrum of $CuInS_2$ thin film at annealing temperature of 250 ℃.

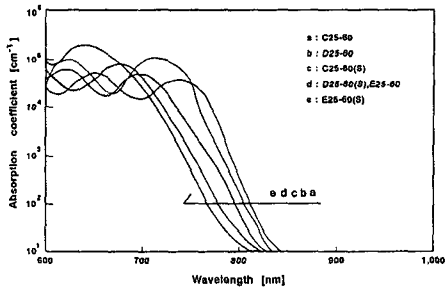

Fig. 3. Optical absorbance spectra of $CuInS_2$ thin films by Cu/In ratios.

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

While, under Cu/In composition ratio of 0.96, we knew that because electron carrier was increased, the lower Cu/In ratio was, the fundamental absorption of n-type $CuInS_2$ thin film moved onto the longer wavelength and the absorption coefficient decreased than 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 films at various Cu/In ratios by extrapolation methods for getting energy band gap.

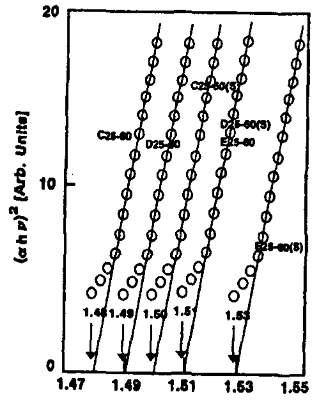

Fig. 4. Plots of $(\alpha h\nu)^2$ versus the incident photon $h\nu$ for $CuInS_2$ thin films by Cu/In ratios.

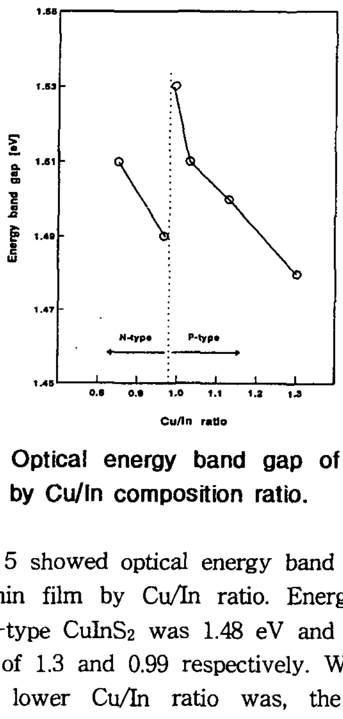

Fig. 5. Optical energy band gap of $CuInS_2$ thin films by Cu/In composition ratio.

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 and 1.53 eV at Cu/In of 1.3 and 0.99 respectively. 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 of 0.96 and 0.84 respectively. We knew that the lower Cu/In ratio was, the lower absorption coefficient and optical energy band gap of n-type $CuInS_2$ were. And we knew that the band gap increase of n-type $CuInS_2$ occurred from electron density increase.

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 accepted from Cu/In composition ratio of 0.84 to 1.3. p-type $CuInS_2$ thin films were appeared at only over Cu/In composition ratio of 0.99. Under Cu/In composition ratio of 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 with Cu/In of 1.3 and 0.99 was 1.48 eV and 1.53 eV respectively. Also energy band gap of n-type $CuInS_2$ was 1.49 eV and 1.51 eV at Cu/In 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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