Preparation of $AgInS_2$ Thin Films by Sulfurization of Ag/In Precursors for Solar Cell Application

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This paper describes preparation of $AgInS_2$ thin films as an absorption layer material for a top cell of tandem solar cells. The film has been prepared by sulfurization of evaporated Ag/In metal precursors. Ag/In ratios in the films were controlled by changing Ag/In ratios in the vacuum chamber. The annealing temperature of 300 ℃ was found to be appropriate for sulfurization in our case.

Keywords: $AgInS_2$, solar cell, sulfurization, Ag/In precursor

1. Introduction

Recently, I-III-VI_2 chalcopyrite semiconductors are developed as promising materials for high efficiency thin film solar cells. $Cu(InGa)Se_2$ thin film solar cells have the best efficiency of 19.5 % [1]. However, a higher efficiency is hardly obtained with a single junction solar cell. Hence, in order to obtain higher efficiency, a tandem solar cell is considered to be effective. $AgInS_2$ has appropriate bandgap energy of 1.9 eV for an absorber layer for a top cell of the tandem solar cell [2]. Thin $AgInS_2$ film has been synthesized by chemical spray pyrolysis [3], vacuum evaporation [4] and hot wall epitaxy [5]. However, thin $AgInS_2$ films grown by sulfurization of metal precursors have not been reported yet. This method is successfully applied to $CuInS_2$ thin film preparation [6]. In this work, we have prepared $AgInS_2$ thin films by sulfurization of evaporated Ag/In precursors.

2. Experiments

The Ag/In precursors were deposited by vacuum evaporation on glass substrates. Ag/In ratios in the films were controlled by changing Ag/In ratios in the vacuum chamber so that the ratios in the films were ranging from 0.4 to 1.4. The precursors were sulfurized in an H_2S atmosphere at 300 to 600 ℃ for 60 min. Composition and crystallinity of the films were evaluated with an EPMA and an XRD, respectively. Resistivity was measured by van der Pauw method. Transmittance spectra were measured to estimate the band-gap.

3. Results and Discussion

Figure 1 shows a relationship between the composition in the films and that of the evaporation source in the vacuum chamber annealed at 500 ℃. Ag/In ratios in the films are found to be proportional to those of the evaporation sources. On the contrary, S/(Ag+In) ratios decreased with increasing the Ag/In ratios of the sources. Figure 2 shows annealing temperature dependence of Ag/In ratios in the films with those in the chamber as a parameter.

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Annealing temperatures hardly affect film compositions except in the case of 300℃. Films with Ag/In=1.0 are obtained with the Ag/In source ratio of around 1.2. This suggests that evaporation rate for In during the deposition process is larger than that for Ag.

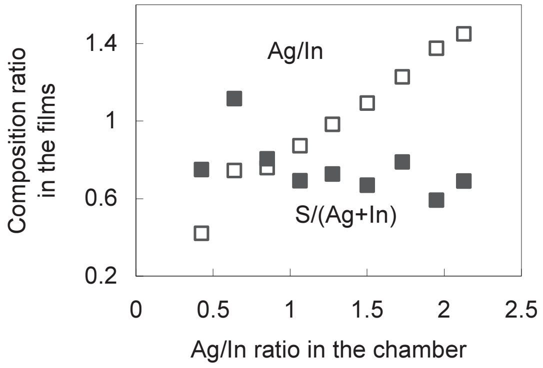

Figure 1　Relationship between composition ratios in the films and those in the chamber.

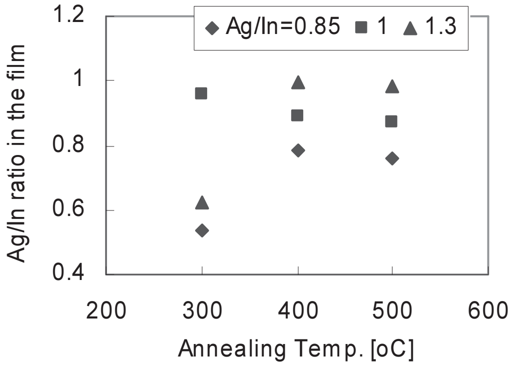

Figure 2　Annealing temperature dependence of Ag/In ratios in the films. Parameter is Ag/In ratio in the chamber.

XRD patterns for the films annealed at 300 to 600 ℃ shown in Fig. 3 reveal that the peak from (112) of chalcopyrite phase is observed at each temperature. The peaks from orthorhombic phase become higher as the annealing temperature increases. This is probably due to the stability temperature difference between these forms. That is, the chalcopyrite form is stable below 620 ℃ while the orthorhombic form above 620 ℃ [7]. Secondary phases, such as InS, can be contained in the films. The temperature of 300 ℃ is appropriate for annealing in this work because the composition of secondary phases including the orthorhombic form increases with increasing the annealing temperature.

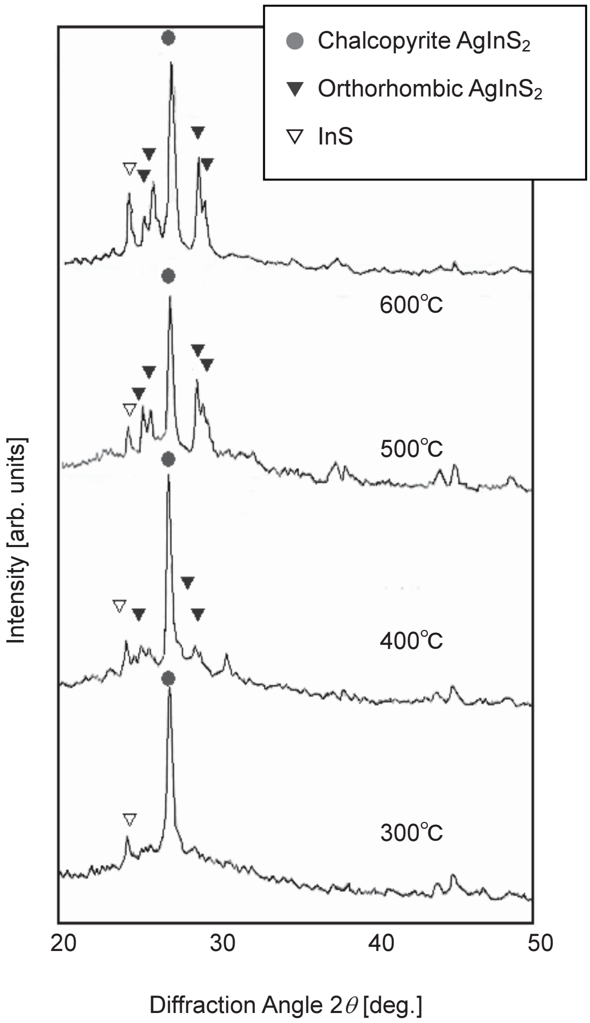

Figure 3　XRD patterns of films annealed at 300 ℃ to 600 ℃. Closed circles indicate the peaks from chalcopyrite (112) phase.

Figure 4 shows surface morphology of Ag-rich (a) and In-rich (b) films. These films have Ag/In ratios of 1.23 and 0.74, respectively. When the largest grains of each film are compared mutually, the Ag-rich film has a larger grain than the In-rich film. The largest grain sizes for Ag- and In-rich films were about 6 μm and 1 μm, respectively.

However, uniformity of the In-rich film in grain size is superior than that of the Ag-rich film.

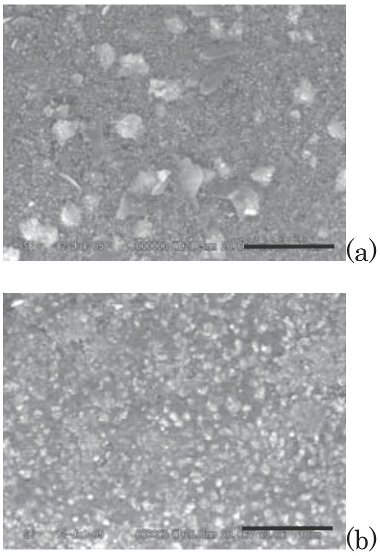

Figure 4　SEM images for Ag-rich (a) and In-rich (b) films. The bars denote 10 μm.

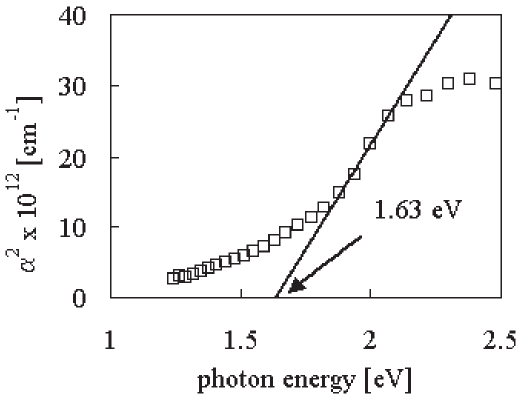

Figure 5　Typical α^2-hν plot for estimating bandgap.

Resistivities of almost stoichiometric films (Ag:In:S=0.98:1:1.69, 1.05:1:1.79, 1.00:1:1.75) are ranging from 1.5 to 3.5 Ωcm. Those of non-stoichiometric films were too high to measure.

Figure 5 shows a typical α^2-hν plot. The absorption coefficients were calculated from transmittance measurement data with a constant reflectivity of 0.42. The bandgap for the stoichiometric film is estimated to be 1.63 eV from the figure. The value is fairly less than that for bulk crystal (1.9 eV). Further investigation is required to understand such decrease.

4. Summary

In conclusion, AgInS$_2$ thin films have been prepared by sulfurization of evaporated Ag-In precursors. Ag/In ratios in the films are controlled by changing Ag/In ratios in the vacuum chamber. The annealing temperature of 300 ℃ is found to be appropriate for sulfurization with respect to crystallinity at the present time. Further annealing is required to investigate the crystallinity of the films annealed below 300 ℃.

Acknowledgement

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