

CuInSe₂ 박막의 구조적 전기적 특성

김영준, 양현훈, 정운조, 박계춘
목포대학교 전기공학과

Structural and Electrical Properties of CuInSe₂ Ternary Compound Thin Film

Young-Jun Kim, Hyeun-Hun Yang, Woon-Jo Jeong, Gye-Choon Park
Dept. of Elect. Eng., Mokpo National University, muan, Chonnam, 453-729, Republic of Korea
e-mail: yjunk@mail.dongac.ac.kr

Abstract - Process variables for manufacturing the CuInSe₂ thin film were established in order to clarify optimum conditions for growth of the thin film depending upon process conditions (substrate temperature, sputtering pressure, DC/RF Power), and then by changing a number of vapor deposition conditions and Annealing conditions variously, structural and electrical characteristics were measured. Thereby, optimum process variables were derived.

For the manufacture of the CuInSe₂, Cu, In and Se were vapor-deposited in the named order. Among them, Cu and In were vapor-deposited by using the sputtering method in consideration of their adhesive force to the substrate, and the DC/RF power was controlled so that the composition of Cu and In might be 1 : 1, while the surface temperature having an effect on the quality of the thin film was changed from 100[°C] to 300[°C] at intervals of 50[°C].

1. Introduction

Looking into the global status of developing the solar cell of the Cu-III-V family, it can be known that the solar cell based on CuInSe₂ has demonstrated the highest efficiency so far, as shown in the references.

Studies on a tandem type of the ternary compound of the Cu-III-V family are little conducted. This study is to manufacture the CuInSe₂ compound thin film of n-type as a program for developing the leading technology for manufacturing a tandem type of the solar cell of the Cu-III-V family which enables a high efficiency of 22[%] or higher to be accomplished by using only the ternary compound semiconductor thin film of the Cu-III-V family as manufactured by the SEL method which enables it to be manufactured at a low cost through the much simpler process than the process for manufacturing a quaternary or pentad compound to absorb a spectrum across the wide wavelength zone of the solar light in each unit lamination layer.

2. Experiment

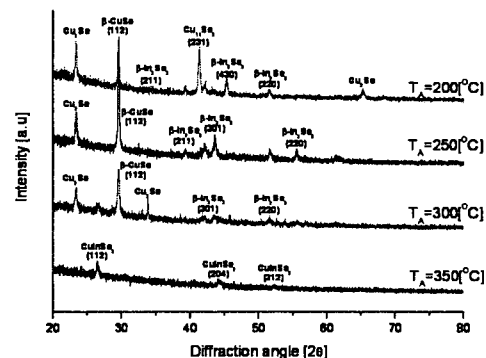
In this experiment for manufacturing the CuInSe₂ ternary compound thin film, deposition was conducted by using the sputtering method and the evaporation method, and the Annealing was used in the electric furnace, and thereby, we intended to get a single-phase compound thin film. Thus, optimum process variables were derived by varying several deposition factors and heat treatment conditions differently and then measuring structural and electrical characteristics depending upon such variation.

In this experiment, Cu and In were deposited by using the sputtering method enabling us to expect the stronger adhesive force with a substrate, while Se was deposited by using the thermal evaporation method because its low melting point prevents sputtering from being available. Since the sputtering rate and the electric conductivity of Cu is high, the DC sputtering method was used for deposition thereof. Meanwhile, for deposition of In, the RF sputtering method was used so that more stable sputtering might be available. Also, the sputtering rate depending upon the DC/RF power was controlled so that the composition ratio of Cu versus In might be around 1 : 1, and the substrate temperature affecting greatly the quality of the thin film was varied in the range of 100[°C] to 300[°C] at intervals of 50[°C].

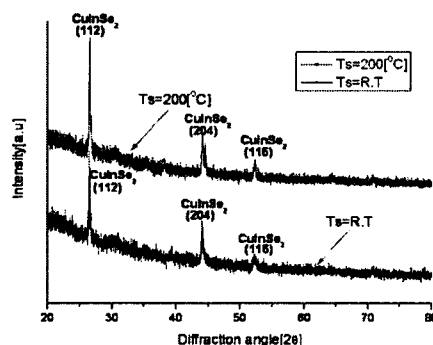
3. Results and Discussion

3.1 Crystallographic Characteristics of CuInSe₂

The diffract fringe of X-ray, which depended upon the substrate temperature and the heat treatment temperature of the manufactured CuInSe₂ thin film, was investigated. Fig. 1 represents a case that a sample manufactured at the substrate temperature of 100[°C] was thermally treated at 200[°C]-350[°C]. Until the heat treatment temperature got to be 300[°C], second-order phases of Cu₂Se, Cu₁₁In₉, β-CuSe and β-In₂Se₃ appeared, and at the heat treatment temperature of 350[°C], such second-order phases disappeared and only the single phase of CuInSe₂ was observed. At the low heat treatment temperature of 200[°C], the phase of Cu₁₁In₉, an excess of Cu appeared, and at the heat treatment temperature of 250[°C] or higher, such phase, an excess of Cu disappeared, and second-order phases of β-In₂Se₃ and the like appeared. This variation is well consistent with the variation of the surface configuration at the heat treatment of 250[°C]. Such second-order phases did not appear at the heat treatment temperature of 350[°C]. In order to investigate this phenomenon more particularly, all of the samples as manufactured at different substrate temperatures were thermally treated at 350[°C], and the result was shown in Fig. 2. As expected, second-order phases were not observed at all, and only single phases of CuInSe₂ appeared



<Fig. 1> XRD results by substrate temperature. (Ts=100[°C])



<Fig. 2> XRD results by heat treatment temperature. (Ta=350[°C])

3.2 Electrical Characteristics of CuInSe₂

In order to examine the composition ratio of each element of CuInSe₂, the substrate temperature was varied in the range of room temperature to 200[°C] and the heat treatment temperature was varied in the range of 200[°C] to 350[°C] on the basis of the result of conducting the EDX analysis and the result of measuring the Hall effect to identify the conduction pattern, the carrier concentration and the Hall mobility thereof.

As a result, p-type and n-type appeared alternately. In order to analyze a cause of this result, an extent of an error beyond stoichiometry, which is represented by the value of ΔS, was obtained from the expression of $\Delta S = (2[Se]/[Cu+3In]) - 1$. It is known that if its value is (+), p-type is available, while if its value is (-), n-type is available. It can be known that this rule is well consistent with the experimental result showing n-type generally. Also, it can be known from the experimental result that if the composition ratio of each element is appropriately adjusted, p-type or n-type can be artificially acquired. The object of this experiment is to acquire CuInSe₂ of n-type. The carrier concentration and the Hall mobility thereof are generally lower than those of CuInSe₂ of p-type, but it is thought that there will be no difficulty in using it as an absorption layer. However, at the heat treatment temperature of 250[°C] or lower, no compound is formed at all. This has been ever identified also through the SEM photo. In order to examine a relation between the composition ratio thereof at the heat treatment temperature of 350[°C] or higher and the electrical characteristics thereof, the Hall effect was measured and the result was shown in Table 1. Both samples have almost the stoichiometric composition. It can be known that as its composition gets to be closer to the stoichiometric composition, p-type is more strongly shown. It was also identified that in order to show n-type clearly in the condition of the heat treatment temperature of 500[°C] for 1 hour, the amount of In had to be more increased.

<Table. 1> Best condition and result table of CuInSe₂ thin film fabrication

A.T 500[°C]	Cu-In:Se [at%]	ΔS	CT	Cc	HM	R
1h	20.70:27.00:52.30	0.028	n	2.12×10 ¹⁹	1.89	1.5
2h (250[°C] 20Min)	23.94:24.19:51.87	0.0749	p	5.37×10 ¹⁸	2.3×10 ⁴	4.8

A.T=Annealing Temp, ΔS=Non-stoichiometry,
CT:Conduction type, HM:Hall mobility[cm²/V·s]
R:Resistivity[Ω·cm], Cc=Carrier concentration [cm⁻³]

4. Conclusion

In this experiment, the CuInSe₂ thin film was let to grow by using the sputtering method and the evaporation method to vary the substrate temperature on the glass substrate, the Annealing temperature and the composition ratio, and characteristics thereof were investigated. As a result, the following conclusions could be drawn:

- (1) Though it is known that in the case of CuInSe₂, intrinsically, a thin film of p-type is acquired with ease, while it is difficult to embody a thin film of n-type, in this experiment, the CuInSe₂ thin film of n-type was embodied with ease.
- (2) In the CuInSe₂ thin film, phase transition took place in the vicinity of 250[°C], and a thin film of a single phase was acquired at the heat treatment temperature of 350[°C].
- (3) The carrier concentration, the Hall mobility and the resistivity of the CuInSe₂ thin film as acquired through the experiment were 1.27~9.88×10¹⁷[cm⁻³], 49.95~185[cm²/V·s] and 10⁻¹~10⁻²[Ω·cm], respectively. In the light of the above results, it is thought that the CuInSe₂ thin film as acquired in this experiment has physical properties suitable for embodying the solar cell.

References

- [1] C. G. Park, A study on photovoltaic characteristics of CuInS₂/Cds Heterojunction Devices, Theses of Dr., 1994.
- [2] M. A. Contreras, B. Egass, K. Ramanathan, J. U. Hiltner, A. Swartzlander, F. Hasoon and R. Noufi, Prog. in Photovoltaics, Short Communication, July-August 1999.
- [3] J. Zhao, A. Wang, M. Green and F. Ferrazza '19.8% Efficient 'Honeycomb' Textured Multicrystalline and 24.4% Monocrystalline Silicon Solar Cell', Appl. Phys. Lett., 73(14), p. 1991, 1998.
- [4] F. H. Kang, 'Development and Manufacturing of CIS Thin Film Solar Modules', Technical Digest of the Int'l PVSEC-11, Hokkaido, Japan, 1999. pp. 627-630.
- [5] F. O. Adurodiya, M. J. Carter, R. Hill, "Solid-liquid reaction mechanisms in the formation of high quality CuInSe₂ by the stacked elemental layer(SEL) technique", Solar Energy Materials & Solar Cells, Vol.37, 1995, pp.203-216.
- [6] R. Noufi, R. L. Matson, R. C. Powell and C. Har-rington, Solar Cell 16, 479. 1986.
- [7] R. A. Mickelson and W. S. Chen, Proc. 16th IEEE photovoltaic specialists' Conf. (San Diego, CA, 1982), p. 781
- [8] N. G. Dhere, M. C. Lourenco, R. G. Dhere and L. L. Kazmerski, Solar Cell 16, 369. 1986.
- [9] S. Zweigart, D. Schmid, J. Kessler, H. Dittrich, H. W. Schock, "Studies of the growth mechanism of polycrystalline CuInSe₂ thin films prepared by a sequential process", Journal of Growth, Vol.146, 1995, pp.233-238.
- [10] Stoshi YAMANAKA, Makoto KONAGAI and Kiyoshi TAKAHASHI, "Characterization of Copper Indium Diselenide Thin Films by Raman Scattering Spectroscopy for Solar Cell Applications", JAPANE JOURNAL OF APPLIED PHYSICS, Vol.28, No.8, 1989, pp.L1337-L1340.