The Properties of CuInSe$_2$ Thin Films by DC/RF Magnetron Sputtering and Thermal Evaporation Method

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CuInSe$_2$ thin film were prepared in order to clarify optimum conditions for growth of the thin film depending upon process, and then by changing a number of deposition conditions and heat treatment conditions variously, structural and electrical characteristics were measured. Thereby, optimum process variables were derived. For the manufacture of the CuInSe$_2$, Cu, In and Se were deposited in the named order. Among them, Cu and In were 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 annealing temperature having an effect on the quality of the thin film was changed from 200 ℃ to 350 ℃ at intervals of 50 ℃.

Keywords : CuInSe$_2$, Thin film, Sputtering, Ternary compound

1. INTRODUCTION

Looking into the global status of developing the solar cell of the Cu-Ⅲ-Ⅵ family, it can be known that the solar cell based on CuInSe$_2$ has demonstrated the highest efficiency so far, as shown in the references[1-5]. Studies on a tandem type of the ternary compound of the Cu-Ⅲ-Ⅵfamily are little conducted[6-9]. This study is to manufacture the CuInSe$_2$ 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-Ⅵ 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-Ⅵ 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[10-13].

2. EXPERIMENT

In this study for manufacturing the CuInSe$_2$ ternary compound thin film, deposition was conducted by using the sputtering method and the evaporation method, and the annealing process was used in the electric furnace, and thereby, we intended to get a single-phase compound thin film. Thus, varying several deposition factors and annealing conditions differently and then measuring structural and electrical characteristics depending upon such variation derived optimum process variables.

In this experiment, Cu/In stack layers 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 ℃ to 300 ℃ at intervals of 50 ℃.

3. RESULTS AND DISCUSSION

3.1 Deposition rate depending upon DC/RF power and microstructure

A sputtering yield and a deposition rate are varied depending upon the ion energy, and the accelerated voltage as applied can control the ion energy.

In order to investigate the depositing rate of Cu, the thickness and the surface configuration of the thin film, which was formed as the DC power was varied in the range of 400 ㎃ to 600 ㎃, were measured with FE-SEM, and the result was shown in Fig. 1. As shown in the figure, it can be known that they were almost linearly varied depending upon the DC power. This means, it is thought, that if the DC power is increased, the energy of Ar ion incident upon the target gets to be greater, and it leads to an increase in the sputtering yield and consequently an increase in the depositing rate.

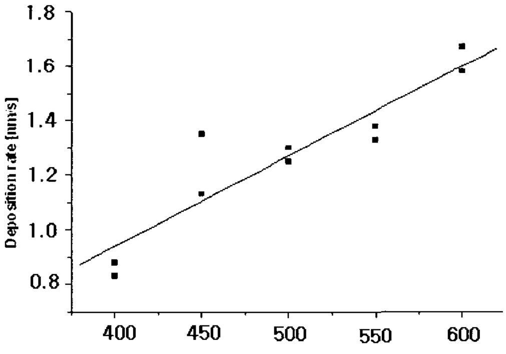


Fig. 1. Deposition rate of Cu by DC power.

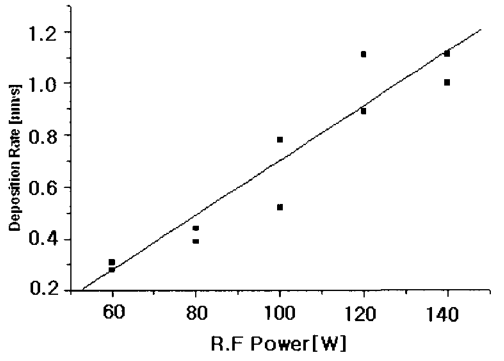
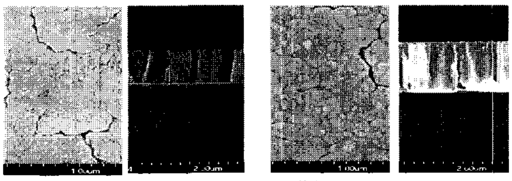


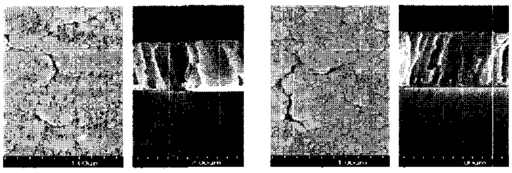
Fig. 2. Deposition rate of In by RF power.

Because the electric conductivity and the heat conductivity of In are lower than those of Cu, the RF power was used for deposition thereof for the purpose of accomplishing a similar sputtering rate. Compared with the case that the DC power was used, sputtering, which was substantially stable, could be available. The depositing rate of In depending upon variation of the RF power in the range of 60 W to 140 W was shown in Fig. 2, and it could be known that as the RF power was increased, the depositing rate was almost linearly increased.

Each surface configuration of the thin film depending upon the deposing rate of Cu and In was measured with FE-SEM, and was shown in Fig. 3 and Fig. 4, respectively. Fig. 3 represents a case that the DC power was used to deposit Cu for 20 minutes, while Fig. 4 represents a case that the RF power was used to deposit In for 30 minutes. It can be known from measurement of the thickness of the thin film with FE-SEM that due to an increase in the thickness of the thin film, the size of the crystal grain is increased.

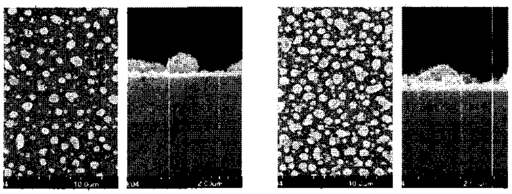


(a) DC 400 mA (b) DC 450 mA

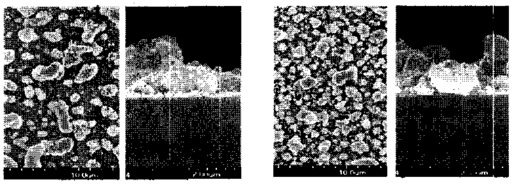


(c) DC 500 mA (d) DC 550 mA

Fig. 3. Surface and cross section morphology of Cu thin film by DC power.



(a) RF 60 W (b) RF 80 W



(c) RF 100 W (d) RF 140 W

Fig. 4. Surface and cross section morphology of In thin film by RF power.

3.2 Crystallographic characteristics of CuInSe$_2$

The diffract fringe of X-ray, which depended upon the substrate temperature and the annealing temperature of the manufactured CuInSe$_2$ thin film, was investigated. Fig. 5 represents a case that a sample manufactured at the substrate temperature of 100 ℃ was annealing Temperature at 200 ℃~350 ℃. Until the annealing temperature got to be 300 ℃, second-order phases of Cu$_x$Se, Cu$_{11}$In$_9$, β -CuSe and β -In$_2$Se$_3$ appeared, and at the annealing temperature of 350 ℃, such second-order phases disappeared and only the single phase of CuInSe$_2$ was observed. At the low annealing temperature of 200 ℃, the phase of Cu$_{11}$In$_9$, an excess of Cu appeared, and at the annealing temperature of 250 ℃ or higher, such phase, an excess of Cu disappeared, and second-order phases of β -In$_2$Se$_3$ and the like appeared.

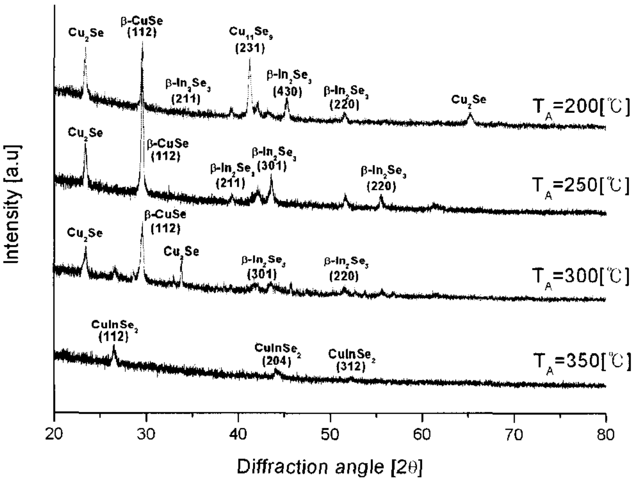


Fig. 5. XRD results by substrate temperature.

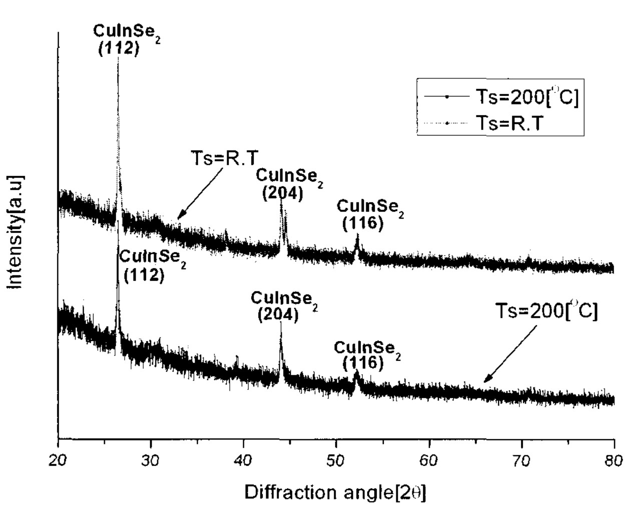


Fig. 6. XRD results by annealing temperature.

This variation is well consistent with the variation of the surface configuration at the annealing of 250 ℃. Such second-order phases did not appear at the annealing temperature of 350 ℃. In order to investigate this phenomenon more particularly, all of the samples as manufactured at different substrate temperatures were annealing Temperature at 350 ℃, and the result was shown in Fig. 6. As expected, second-order phases were not observed at all, and only single phases of CuInSe$_2$ appeared.

3.3 Electrical characteristics of CuInSe$_2$

In order to examine the composition ratio of each element of CuInSe$_2$, the substrate temperature was varied in the range of room temperature to 200 ℃, and the annealing temperature was varied in the range of 200 ℃ to 350 ℃ 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 CuInSe$_2$ of n-type. The carrier concentration and the Hall mobility thereof are generally lower than those of CuInSe$_2$ of p-type, but it is thought that there will be no difficulty in using it as an absorption layer.

However, at the annealing temperature of 250 ℃ 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 annealing temperature of 350 ℃ 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 annealing temperature of 500 ℃ for 1 hour, the amount of In had to be more increased.

Table 1. Best condition and result table of $CuInSe_2$ thin film fabrication.

A.T.	Cu:In:Se [at%]	Δ S	C.T.	Cc	H.M.	R
500[℃]	20.70:27.00:52.30	0.028	n	2.12×10^{19}	1.89	1.5
350[℃]	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,
C.T.: Conduction type, H.M.: Hall mobility[$cm^2/V\cdot s$]
R: Resistivity[10^{-1} Ωcm], Cc: Carrier concentration [cm^{-3}]

4. CONCLUSION

The $CuInSe_2$ 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) Process conditions, which enabled the $CuInSe_2$ thin film having the desired composition ratio to be acquired by controlling each depositing rate of Cu, In and Se, was established. (2) Though it is known that in the case of $CuInSe_2$, 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 $CuInSe_2$ thin film of n-type was embodied with ease. (3) In the $CuInSe_2$ thin film, phase transition took place in the vicinity of 250 ℃, and a thin film of a single phase was acquired at the annealing temperature of 350 ℃. (4) The carrier concentration, the Hall mobility and the resistivity of the $CuInSe_2$ thin film as acquired through the experiment were $1.27\sim9.88\times10^{17}$ cm^{-3}, $49.95\sim185$ $cm^2/V\cdot s$ and $10^{-1}\sim10^{-2}$ $\Omega\cdot cm$, respectively. In the light of the above results, it is thought that the $CuInSe_2$ thin film as acquired in this experiment has physical properties suitable for embodying the solar cell.

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