Cu2ZnSn(S,Se)4 Thin Films Fabricated by Sequential Evaporation using Cu2ZnSnSe4 Compound and Their Photovoltaic Applications

Toshiyuki Yamaguchi, Mitsuki Nakashima and Tatsuya Sakamoto

ABSTRACT

Cu2ZnSnSe4 compound was synthesized and then used it as an evaporation material to fabricate Cu2ZnSn(S,Se)4 thin films for solar cell applications by sequential evaporation process. From EPMA analysis, the S content in Cu2ZnSn(S,Se)4 thin films increased and the Se content decreased with increasing the amount of S in the evaporation materials. XRD study showed that the thin films had a kesterite phase in Cu2ZnSn(S,Se)4. From SEM micrographs, the grain size in the thin films decreased with increasing the amount of S. Cu2ZnSn(S,Se)4 thin film solar cells fabricated by this process demonstrated V_{oc}=255mV and J_{sc}=25.5mA/cm².

INTRODUCTION

Thin film solar cells based Cu2ZnSn(S,Se)4 (CZTSSe) kesterite absorbers have drawn considerable attention due to their outstanding performance and earth-abundant composition in contrast to Cu(In,Ga)Se2 [1] and CdTe [2] based photovoltaics. CZTSSe possesses a direct band gap in the range from about 1.0eV (CZTSe) to 1.5eV (CZTS) by increasing the S/(S+Se) ratio from 0 to 1 [3]. Therefore, these absorber materials enable the realization of a high conversion efficiency of about 30% under terrestrial conditions according to the Schockley and Queisser limit [4]. Thus, numerous vacuum and non-vacuum techniques have been successfully used in preparing CZTSSe thin films [5-21]. The recent world-record in CZTSSe thin film solar cells with a conversion efficiency of 12.6% was presented, which was fabricated using the hydrazine-based solution deposition technique [15]. The hydrazine is highly toxic and very unstable, which requires extreme caution during handling. In almost researches including the hydrazine-based solution technique, CZTSSe thin films were fabricated by using two-step technique which consisted of the processes of the precursor preparation and the annealing. One-step process using only deposition technique for fabrication of CZTSSe thin film is a
simple fabrication process and useful industrially. On the other hands, Kim et al. have reported that the compounds of CTSe and ZnSe were used for preparation of precursor in order to fabricate CZTSe thin films [11]. Previously we have synthesized CZTSe compound and then used it as evaporation material to prepare a precursor for selenization process in order to fabricate CZTSe thin films for solar cell applications [21]. In this study, we tried to fabricate CZTSSe thin films by one-step evaporation process using the CZTSe compound and applied to the photovoltaic devices.

**EXPERIMENTAL**

CZTSe compound was synthesized by reacting high-purity elements (Cu:Zn:Sn:Se = 25:12.5:12.5:50 at%) in an evacuated quartz ampoule. The elements were reacted first at 200°C for 4 hours and then slowly heated to 1100°C in order to assure a congruent melt. Next the material was slowly cooled to 650°C and was kept for 4 hours to ensure homogenization and was finally cooled down to room temperature. The thermal treatments as described above were repeated three times. CZTSSe thin films were prepared by the sequential evaporation process using the ULVAC VPC-1100 vacuum evaporation apparatus. The temperature profiles of our sequential evaporation process for fabricating CZTSSe thin films is shown in Fig. 1. Mo layer used as a back contact was prepared by rf magnetron sputtering onto soda-lime glass substrate in Ar ambient. Before fabrication of CZTSSe thin films, the Mo/soda-lime glass substrate was heated in vacuum for 5min at 600°C. After cooling down to 300°C, in the first step, Cu-Zn-Sn-Se-S layer was evaporated from CZTSe compound and S element onto the Mo/soda-lime glass substrate. In the second step, Zn-Sn-Se layer was deposited from each element at 575°C. Finally, only NaF was effused at the same substrate temperature. The mole ratio of the evaporation materials was kept at CZTSe:Zn:Sn: NaF =1.2:3.5:1.2:0.048. The amount of S in the evaporation materials was changed from 0 to 0.3g under the constant at Se=2.0g. The solar cells were completed by the deposition of a CdS layer of about 50nm in a chemical bath, rf sputtering of a thin intrinsic ZnO layer, dc sputtering of a 350nm thick ZnO:Ga transparent conductive layer and Al grid contact. The composition of thin films was determined by electron probe microanalysis (EPMA) with energy dispersive spectrometry (EDS) detector. The crystalline structure of the thin films was examined by the X-ray diffraction (XRD). The surface morphologies of the thin films were observed with scanning electron microscopy (SEM). Current-Voltage characteristics of solar cells were measured using standard 1-sun (AM1.5, 100mW/cm²) illumination.
RESULTS AND DISCUSSIONS

Figure 2 shows the dependence of the film composition ratio determined by EPMA analysis on the amount of S in the evaporation materials. The contents of Cu, Zn and Sn in the thin films were nearly constant. The Cu/(Zn+Sn) mole ratios were in the range from 0.57 to 0.65, the Zn/Sn mole ratios range were from 1.11 to 1.42. All thin films had a composition of Cu-poor and Zn-rich, which was suitable for fabrication of solar cells. The S content in the thin films increased and the Se content decreased with increasing the amount of S in the evaporation materials. The S/(S+Se) mole ratio in the thin films increased from 0 to 0.41. S was incorporated into the thin films by using the temperature profile shown in Fig. 1.

Figure 1. Temperature profile for preparation of CZTSSe thin films by sequential evaporation process.

Figure 2. Dependence of the film composition on the amount of S in the evaporation materials.
Figure 3 shows the XRD patterns of the thin films prepared at various amount of S in the evaporation materials. XRD studies revealed that the all thin films had a kesterite CZTSSe structure, and the peaks of Mo used as a back electrode contact were also observed. All XRD peaks corresponding to CZTSSe with a kesterite structure were slightly shifted toward a higher angle. This indicates that a part of Se in CZTSe was substituted by S. CZTSSe thin films were successfully fabricated by this approach.

Figure 4 shows the surface and cross-sectional SEM images of CZTSSe thin films. As the amount of S in the evaporation materials increased, the CZTSSe film thickness decreased from 2 µm to 1 µm and the grain sizes decreased also. The CZTSSe thin films were formed densely, but had a few voids visible at the CZTSSe-Mo interface. The conversion efficiency of polycrystalline solar cells improves with increasing grain size of the absorber layer as the recombination rate of the photogenerated carriers can be reduced. Thus, large grains are required for the fabrication of high efficiency solar cells.

For CZTSSe thin film solar cells, current density J and voltage V characteristics were measured in-house under 1-sun illuminated condition. The J-V characteristics of CZTSSe thin film solar cells prepared by sequential evaporation at S=0g and S=0.1g are shown in Fig. 5. In this case, an open circuit voltage $V_{oc}$ and a shunt circuit
current density $J_{sc}$ decreased with increasing the amount of S in the evaporation materials. For the sample prepared at S=0.1g, the cell performance of $V_{oc}=241$ mV, $J_{sc}=9.06$ mA/cm$^2$, a fill factor FF=0.30 and a conversion efficiency $\eta=0.66\%$ was obtained. The best solar cell in this study showed $V_{oc}=255$ mV, $J_{sc}=25.5$ mA/cm$^2$, FF=0.31 and $\eta=2.04\%$ as shown in Fig. 5, which was fabricated at S=0g. In comparison with the previous data ($V_{oc}=213$ mV, $J_{sc}=20.04$ mA/cm$^2$) for a solar cell prepared by two-step process (selenization process) using CZTSe compound [14], this cell parameter was improved.

**SUMMARY**

We successfully fabricated CZTSSe thin films and solar cells by one-step process (sequential evaporation process) using CZTSe compound and characterized their properties. Thus the S/(S+Se) mole ratio in CZTSSe thin films could be changed by this approach. The best solar cell with the performances of $V_{oc}=255$ mV, $J_{sc}=25.5$ mA/cm$^2$, FF=0.31 and $\eta=2.04\%$ was demonstrated in this study. The performance of CZTSSe thin film solar cells was improved in comparison with the previous data for a solar cell prepared by two-step process using CZTSe compound. Therefore, it is considered that the sequential evaporation process using CZTSe compound is a useful technique.

**Acknowledgements**

This study was supported in part by a Grant-in-Aid for Scientific Research (No.26420888) from the Ministry of Education, Culture, Sports, Science and Technology in Japan.
REFERENCES