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전자빔 증착기로 제조된 $CuInS_2$박막의 전기적,구조적 특성

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Electrical and Structural Properties of $CuInS_2$ thin films fabricated by EBE (Electrical Beam Evaporator) Method

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Abstract : Ternary chalcopyrite $CuInS_2$ thin film material is very promising for photovoltaic. Power generation because of its excellent optical and semiconductor properties, $CuInS_2$ thin films were performed from S/In/Cu/SLG stacked elemental layer (SEL) method with post annealing treatment. $CuInS_2$ thin films were appeared from 0.84 to 1.27 of Cu/In composition ratio and sulfur composition ratios of $CuInS_2$ thin films fabricated. Analysis of the optical energy band gap of $CuInS_2$ value of 1.5eV interior and exterior.

Key Words : $CuInS_2$, thin film, ternary compound,

1. 서 론

The ternary Compound Copper Indium disulfide ($CuInS_2$) with band gap of about 1.5eV and a large absorption coefficient which are well suited for the photovoltaic conversion of Solar energy.

But there is a distinct discrepancy between theoretical and actual efficiency of around 12%. Also the ability to deposit thin films of $CuInS_2$ on many substrates is an added advantage to produce efficient photoelectron for solar cell and other optoelectronic devices.

The decisive requirements for the efficient performance of these devices are compositional uniformity and crystalline.

The production of $CuInS_2$ thin film 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 Com-pared 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 stacked layer, SEL were post annealed under a sulfur ambience. Also, In order to accept optimum conditions of single phase $CuInS_2$ formation of good photovoltaic device, structural, electrical characteristics were studied.

2. 실 험

$CuInS_2$ thin films were deposited by stepwise flash evaporation at a base pressure of $\sim 2\times10^{-5}$ torr. A short electrical pulse to a relay to which a feeder was attached, ensured that the material into the tungsten boat and molybdenum boat in steps.

Uniformity in the grain size of the powdered material ensured constant amount of fall in each step.

Films were grown onto cleaned glass substrates held at different temperatures. We used $CuInS_2$ layers deposited on a soda-lime-glass sample, by annealing of S/In/Cu stacked layers which were deposited sequentially with optimum substrate temperature of 70℃.

The stacked element layer structure with total thickness of 1.5㎛ was obtained by sequential deposition of the elemental layers on soda-lime-glass substrates maintained at room temperature.

At this time, SLG/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 soda-lime-glass at 10^{-5} Torr. The thickness of $CuInS_2$ thin film was about 1.5㎛ which was enough to obtain 1×10^4 cm^{-1} of absorption coefficient. Micro-structural studies were carried out by XRD (D/MAX-1200, Rigaku Co.) and SEM (JSM-5400, Jeol Co.). Electrical properties were measured by Hall Effect Measurement System (HL5500PC, Accent Optical Technology Ltd.).

3. 결과 및 검토

3.1 Structural Characteristic

Table 1.described sample numbers of $CuInS_2$ thin films by initial deposition ratios and Composition ratio after accepted from EDAX analyses in particular, EDAX analysis of the $CuInS_2$ thin films with Cu/In composition ratio of 1.27 was shown at Figure.

From the results of XRD, We know that the (112) peaks of single phase $CuInS_2$ thin films were appeared from 0.84 to 1.27 of Cu/In ratio and sulfur composition ratios of $CuInS_2$ thin films fabricated in S ambience were all over 50 atom%.

The Corresponding XRD traces of the above films are shown in Fig.1. Fig.1 shows the XRD spectrum of these $CuInS_2$ films which showed crystalline nature with reflection from(112)(220) and (204) planes. It may be observed that the peak intensity increased with the increasing annealing temperature.

Table 1. Grain boundary Parameters for $CuInS_2$ films. Δy(non-stoichiometry) (s) sulfurization

Sample No.	Type	Cu/In	Δy	Carrier Con [cm^{-3}]	Mobility [㎠/Vsec]	Resistivity [Ωcm]	Hall Coefficient
C25-60	P	1.27	0.05	9.4×10^{18}	11.88	5.6×10^{-2}	6.7×10^{-2}
D25-60	N	0.97	-0.01	1.3×10^{15}	44.80	1.0×10^{-1}	-4.7×10^{-2}
E25-60	N	0.84	-0.04	1.5×10^{15}	50.46	8.0×10^{1}	-4.1×10^{-2}
H25-60	P	1.09	0.02	1.0×10^{18}	8.91	6.7×10^{-1}	5.6×10^{-2}
I25-60	P	1.01	0.002	1.6×10^{18}	30.91	1.2×10^{-1}	3.9×10^{-2}
J25-60	p	1.03	0.01	7.6×10^{17}	14.80	5.6×10^{-1}	8.3×10^{-2}
Sample No.	Type	Cu/In	Δy	Carrier Con [cm^{-3}]	Mobility [㎠/Vsec]	Resistivity [Ωcm]	Hall Coefficient
Cs25-60	P	1.13	0.03	3.4×10^{18}	14.80	1.3×10^{-1}	1.9×10^{0}
Ds25-60	P	1.03	-0.009	7.5×10^{17}	12.46	6.7×10^{-1}	8.3×10^{0}
Es25-60	p	0.99	-0.001	2.1×10^{15}	28.10	1.1×10^{2}	3.0×10^{3}

From XRD results of Fig. 1(a) for crystal structure, it was found that the peak 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 angle (2Θ) of 46.25° was made well at substrate temperature of 70℃, annealing temperature of 250℃ and annealing time of 60min.

It can be seen that single phase $CuInS_2$thin film with chalcopyrite structure was 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 60min as optimum annealing conditions.

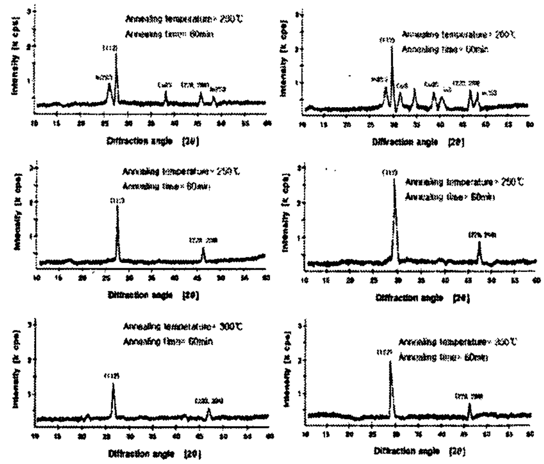

Fig.1. XRD spectrum of $CuInS_2$ thin films by annealing temperature. ((a) vacuum, (b) sulfurization)

And Fig.1(b) showed the XRD results of thin films annealed in S ambience at various temperatures. The XRD spectra peak spuctrum of multi-phases of $CuInS_2$, In_2S_3, InS, Cu_2S and CuS appeared at an-nealing temperature of 200℃ in S ambience.

The (112) XRD peak spuctrum of single phase of $CuInS_2$ thin films at annealing temperature of 250℃ and annealing time of 60 min in S ambience appeared a little (about 11%) higher than in only Vacuum.

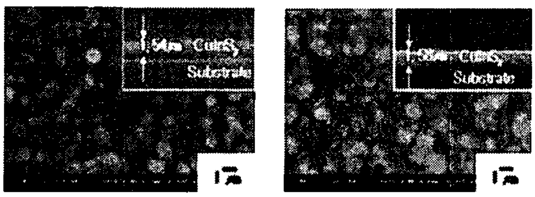

Fig.2 SEM photograph of $CuInS_2$ thin film at Cu/In composition ratio of 1.03.
(×10,000, (a) vacuum, (b) Sulfurization)

3.2 Electrical characteristic

We know 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 though 0.99Ωcm.

But when the Cu/In composition ratio was below 0.97, Conduction types of $CuInS_2$ thin films were n-type, and their resistivities were around 80 though 100Ωcm. And $CuInS_2$ thin films annealed in S ambi-ence were all p-conduction type with resistivities of around 10^{-1} Ωcm. The nature of the charge carriers was seen to be determined (Table 1) by the relative amount of In and sulphur in the films.

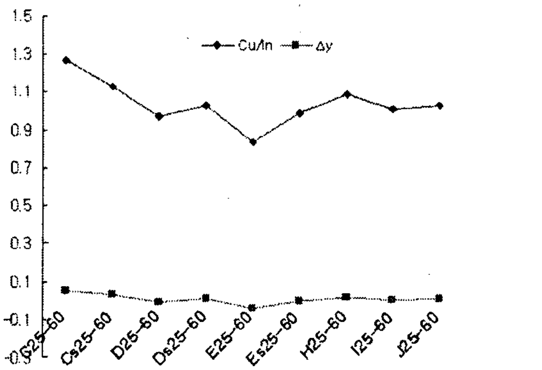

Fig.3 Electrical properties of $CuInS_2$ films formed at 300k having different Cu/In ratio

In-rich films showed n-type conductivity while sulphur-rich rich films showed p-type conductivity. The compositional deviations from the ideal chemical formula for $CuInS_2$ material can be conveniently described by non-molecularity (Δx=[Cu/In]-1) and non-stoichiometry (Δy= [{2S/(Cu+3In)}-1]).

The variation of Δx would lead to the formation of equal number of doner and accepters and the films would behave like a compensated material. The Δy parameter is related to the electronic defects and would determine the type of the majority charge carriers.

Films with $\Delta y > 0$ would behave as p-type material while $\Delta y < 0$ would show n-type conductivity. Dependence of non-stochiometry (Δy) on the carrier type was also apparent(Table 1.) in our films.

4. 결 론

These studies have evaluated a detailed reaction mechanism leading to the formation of $CuInS_2$ from vacuum annealed Cu, In and S elemental layers by the SEL technique. The reaction model was established as follows

(a) The XRD analysis of binary and ternary compound formation at different annealing temperature and time, it could be seen that at low temperatures, binary phase of mainly Cu_2S and In_2S are formed. Various phase transformations occur as the annealing temperature increases.

(b) Single phase $CuInS_2$ thin films were prepared with chalcopyrite structure had the highest peak (112) at diffraction angel (2Θ) of 27.7 and the second peak (220) at diffraction angel (2Θ) of 46.25 was well fabricated at substrate temperature of 70 ℃, annealing temperature of 250℃ and annealing time of 60 min

(c) 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-type with resistivities of around 10^{-1}Ωcm.

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