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A Study of the Properties of CuInS$_2$ Thin Film by Sulfurization

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The copper indium disulfide (CuInS$_2$) thin film was manufactured using sputtering and thermal evaporation methods, and the annealing with sulfurization process was used in the vacuum chamber to the substrate temperature on the glass substrate, the annealing temperature and the composition ratio, and the characteristics thereof were investigated. The CuInS$_2$ thin film was manufactured by the sulfurization of a soda lime glass (SLG) Cu/In/S stacked [1] elemental layer deposited on a glass substrate by vacuum chamber annealing [2] with sulfurization for various times at a temperature of substrate temperature of 200°C. The structure and electrical properties of the film was measured in order to determine the optimum conditions for the growth of CuInS$_2$ ternary compound semiconductor CuInS$_2$ thin films with a non-stoichiometric composition. The physical properties of the thin film were investigated under various fabrication conditions [3,4], including the substrate temperature, annealing temperature and annealing time by X-ray diffraction (XRD), field Emission scanning electron microscope (FE-SEM), and Hall measurement systems. [5] 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 the quality of the film was varied in the range of room temperature (RT) to 300°C at intervals of 100°C, and the annealing temperature of the thin film was varied RT to 550°C in intervals of 100°C.

Keywords: CuInS$_2$, Thin film, Sulfurization

1. INTRODUCTION

Chalcopyrite Copper indium disulfide (CuInS$_2$) thin films are the most promising materials for thin film photovoltaic devices due to their energy band gap of 1.5 eV which perfectly matches the solar spectrum for energy conversion. There is a strong demand for renewable energy due to the limited availability of fossil and nuclear fuels and growing environmental problems. Photovoltaic energy conversion has the potential to contribute significantly to the next generation of electrical energy [6]. CuInS$_2$ is the focus of strong research interest among the materials suitable for thin film solar cells, such as amorphous silicon, CdTe and Cu(In,Ga)Se$_2$ [7]. Cu-chalcopyrite semiconductor materials are used as absorber layers in heterojunction solar cell devices.

Polycrystalline solar cells with a Cu(In,Ga)Se$_2$ absorber recently achieved conversion efficiencies of up to 18.8% [8]. Single phase CuInS$_2$ thin film with a chalcopyrite structure has achieved conversion efficiencies of 27~32% as its direct energy band gap of about 1.5eV lies in the optimum solar energy conversion range [9]. CuInS$_2$ is a Se-free compound from the chalcopyrite family and is suitable for solar cells due to its high optical absorption. The development of CuInS$_2$ is attractive because the problematic selenium is substituted by non-toxic sulfur. The open circuit voltage of CuInS$_2$ solar cells is theoretically higher (1.2 V) than that of Cu(In,Ga)Se$_2$ cells. However, up to now the efficiency of CuInS$_2$ solar cells has been limited by open circuit voltage, which is far below the theoretical value. The best conversion efficiency for polycrystalline CuInS$_2$ cells reported so far is 12.7% [10,11]. Thermal evaporation as a method for thin film CuInS$_2$ preparation is a good approach with respect to economic considerations. An important advantage of thermal evaporation as a method for thin film preparation is that films with a large area can be prepared without a vacuum using simple, low-cost equipment. CuInS$_2$ thin film can be easily obtained by sulfurization of the Cu-In precursor. However, thermal evaporation Cu-In precursors with

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excellent morphology have not been obtained. Therefore, in this study related to the manufacture of CuInS$_2$ ternary compound thin film, deposition was conduce using sputtering and evaporation methods, and the annealing with sulfurization process was used in the vacuum chamber, our intention being to obtain a single phase compound thin film. The performance of our study is also described below.

2. EXPERIMENTS

In this study for manufacturing CuInS$_2$ ternary compound thin film, deposition was conducted using sputtering and evaporation methods, and the annealing with sulfurization process was used in the vacuum chamber (10^{-3} torr), with the intention of obtaining a single-phase compound thin film. Thus, varying several deposition factors and annealing conditions differently and then measuring the structural and electrical characteristics depending upon such variations derived the optimum process variables. In this experiment, Cu/In stack layers were deposited using the sputtering method, enabling us to expect a stronger adhesive force with a substrate, while S was deposited using the thermal evaporation method, enabling us to expect a stronger adhesive force with a substrate, while S was deposited 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 the deposition thereof. Meanwhile, for the deposition of In, the RF sputtering method was used so that a 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 the quality of the thin film was varied in the range of RT to 300°C at intervals of 100°C and the annealing temperature of the thin film was varied RT to 550°C in intervals of 100°C.

The thickness of the fabricated CuInS$_2$ thin film was about 1.5 µm, which was sufficient to obtain an absorption coefficient of more than 1×10^4 cm^{-1}. Micro-structural studies were carried out by XRD (D/MAX-1200, Rigaku Co., Shibuya-Ku, Tokyo, Japan) and SEM (JSM-5400, Jeol Co., Akishima, Tokyo, Japan). The electrical properties were measured by a Hall Effect Measurement system (HL5500PC, Accent Optical Technology Co., Oregon, USA), and the optical absorbance was measured by a UV/VIS/NIR Spectrophotometer (CARY 1, Varian Co., NY, USA).

3. RESULTS AND DISCUSSION

3.1 Microstructure properties of CuInS$_2$ thin films

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

In order to investigate the depositing rate of Cu, the thickness and the surface configuration of the thin film, which was formed as DC power was varied in the range of 400 mA to 600 mA, were measured with scanning probe microscope (SPM) and FE-SEM, and the result shown in Fig. 1.

As shown in Fig. 1, it can be seen that they were almost linearly varied depending upon the DC power. This means, it is thought, that if DC power is increased, the energy of Ar ion incident upon the target becomes greater and leads to an increase in the sputtering yield and, consequently, the heat conductivity of In are lower than those of Cu, and RF power was used for the deposition thereof for the purpose of accomplishing a similar sputtering rate. Compared with the case where DC power was
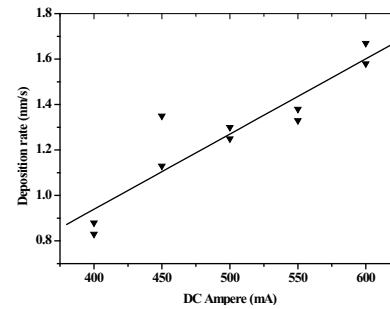

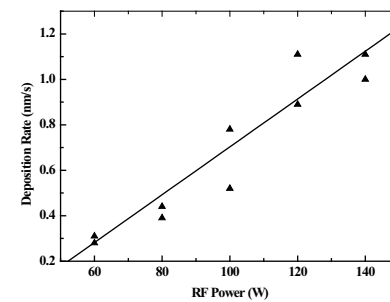Fig. 1. Deposition rate of DC power by Cu thin films.

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

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

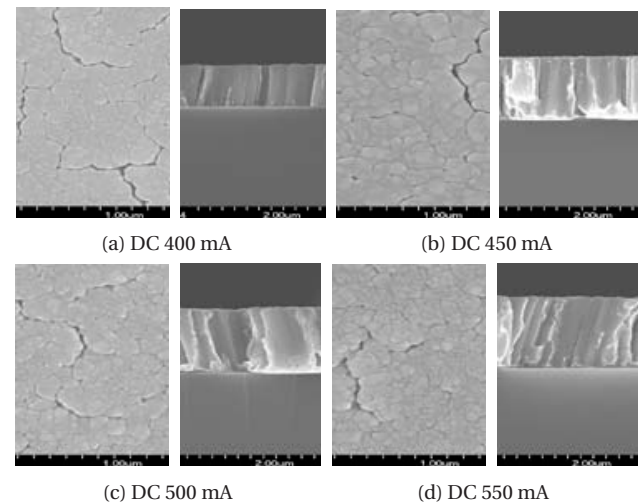(c) DC 500 mA   (d) DC 550 mA

Fig. 3. SEM images of Cu thin film by DC power (surface and cross section).

used, sputtering, which was substantially stable, could be available.

The depositing rate depending upon variation of RF power in the range of 60 W to 140 W is shown in Fig. 2, and it could be known that as 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 Figs. 3 and 4, respectively. Figure 3 represents a case where DC power was used to deposit Cu for 20 minutes, while Fig. 4 represents a case where RF power was used to deposit In for 30 minutes. It can be seen from the measurements of the thickness of the thin film with SPM and FE-SEM that, due to an increase in the thickness of the thin film, the size of the crystal grain is increased.
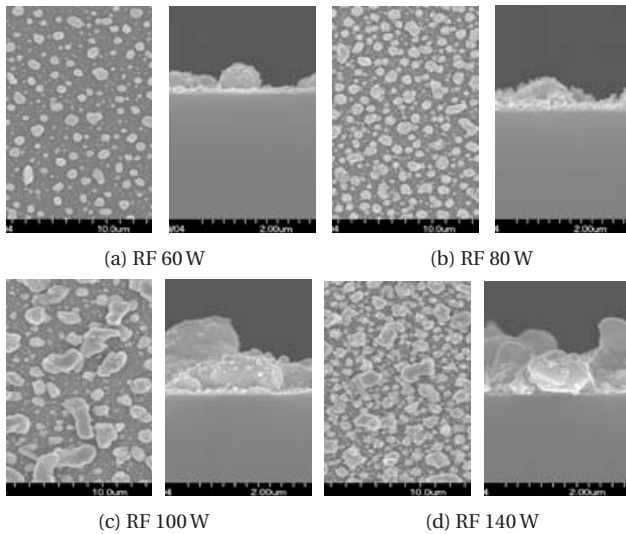
(a) RF 60 W   (b) RF 80 W

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

Fig. 4. SEM images of In thin film by RF power (surface and cross section).
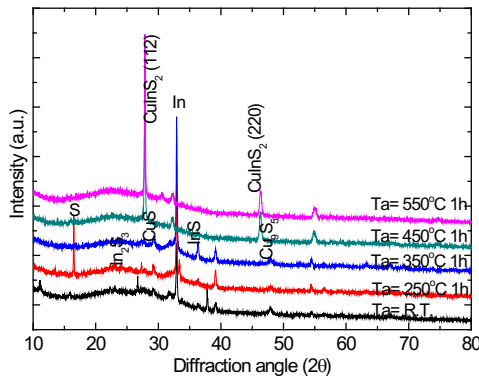

Fig. 5. XRD pattern of $CuInS_2$ thin films by various annealing temperatures (Ts=200°C, Ta=R.T~550°C)

The diffract fringe of an X-ray, which depended upon the substrate temperature and the annealing temperature of the manufactured $CuInS_2$ thin film, was investigated. Figure 5 represents a case where a sample manufactured at a substrate temperature of 200°C was annealing temperature at R.T~550°C. Until the annealing temperature rose to 350°C, second-order phases of CuS, Cu_9In_8, and In_2S_3 appeared, and at an annealing temperature of 450°C, such second-order phases disappeared and only the single phase of $CuInS_2$ was observed. At a low annealing temperature of 250°C, the phase of $Cu_{11}In_9$, an excess of Cu appeared, and at annealing temperatures of 350°C or higher, an excess of Cu disappeared and second-order phases of β-In_2S_3 and the like appeared.

This variation is consistent with the variation of the surface configuration at an annealing of 350°C. Such second-order phases did not appear at an annealing temperature of 450°C. In order to investigate this phenomenon more carefully, all samples manufactured at different substrate temperatures were annealing temperature of 450°C, and the results shown in Fig. 5. As expected, second-order phases were not observed at all, and only single phases of $CuInS_2$ appeared.

3.2 Electrical properties of $CuInS_2$ thin films

In order to examine the composition ratio of each element of

Table 1. Electrical properties measurement of $CuInS_2$ thin films after annealing at various temperatures.

Sample No.	Conduction type	Carrier concentration (cm^3)	Hall mobility $(cm^{2/v \cdot s})$	Resistivity $(\Omega \cdot cm)$
RT	P	1.2105×10^{18}	126.24989	9.4669×10^{-3}
250°C	p	3.7062×10^{16}	130.42523	24.76154
350°C	P	6.8874×10^{17}	151.89705	9.06315
450°C	P	7.096×10^{18}	53.01726	1.6574×10^{-2}
550°C	p	7.9825×10^{17}	605.08693	0.53114

$CuInS_2$, the substrate temperature was varied in the range of RT to 200°C, and the annealing temperature was varied in the range of RT to 550°C on the basis of the results of conducting the energy dispersive X-ray spectrometer (EDX) analysis and measuring the Hall effect to identify the conduction pattern, the carrier concentration and the Hall mobility thereof.

As a result, p-type appeared. In order to analyze the cause of this result, an extent of an error beyond stoichiometry, which is represented by the value of $\triangle$S, was obtained from the expression of $\triangle$S = {2[S]/[Cu+3In]}-1. It is known that if its value is (+), p-type is available, while if its value is (-), n-type is available. Also, it can be seen from the experimental results 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 $CuInS_2$ of n-type. The carrier concentration and the Hall mobility thereof are generally lower than those of $CuInS_2$ of p-type, but it is thought that there will be no difficulty in using it as an absorption layer.

However, at an annealing temperature of 250°C or lower, no compound is formed at all. This has also been identified through the SEM photo. In order to examine a relation between the composition ratio thereof at an annealing 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 almost have the stoichiometric composition. It can be seen that as its composition gets closer to the stoichiometric composition, the p-type is more strongly shown. It was also identified that in order to show the n-type clearly in the condition of an annealing temperature of 450°C for 1 hour, the amount of In had to be increased further.

3.3 Optical properties of $CuInS_2$ thin films

The optical absorption spectra of $CuInS_2$ tin films with chalcopyrite structure at RT to 300°C at intervals of 100°C and the annealing temperature of thin film was varied RT to 550°C in intervals of 100°C were shown in Fig. 6.

The fundamental absorption wavelength, absorbance, and the energy band gap of p-type $CuInS_2$ thin film with room temperature to 200°C and an annealing temperature of 450°C was 828 nm, 2×10^{-4} cm^{-1}, and 1.503 eV, respectively. The energy band gap of p-type $CuInS_2$ was 1.45 eV and 1.56 eV at an annealing temperature of RT to 550°C respectively.

We know that the increased annealing with the sulfurization process was fundamental absorption moved onto the shorter wavelength, and the absorption coefficient decreased.

In this case, we concluded that a decrease in the reactive defect density made the grain size smaller and the last energy band gap larger.

4. CONCLUSIONS

The $CuInS_2$ thin film was manufactured using sputtering and
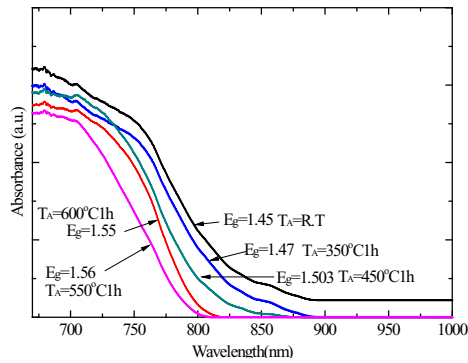
Fig. 6. Absorbance spectra of CuInS$_2$ thin films measured after various annealing temperatures.

evaporation methods, and the annealing with sulfurization process was used in the vacuum chamber to vary the substrate temperature on the glass substrate, the annealing temperature and the composition ratio, and the characteristics thereof were investigated. As a result, the following conclusions could be drawn: (1) process conditions, which enabled the CuInS$_2$ thin film having the desired composition ratio to be acquired by controlling each depositing rate of Cu, In and S, was established; (2) in the CuInS$_2$ thin film, phase transition took place in the vicinity of 350°C to 1h, and a thin film of a single phase was acquired at an annealing temperature of 450°C to 1 hour; (3) the annealing with sulfurization process was used in the Vacuum chamber of S ambient carrier concentration, the Hall mobility and the resistivity of the p-type CuInS$_2$ thin film as obtained through the experiment were 7.096×10^{17} cm^{-3}, 53 cm^2/V and 1.65×10^{-2} Ω·cm, respectively. Also, optical energy band gaps of the films in S ambient appeared a little larger than those in the vacuum only.

The largest optical energy band gap of CuInS$_2$ thin film in the Vacuum Chamber of S ambient was 1.503 eV. In light of the above results, it is thought that the CuInS$_2$ thin film as obtained in this experiment has suitable physical properties to embody solar cells.

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