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$Cu_2ZnSn(S,Se)_4$ thin-film solar cells prepared by sulfurization using $Cu_2ZnSnSe_4$, NaF and KF compounds

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Abstract

$Cu_2ZnSn(S,Se)_4$ thin films were fabricated by sulfurization of the precursor evaporated from $Cu_2ZnSnSe_4$, NaF and KF compounds. From Raman analysis, the precursor prepared without NaF had mixed Cu_2SnSe_3 and $Cu_2ZnSnSe_4$ structure, and Cu_2SnSe_3 structure became dominant by adding NaF. After sulfurization, $Cu_2ZnSn(S,Se)_4$ was formed in all samples, even if the precursors had different structures. EPMA analysis revealed that the S/(Se+S) molar ratios in the sulfurized films were in the range between 0.95 and 0.97. The open circuit voltage V_{oc} and the short circuit current density J_{sc} of $Cu_2ZnSn(S,Se)_4$ thin-film solar cells fabricated using NaF and KF improved more than those of the solar cell fabricated using only KF.

1. Introduction

Earth-abundant materials of copper-zinc-tin-chalcogen-based kesterites such as Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe), and $Cu_2ZnSn(S,Se)_4$ (CZTSSe) are expected as good substitute materials for solar cell containing any rare metals. Now, the CZTSSe thin-film solar cells fabricated by a hydrazine-based solution deposition process which requires extreme caution during handling have achieved the record efficiency of 12.6% [1]. On the other hand, Lee et al. have achieved high conversion efficiency of 11.6% in the CZTSe thin-film solar cell which was fabricated by four-source thermal co-evaporation and selenization [2]. However, the conversion efficiencies of these are still lower than the $Cu(In,Ga)Se_2$ thin-film solar cell containing rare metal of indium which achieved the conversion efficiency more than 20% [3]. In recent years, the alkaline metals doping techniques were reported as one of the methods for improvement of the cell performances in $Cu(In,Ga)Se_2$ solar cells [3-5]. Previously, we have synthesized CZTSe compound and then used it as evaporation material to fabricate CZTSe thin films and solar cells, and investigated the effect of addition of NaF to CZTSe thin-film solar cell [6]. Moreover the synthesized CZTSe compound was used as evaporation material to fabricate CZTSSe thin films and solar cells, and investigated the effect of addition of KF to CZTSSe thin-film solar cell [7]. As a results, the improvement of the cell performances were confirmed by each alkaline metals addition. However, the effect of the co-addition of NaF and KF to CZTSSe thin-film solar cell has not yet been reported. In this study, we investigated the effect of NaF and KF co-doping to the CZTSSe thin-film for improvement of CZTSSe solar cell performance.

2. Experimental

The precursors were fabricated at substrate temperatures and evaporation times specified. First, substrates were preheated for 5 min at 600 °C with the subsequent evaporation of CZTSe compound at a substrate temperature of 300 °C. Next, Zn, Sn, and Se were co-evaporated at a substrate temperature of 500 °C. Finally, NaF, KF and Se were co-evaporated at a substrate temperature of 350 °C. The molar ratio of the evaporation materials were held constant at CZTSe:Zn:Sn=1.2:3.0:1.0 and KF/CZTSe=3.0%. The NaF/CZTSe molar ratio was varied from 0 to 10 %. Next, the precursors were set in the vacuum-sealed glass ampoules with elemental S and Sn shots, and then sulfurized under mixed S and Sn atmosphere with a Sn/S molar ratio of 0.2 for 30 min at 500 °C. We fabricated solar cells with a configuration of Al grid contact/Ga-doped ZnO transparent conducting layer/non-doped ZnO/CdS buffer layer/CZTSSe absorber layer/Mo back contact/SLG substrate. The details of fabrication process were described in our previous paper [6]. Compositions of the obtained thin films were determined from the results of the electron probe microanalysis (EPMA) performed by energy dispersive spectrometry (EDS) detector. The crystalline structure 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 (J–V) characteristics and quantum efficiencies (QE) of the fabricated solar cells were measured using standard 1 sun (AM1.5, 100 mW/cm^2) illumination.

3. Results and discussions

From the EPMA analysis, the Se content in all precursors was around 50 %. In addition, all precursors became Cu-poor composition of less than 25 % Cu content. After sulfurization, the S/(S+Se) molar ratio was approximately constant within 0.95 to 0.97. This indicates that Se in the precursor is substituted for S selectively by sulfurization.

Figure 1 shows the Raman spectra of the precursors and the sulfurized thin films which were prepared by changing NaF/CZTSe molar ratio under the constant of KF/CZTSe molar ratio of 3.0%. This figure shows the lines at 172cm^{-1},

$183 cm^{-1}$, $194 cm^{-1}$, $287 cm^{-1}$ and $337 cm^{-1}$ corresponding to the CZTSe, CTSe, and CZTS phases, respectively, for a comparison. Raman peaks corresponding to Cu_2SnSe_3 (CTSe) and CZTSe was observed for the precursor of NaF/CZTSe=0% which means only KF addition. Therefore, it is considered that the CTSe is coexisting with the CZTSe in this precursor. In the precursors which added NaF, the dominant Raman peak of CTSe was observed, which means that CZTSe compound in the evaporation materials disintegrated to CTSe during the vapor deposition. After sulfurization, the Raman peak was observed near $337 cm^{-1}$ indicating CZTS in all thin films. It is considered that this Raman peak corresponds to CZTSSe because the sulfurised thin films have high S/(S+Se) molar ratio range of 0.95 to 0.97 from EPMA analysis. From the above, even if the structure of precursor was different compound such as CTSe and/or CZTSe, it indicated that the CZTSSe structure was successfully formed by sulfurization process.

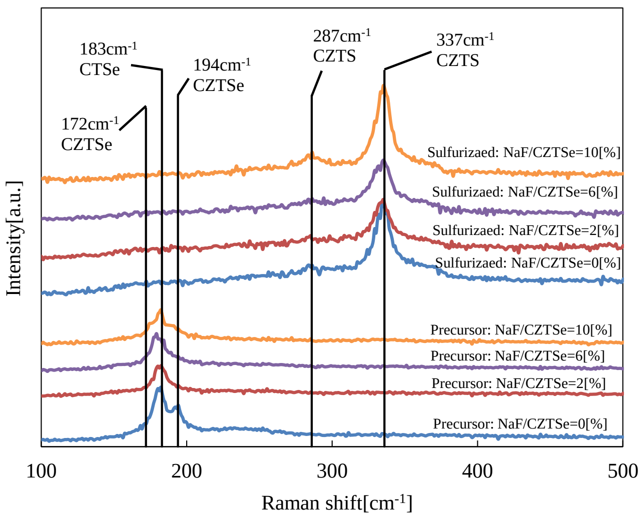

Figure 1 Raman spectra of the precursors and the sulfurized thin films prepared by changing NaF/CZTSe molar ratio.

Figure 2 shows the open-circuit voltage V_{oc} and the short-circuit current density J_{sc} of the CZTSSe thin-film solar cells which fabricated by changing NaF/CZTSe molar ratio. In the sample of NaF/CZTSe=0% which added only KF, V_{oc} was 560 mV, and Jsc was 5.4 mA/cm^2. The samples which added KF and NaF demonstrated the values of V_{oc} over 600 mV, and those were higher V_{oc} than the sample without NaF addition. Moreover, the great increase in J_{sc} was confirmed with addition of NaF, and there were several samples which J_{sc} increased more than double in comparison with the non-NaF sample. Therefore, it is considered that the adding both KF and NaF is a useful technique for improving the CZTSSe solar cell performance. The CZTSSe solar cell with the highest conversion efficiency in this study demonstrated V_{oc} = 674 mV, J_{sc} = 12.6 mA/cm^2, FF = 0.37 and η = 3.12%, which fabricated at NaF/CZTSe=6%.

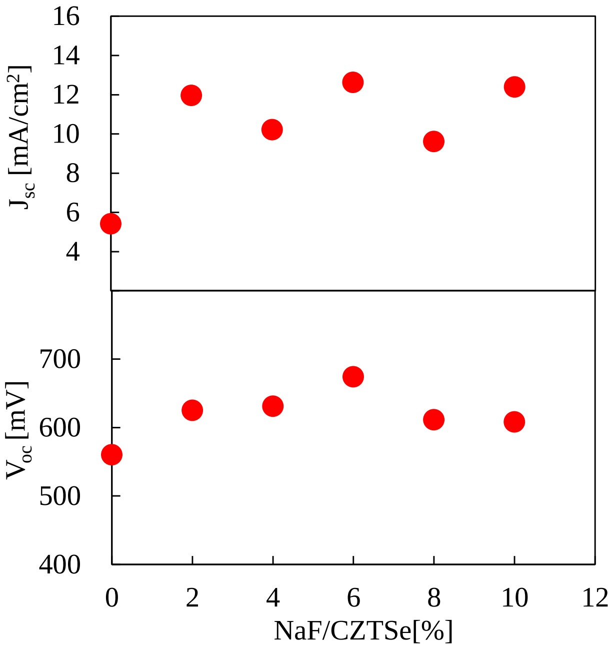

Figure 2 V_{oc} and J_{sc} of the CZTSSe thin-film solar cells fabricated by changing NaF/CZTSe molar ratio.

3. Conclusions

CZTSSe thin films and solar cells were fabricated by sulfurization of the precursor evaporated from $Cu_2ZnSnSe_4$, NaF and KF compounds. The precursors having CTSe phase were prepared by evaporation from CZTSe compound, and the CZTSSe phase was successfully formed after sulfurization. The CZTSSe solar cell performances were increased greatly by adding both KF and NaF to the precursor.

Acknowledgements

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