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SEL 법으로 제조된 $CuInS_2$ 화합물 반도체 박막의 전기적 특성

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Abstract

Single phase $CuInS_2$ thin film with a highest diffraction peak (112) at a diffraction angle (2Θ) of 27.7° was well made by SEL method at annealing temperature of 250 ℃ and annealing hour of 60 min in vacuum of 10^{-3} Torr or in S ambience for an hour. And the peak of diffraction intensity at miller index (112) of $CuInS_2$ thin film annealed in S ambience was shown a little higher about 11 % than in only vacuum. Single phase $CuInS_2$ thin films were appeared from 0.85 to 1.26 of Cu/In composition ratio and sulfur composition ratios of $CuInS_2$ thin films fabricated in S ambience were all over 50 atom%. Also when Cu/In composition ratio was 1.03, $CuInS_2$ thin film with chalcopyrite structure had the highest XRD peak (112).

And lattice constant a and grain size of the thin film in S ambience were appeared a little larger than those in only vacuum. The largest lattice constant of a and grain size of $CuInS_2$ thin film in S ambience was 5.63 Å and 1.2 ㎛ respectively. And the films in S ambience were all p-conduction type with resistivities of around 10^{-1} Ω cm.

Keywords: $CuInS_2$ thin film, SEL, S ambience, Lattice constant, Resistivity

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. But there is a distinct discrepancy between theoretical and actual efficiency of around 12 %. So, it's necessary to grow $CuInS_2$ thin film with good crystalline quality for solar cell with higher efficiency.

Recently, various techniques are reported for the preparation of $CuInS_2$ thin films such as elemental co-evaporation, sputtering and electro-deposition. For a commercial process, the fabrication of $CuInS_2$ thin films over large areas with good reproducible optical semiconductor properties is essential. And it becomes necessary to produce good $CuInS_2$ thin films through a low-cost, eco-friendly and easily scalable process for mass production of films for PV applications.

The production of $CuInS_2$ thin film from the Stacked Elemental layers (SEL) is a very promising method since good control of the individual material and film uniformity could be achieved over a large area compared with the co-evaporation technique. However, the problem which has hindered development of this technique was the poor quality crystalline structures obtained by vacuum annealing of the films.

In this work, we present the successful growth of single phase $CuInS_2$ thin film by Electron Beam Evaporation (EBE) method. $CuInS_2$ thin films were fabricated by annealing in vacuum the SEL of S/In/Cu deposited on slide glass substrate by sequence. In additions, to compensate the compositional shift due to desorption of S during the annealing of S/In/Cu stacked layer, SEL were post-annealed under a sulfur ambience. Also, In order to accept optimum conditions of single phase $CuInS_2$ formation for good photovoltaic devices, structural and electrical characteristics were studied.

2. Experiment

$CuInS_2$ thin films were made on substrate slide glasses by annealing of S/In/Cu stacked layers which were deposited sequentially with optimum substrate temperature of 70 ℃. At this time, S/In/Cu stacked layers were prepared by sequential EBE of S, In, Cu with thickness of 7,500 Å, 5,500 Å and 2,400 Å respectively for stoichiometric composition of $CuInS_2$ thin films on sodalime slide substrate glass at 10^{-6} Torr. and the SEL were annealed at temperature ranging from 50 ℃ to 350 ℃ in vacuum of 10^{-3} Torr or in S ambience for an hour. S ambience was prepared by excess sulfur supplement at 5 Å/s rate in qurtz tube to compensate the compositional shift due to desorption of sulfur during annealing.

The thickness of $CuInS_2$ thin film was about 1.5 ㎛ which was enough to obtain $1 \times 10^4 cm^{-1}$ of absorption coefficient.

Micro-structural studies were carried out by XRD (D/MAX-1200, Rigaku Co.) and SEM (JSM-5400, Jeol Co.). Composition ratio was analyzed by ESCA (SSX-100, Surface Science Instrument Co.). Electrical properties were measured by Hall Effect Measurement System (HL5500PC, Accent Optical Technology Ltd.).

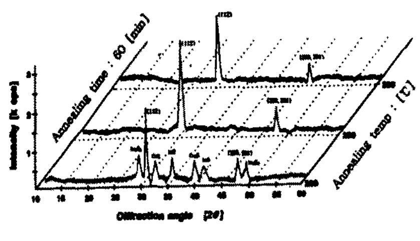
3. Results and Discussion

3.1 Structural characteristic

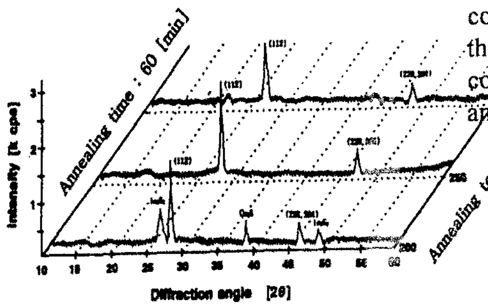
From XRD results of Fig. 1(a) for crystal structure, it was found that the peaks of multiphases of $CuInS_2$, In_2S_3 and Cu_2S appeared at annealing temperature of 200 ℃. The highest (112) peak of single $CuInS_2$ thin film was showed at annealing temperature of 250 ℃. Single phase $CuInS_2$ with the diffraction peak (112) at diffraction angle (2Θ) of 27.7° and the 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 250 ℃. So, we can say these annealing temperature of 250 ℃ and annealing time of 60 min as optimum annealing conditions.

And Fig. 1(b) showed the XRD results of thin films annealed in S ambience at various temperatures. The peaks of multi-phases of $CuInS_2$, In_2S_3, InS, Cu_2S and CuS appeared at annealing temperature of 200 ℃ in S ambience. The (112) peak of single phase of $CuInS_2$ thin film at annealing temperature of 250 ℃ and annealing time of 60 min in S ambience appeared a little(about 11%) higher than in only vacuum.

While, XRD patterns of $CuInS_2$ thin films at various Cu/In composition ratios were shown at Figure 2. When Cu/In composition ratio was 1.03, $CuInS_2$ thin film had the highest peak (112).



(a)



(b)

Fig. 1. XRD patterns of $CuInS_2$ thin films by annealing temperature. (a) in vacuum, (b) in S ambience)

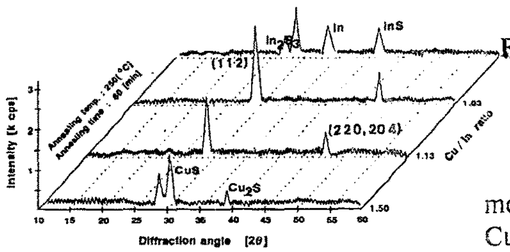


Fig. 2. XRD patterns of $CuInS_2$ thin films by Cu/In composition ratio.

In particular, ESCA spectrum of the $CuInS_2$ thin film with Cu/In composition ratio of 1.03 was shown at Figure 3. From the results of XRD and ESCA, we knew that the (112) peaks of single phase $CuInS_2$ thin films were appeared from 0.85 to 1.26 of Cu/In ratio and sulfur composition ratios of $CuInS_2$ thin films fabricated in S ambience were all over 50 atom% .

Fig. 3. ESCA spectrum of $CuInS_2$ thin film with Cu/In composition ratio of 1.03.

From extrapolation with Miller index of XRD results, Bragg condition equation and Nelson-Riley correction equation, we could accept lattice constant of a $CuInS_2$ thin film as like Fig. 4. The largest lattice constant of a $CuInS_2$ thin film in S ambience was 5.63 Å.

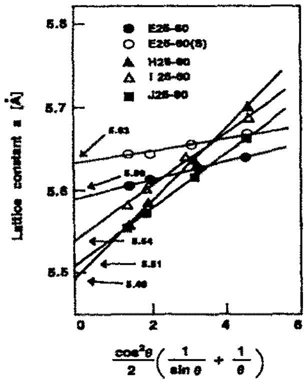
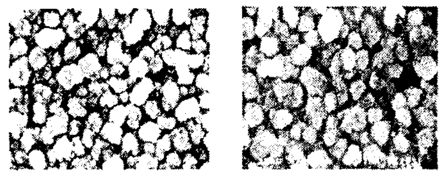


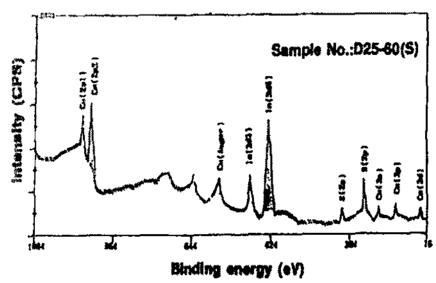
Fig. 4. Lattice constant a $CuInS_2$ thin films by composition ratio.

And Photo 1 showed the surface morphology of the $CuInS_2$ thin film at Cu/In composition ratio of 1.03. we knew that the largest grain size of $CuInS_2$ thin film in S ambience was 1.2 ㎛.



(a) (b)

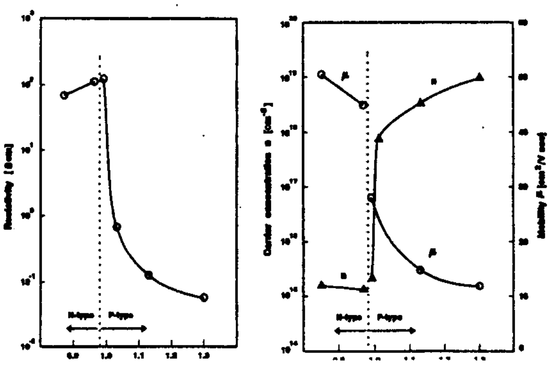
Photo. 1. SEM photograph of $CuInS_2$ thin film at Cu/In composition ratio of 1.03. (×10,000, (a) in vacuum, (b) in S



ambience)

3.2 Electrical characteristic

Table 2 showed electrical characteristics of fabricated single phase $CuInS_2$ thin films by composition ratio. Fig 5(a) represented conduction types and resistivities and Fig. 5(b) showed carrier concentrations and mobilities obtained from Hall Effect analyses to convince the variety of resistivities of the $CuInS_2$ thin films. We knew that p-type $CuInS_2$ thin films were appeared when the Cu/In ratio was above 0.99, and their resistivities were around 0.05 through 0.99 Ω㎝. But when the Cu/In composition ratio was below 0.96, conduction types of $CuInS_2$ thin films were n-type, and their resistivities were around 80 through 100 Ω㎝. And $CuInS_2$ thin films annealed in S ambience were all p-conduction type with resistivities of around 10^{-1} Ω㎝. Also, from results of Fig. 5(a) and Fig. 5(b), the varieties of resistivities were well corresponded with varieties of carrier concentrations and mobilities.



(a) (b)

Fig. 5. Electrical characteristics of $CuInS_2$ thin films by composition ratio.
((a) resistivities, (b) carrier concentrations and mobilities)

4. Conclusion

Single phase $CuInS_2$ thin film with chalcopyrite structure had 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.

And the peak of diffraction intensity at miller index (112) of $CuInS_2$ thin film annealed in S ambience was shown a little higher about 11 % than in only vacuum of 10^{-3} Torr. Also, lattice constant of a and grain size of the film in S ambience were appeared a little larger than those in only vacuum.

Sulfur composition ratios of $CuInS_2$ thin films fabricated in S ambience were all over 50 atom%. And the films in S ambience were all p-conduction type with resistivities of around 10^{-1} Ω㎝.

We found that the polycrystalline p-type $CuInS_2$ thin film was well made in S ambience than in only vacuum.

Acknowledgements

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