

Cu₂ZnSn(S,Se)₄ Thin Film Solar Cells Fabricated by Sulfurization Using Cu₂ZnSnSe₄ and KF Compounds

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Abstract

Cu₂ZnSn(S,Se)₄ thin films were fabricated by sulfurization of the precursor evaporated from Cu₂ZnSnSe₄ and KF compounds. From Raman analysis, the precursor had a Cu₂SnSe₃ structure and transformed to Cu₂ZnSn(S,Se)₄ structure after sulfurization, which was a first approach to produce Cu₂ZnSn(S,Se)₄ thin films. EPMA analysis revealed that the S/(S+Se) mole ratios in the sulfurized films were in the range between 0.94 and 0.99. The open circuit voltage Voc of Cu₂ZnSn(S,Se)₄ thin film solar cells fabricated using KF improved more than one of the solar cell fabricated without KF, especially the best solar cell demonstrated Voc=698mV.

1. 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]. Their bandgap energies are tunable to optimum values for matching the solar spectrum. Thus, numerous vacuum and non-vacuum techniques have been successfully used in preparing CZTSSe thin films. The highest conversion efficiency (η) of up to 12.6% with an open circuit voltage (V_{oc}) of 513.4 mV, a short circuit current density (I_{sc}) of 35.2 mA/cm² and a fill factor (FF) of 0.698 was demonstrated using CZTSSe thin film absorber prepared with the hydrazine-based solution deposition and annealing processes [4]. Previously we have synthesized CZTSe compound and then used it as evaporation material to fabricate CZTSe and CZTSSe thin films and solar cells [5, 6]. These thin films were fabricated by one-step process using only deposition technique. Our CZTSe solar cell showed V_{oc} =274 mV, I_{sc} =33.3 mA/cm², FF=0.43 and η =3.93% [5], and those of CZTSSe solar cell were V_{oc} =241mV, I_{sc} =9.06mA/cm², FF=0.30 and η =0.66% [6]. In order to improve the cell performances including CZTSSe solar cell with a best efficiency of 12.6%, it is one of the important issue to increase V_{oc} . In recent years, the potassium doping techniques were reported as one of the method for improvement of the Voc in

Cu(In,Ga)Se₂ solar cells [7]. In this study, we proposed a new crystallization process for fabrication of CZTSSe thin films and investigated the effect of potassium doping for improvement of CZTSSe solar cell performance.

2. 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. CZTSSe thin films were prepared on the sputtered Mo/soda-lime glass substrate by the sequential evaporation process using CZTSe compound. 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 the substrate temperature of 300°C, in the first step, Cu-Zn-Sn-Se layer was evaporated from CZTSe compound onto the Mo/soda-lime glass substrate. In the second step, Zn-Sn-Se layer was deposited from each element at 500°C. Finally, only KF and Se were effused at 350°C. The mole ratio of the evaporation materials was kept at CZTSe:Zn:Sn=1.2:3.0:1.0. The KF/CZTSe mole ratio was varied from 0 to 5%. The as-deposited films were set in a vacuum-sealed glass ampoules with elemental sulfur and tin shots. They were sulfurized for 30 min at 550 °C in the sulfur/tin mixing atmosphere. The solar cells using the sulfurized thin films 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 X-ray diffraction (XRD) and Raman spectroscopy. The surface and cross-section 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.

3. Results and discussions

Results of EPMA analysis, the S content in thin films was drastically increased by sulfurization. For example, the composition of the as-deposited thin film prepared at KF/CZTSe=3% was Cu:Zn:Sn:Se=13.7:16.9:17.1:52.3%,

and that of the sulfurized thin film was Cu:Zn:Sn:Se:S=17.1:19.4:12.9:2.8:47.7%. In this experiment, the S/(S+Se) mole ratio in the sulfurized thin films was approximately constant within 0.94 to 0.99. This indicates that Se in the as-deposited thin films is substituted for S selectively by sulfurization.

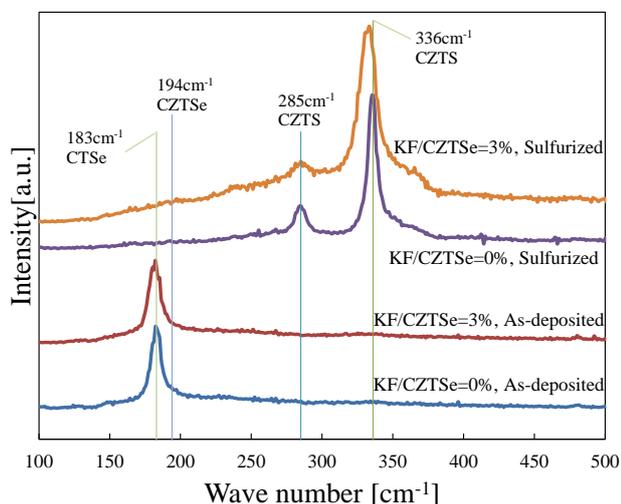


Fig. 1 Raman spectra of the as-deposited and the sulfurized thin films prepared at KF/CZTSe=0% and 3%.

The Raman spectroscopy was carried out for investigation of phase analysis and revealed that CZTSSe thin films were formed after a new crystallization process. Figure 1 shows the Raman spectra of the as-deposited and sulfurized thin films prepared at KF/CZTSe=0% and 3%. This figure shows the lines at 183cm⁻¹, 194cm⁻¹, 285cm⁻¹ and 336cm⁻¹ corresponding to the CTSe, CZTSe, and CZTS phases, respectively, for a comparison. No Raman peak attributed to CZTSe phase was detected in the as-deposited thin films, though the CZTSe compound was used as an evaporation material. The as-deposited thin films were comprised of CTSe mainly. It is considered that CZTSe compound disintegrated to CTSe and other materials by the vapor deposition. After the sulfurization treatment, the Raman peaks of the sulfurized thin films showed almost CZTS phase without CTSe phase. The slight difference of the peak position at around 336cm⁻¹ is due to the small amount of Se in CZTSSe thin film.

Figure 2 shows the current density-voltage characteristics of CZTSSe thin films solar cells prepared at KF/CZTSe=0% and 3%. The cell performances were improved by the KF doping. For CZTSSe thin film solar cell prepared at KF/CZTSe=3%, the cell efficiency was 1.95% with Voc=698mV, Isc=7.52mA/cm², and FF=0.38. Especially, the value of Voc increased from 406mV in CZTSSe solar cell without KF doping to 698mV, which improved greatly more than the Voc of the highest efficient CZTSSe solar cell [4] and our previous data [5, 6].

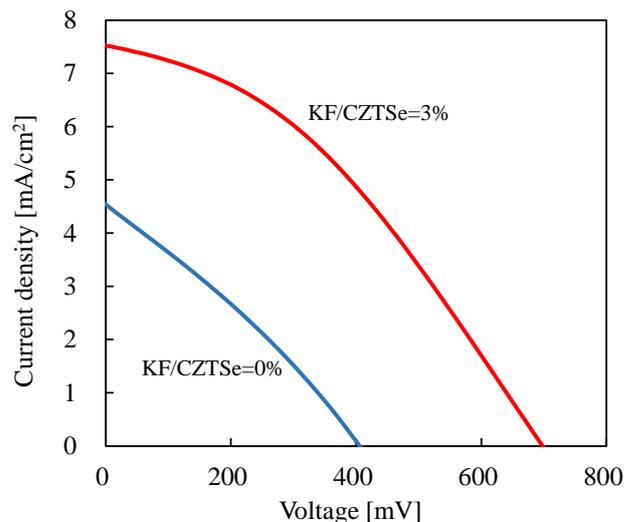


Fig. 2 Current density-Voltage characteristics of CZTSSe thin films solar cells prepared at KF/CZTSe=0% and 3%.

4. Conclusions

CZTSSe thin films were fabricated by sulfurization using a new crystallization process, which was a transformation from CTSe phase to CZTSSe phase. The KF doping technique in this process contributed to the improvement of an open circuit voltage in CZTSSe thin film solar cells. However, the cell performances could be further improved by optimizing the parameters of the crystallization process.

Acknowledgements

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