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Effect of Ag/Sn Mole Ratio of Ag-rich Ag_8SnS_6 Thin Film Prepared by Vacuum Evaporation

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Abstract

Ag_8SnS_6 (ATS) thin films were prepared from a vacuum-evaporated Ag-SnS stacked precursor via annealing in H_2S at 500 °C for 1 hour. The Ag/Sn mole ratio of the starting materials were from 8.0 to 9.0. From X-ray diffraction patterns, single-phase orthorhombic Ag_8SnS_6 were observed from the thin films prepared from the Ag/Sn mole ratio of 8.25 and 8.5. From SEM, the largest grain size was obtained at the Ag/Sn mole ratio of 8.25. In addition, it was found by EDS mapping the elements were uniformly distribute. The absorption coefficients and the band-gap energy of Ag-rich Ag-Sn-S thin films were above 10^4 cm^{-1} and 1.18-1.35eV, respectively. Consequently, we succeeded in obtaining high quality single phase crystals at Ag/Sn=8.25.

1. Introduction

$Cu(In,Ga)Se_2$ (CIGS) thin film solar cell has achieved a conversion efficiency 22.9%, and is expected as a next-generation solar cells [1]. However, CIGS thin film composed of rare metal such as In, Ga, thereby it may increase production cost. Thus, it is not easy for CIGS solar cell to meet high demand of PV market. One of the alternative candidate thin film solar cell is Cu_2SnS_3 (CTS) thin film solar cell, which consists non-toxic and low cost materials. However, conversion efficiency is still 4.8% [2], and further improvement is essential. For searching new materials, we are focusing on Ag-Sn-S thin films which replaced Cu in Cu_2SnS_3 with Ag. Ag_2SnS_3 and Ag_8SnS_6 are reported for these materials up to now [3,4]. Especially, Ag_8SnS_6 has band-gap energy 1.33eV and high absorption coefficient of $10^4 cm^{-1}$. It is close to the ideal band-gap energy (Eg=1.4eV) more than CTS thin film solar cells, therefore Ag_8SnS_6 solar cells can be expected high conversion efficiency. In this research, we investigate the effect of Ag/Sn mole ratio on Ag-rich Ag_8SnS_6 thin film.

2. Experiment

Ag-SnS stacked precursors were prepared on soda lime glass (SLG) by vacuum evaporation. The substrate temperature was at 300°C for SnS and at room temperature for Ag. The Ag/Sn mole ratio of the evaporation materials was changed from 8.0 to 9.0 in step of 0.25. The precursor was crystallized by annealing in H_2S atmosphere for 1 hour at 500 °C. The composition of thin films was determined by energy dispersive spectrometry (EDS). The crystalline structure of the thin films was examined by X-ray diffraction (XRD). The surface morphology of the thin films was observed by scanning electron microscopy (SEM). The transmittance and reflectance data were measured using an UV-visible-NIR spectrophotometry.

3, Result and discussion

Figure 1 shows XRD patters of thin films prepared for different Ag/Sn mole ratio of evaporation materials. The thin films prepared at the Ag/Sn mole ratio of 8.0 was observed (013), (022), (205) and (801) crystal planes of orthorhombic Ag_8SnS_6 phase (PDF file no. 01-0380-0434) and unknown peak at 22.8°. The thin films prepared at the Ag/Sn mole ratio of 8.25 and 8.5, unknown peak disappeared and single-phase orthorhombic Ag_8SnS_6 were observed. At the Ag/Sn mole ratio of 8.75 and 9.0 were observed (110) and (200) crystal plane of monoclinic Ag_2S phase (PDF file no.00-002-0998) and unknown peak. The possible reason is due to the increase amount of Ag.

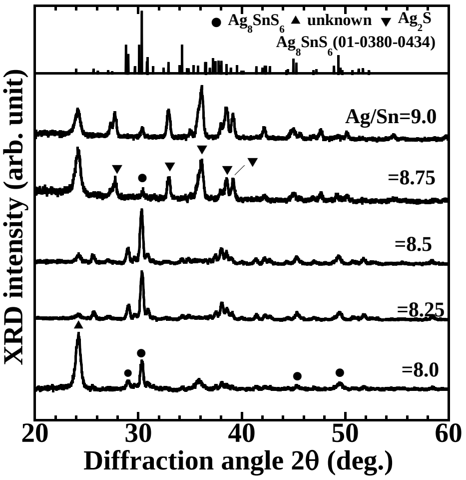

Fig. 1. XRD patters of thin films prepared for different for the Ag/Sn mole ratio

Figure 2 shows composition prepared for different Ag/Sn mole ratio of starting materials. From this result, the thin films prepared at the Ag/Sn mole ratio of 8.0, 8.25 and 8.5 were nearly stoichiometric Ag_8SnS_6. Especially, the thin films prepared at Ag/Sn mole ratio of 8.25 is the closest stoichiometric Ag_8SnS_6, which may be due to disappeared unknown phase. The thin films prepared at the Ag/Sn mole ratio of 8.75 and 9.0 became fat away from stoichiometry, and composition of Sn is very low. A possible reason is reevaporation of Sn.

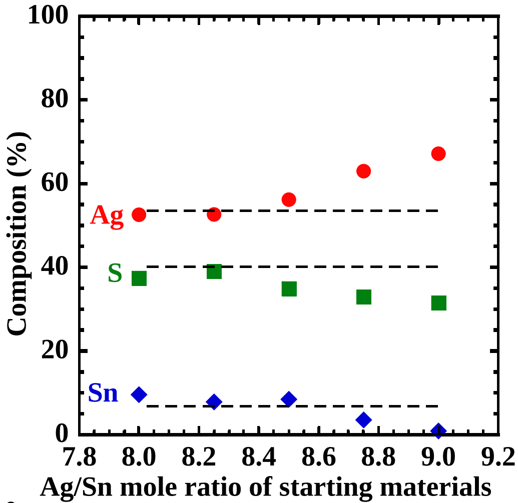

Fig. 2. Composition prepared for different Ag/Sn mole ratio of starting materials

Fig. 3. shows SEM and EDS mapping images for elements prepared for the Ag/Sn mole ratio of 8.0, 8.25 and 8.5. Red, green and blue in the EDS mapping images show Ag, Sn and S elements, respectively. From SEM images, the largest grain obtained Ag/Sn mole ratio of 8.25, which was about 1 μm. It is considered that the crystal growth was promoted by the disappearance of unknown. From EDS mapping, at the Ag/Sn mole ratio of 8.0 and 8.5 were seen bias of elements such as S. In contrast, at the Ag/Sn mole ratio of 8.25, each element was uniformly distributed. To analyze optical properties, we measured transmittance and reflectance using an UV-visible-NIR spectrophotometry. The absorption coefficient estimated by transmittance and reflectance were obtained above 10^4 cm^{-1} for all samples. In addition, we calculated the band-gap energy from $(\alpha h\nu)^2$-$h\nu$. The estimated band-gap energy of Ag/Sn mole ratio of 8.25 was 1.35 eV. From these optical properties, it was found that Ag_8SnS_6 thin film can be thinned and has potential as an absorber layer.

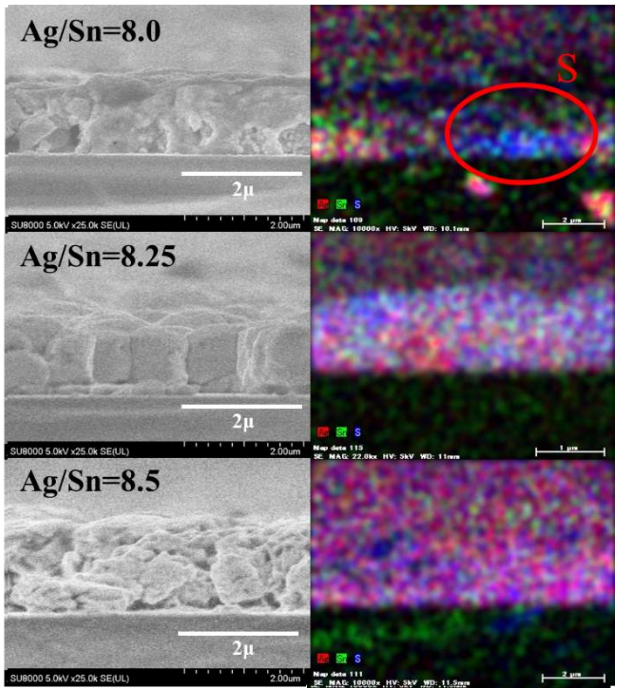

Fig. 3. SEM and EDS mapping image prepared for different for the Ag/Sn mole ratio of 8.0, 8.25 and 8.5

4. Conclusions

From the thin films prepared at the Ag/Sn mole ratio of 8.25 and 8.5, unknown peak disappeared and single-phase orthorhombic Ag_8SnS_6 were observed. Especially, the mole ratio of 8.25 obtained the largest grain about 1 μm from SEM image. In addition, it was found the absorption coefficients and the band-gap energy of Ag-rich Ag-Sn-S thin films were above 10^4 cm^{-1} and 1.18-1.35 eV, respectively. From these result, we succeeded in fabricating high quality thin film at the Ag/Sn mole raitio of 8.25.

Acknowledgements

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