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Characteristics of $Cu_2ZnSnSe_4$ and $Cu_2ZnSn(Se,S)_4$ absorber thin films prepared by post selenization and sequential sulfurization of co-evaporated Cu–Zn–Sn precursors

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ABSTRACT

$Cu_2ZnSnSe_4$ and $Cu_2ZnSn(S,Se)_4$ absorber films processed from co-evaporated Cu–Zn–Sn precursor films by post selenization and sequential sulfurization were investigated by varying Cu/(Zn + Sn) ratio and selenization/sufurization temperatures. Structural, electrical and optical properties were largely dependent on the experimental parameters. The selenization process of the Cu–Zn–Sn precursors was successful in producing $Cu_2ZnSnSe_4$ phase with dense microstructure when the Cu/(Zn + Sn) ratio of 0.8 was initially used. The absorber led to a photovoltaic cell efficiency of ~1.04% with a short circuit current of ~21.9 mA/cm^2. Sequential sulfurization of the selenized films resulted in completely-transformed $Cu_2ZnSn(S,Se)_4$ phase with a minor secondary phase of Cu_2S. Cell performance was not improved after sulfurization primarily due to poor microstructural features that became worse with increasing the Cu/(Zn + Sn) ratio.

1. Introduction

In recent years, $Cu_2ZnSnSe_4$ (CZTSe) and Cu_2ZnSnS_4 (CZTS) quaternary semiconductor compounds have drawn significant interest for solar cell applications due to a sufficiently large absorption coefficient of $>10^4\ cm^{-1}$ and a direct band gap energy of >1.0 eV [1–5]. Furthermore, the constituent components Zn and Sn are highly earth-abundant elements, compared to the scarce and expensive ones such as In and Ga that are major portions of the known ~20% efficiency $Cu(In,Ga)Se_2$ (CIGSe) solar cells [6]. Various vacuum processes including evaporation, sputtering and pulsed laser deposition have been reported to prepare CZTSe or CZTS films. The recent achievement of ~9.15% efficiency for the CZTSe solar cells co-evaporated from elementary Cu, Zn, Sn and Se pellets has demonstrated high potentials as a future photovoltaic candidate [7]. Zoppi et al. have reported CZTSe solar cells prepared by selenization of sequentially sputtered Cu–Zn–Sn films with efficiencies of ~3.2% [8]. In addition, Moholkar et al. have shown a conversion efficiency of 4.13% for CZTS prepared by pulsed laser deposition when the ratio Cu/(Zn + Sn) of 1.1 was used [9].

The band gap engineering has been recognized as one of the practical ways to enhance the performance of thin film solar cells. The incorporation of sulfur into the CIGSe results in a slight increase in open circuit voltage V_{oc} due to the increase of band gap energy [10]. It is known that introducing S into CIGSe increases the level of conduction band E_c and reduces the energy portion of valance band E_v in a fairly equal proportion [11]. The shift in band gap depends strongly on annealing conditions [12]. For instance, higher annealing temperatures and longer times lead to more S incorporation and improve V_{oc}. In a similar way, application of the sulfurization process for CZTSe is expected to bring the similar effect of the band gap increase. However, there has been no report dealing with the sequential sulfurization effect of the selenized CZTSe absorbers on their electrical, optical and cell performance in any vacuum or nonvacuum process.

In this work, the post selenization of vacuum-evaporated Cu–Zn–Sn precursors is investigated in terms of selenization temperature and the elemental ratio Cu/(Zn + Sn), and then the subsequent sulfurization process is applied for further modification toward a higher band gap. As a comparative result, we suggest the potential of the post-selenized CZTSe absorber solar cells with an actual demonstration of cell efficiency as well as the observed effect of the sulfurization process.

2. Experiments

Precursor layer of CZTSe thin films was first prepared by thermal evaporation of metallic Cu, Zn and Sn pellets. The evaporation chamber was evacuated up to a base pressure of 4×10^{-6} Torr. The films were grown on a Mo-coated soda lime silicate glass substrate held at room temperature. During the deposition, the substrate holder was rotated for uniform deposition. The film with certain Cu/(Zn + Sn) ratio in the range of 0.8–1.1 was deposited by adjusting the pre-calibrated evaporation rate of each element for the desired target thickness. Total thickness of the

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deposited Cu–Zn–Sn precursor layer was about 800 nm. Selenization process was then carried out at different temperature between 500 °C and 570 °C for 20 min under N_2 flow by placing Se pieces inside a quartz tube in a furnace. As an additional step for sulfurization, only the 530 °C-selenized samples were exposed to a gas mixture of H_2S and N_2 at 530 or 570 °C for 20 min in atmospheric pressure.

Solar cells (having ~0.42 cm^2 of each cell area) based on a typical cell structure of glass/Mo/CZTSSe/CdS/i:ZnO/ZnO:Al/Al (without an antireflection layer) were fabricated. A CdS buffer layer of ~30 nm in thickness was deposited by chemical bath deposition on the absorber layer, and then the i:ZnO (~50 nm) and ZnO:Al (~350 nm) thin films were prepared by RF magnetron sputtering. An Al top grid on the ZnO window layer was deposited by thermal evaporation.

Phase analysis was performed by using an X-ray diffractometer (XRD: Rigaku B/Max-2500/PC, Tokyo, Japan) with Cu Kα radiation. Surface morphology and cross sectional images of the films were observed using a field-emission scanning electron microscope (FESEM: S-4700, Hitachi, Osaka, Japan). Atomic distributions for the selected samples were determined by an energy dispersive spectrometer (EDS: EMAX, Horiba, Kyoto, Japan) interfaced with the FESEM. Electrical properties including dark resistivity, Hall mobility and carrier concentration were measured at room temperature using a standard Hall measurement system (Model HMS-3000, Ecopia Co., Korea) in the van der Pauw configuration. Optical transmission and reflection of the films were analyzed at room temperature in the spectral range of 300–1800 nm using a UV–visible spectrophotometer (JASCOV530, Jasco, Japan). The current–voltage characteristics of the solar cells were measured under AM 1.5 spectrum with 1000 Wm^{-2} illumination at 25 °C.

3. Results and discussion

3.1. Effect of post-selenization of the evaporated Cu–Zn–Sn precursor

Fig. 1 shows the effect of selenization temperature of 500–570 °C on the XRD patterns of thin films selenized from the evaporated Cu–Zn–Sn precursor as exemplified with a Cu/(Zn + Sn) ratio of 0.8. All XRD patterns show polycrystalline CZTSe phase as a main phase along with either secondary Cu_2Se or $Cu_{2-x}Se$ phase. It is apparent that the selenization process easily converts the Cu–Zn–Sn precursor into CZTSe phase in this temperature range. Interestingly, the secondary phase of Cu–Se tends to transfer gradually from $Cu_{2-x}Se$ (JCPDS 00-006-0680) into stoichiometric Cu_2Se (JCPDS 03-065-2982) as the selenization temperature increases. The peak shift toward the lower angle between 44° and 45° is more clearly seen in the inset of Fig. 1 as indicated by an upward tilted arrow. This observation is understandable when assumed that Cu continuously fills in the vacant (or deficient) Cu site in $Cu_{2-x}Se$ while more Se becomes evaporated with increasing selenization temperature.

Fig. 2 shows the XRD patterns of the Cu/(Zn + Sn) ratio from 0.8 to 1.1 at the fixed selenization temperature of 530 °C. Increasing the ratio did not create any other phase but seemed to influence the degree of crystallization for both the CZTSe and $Cu_{2-x}Se$ phases. For instance, much stronger intensity peaks of the $Cu_{2-x}Se$ phase were found at the ratio of 1.1. It is obvious that the relatively larger amount of Cu facilitates crystallization with a sufficient supply of Cu and simultaneously induces more segregation of $Cu_{2-x}Se$ [13]. Similarly, it is known that Cu-rich composition in CZTSe promotes crystallization of CZTSe with the segregation of Cu–Se secondary phase [14,15].

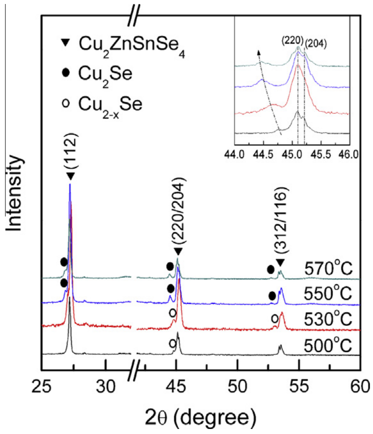

Fig. 1. XRD patterns of thin films selenized at different temperature from the Cu–Zn–Sn precursor film having the Cu/(Zn + Sn) ratio of 0.8.

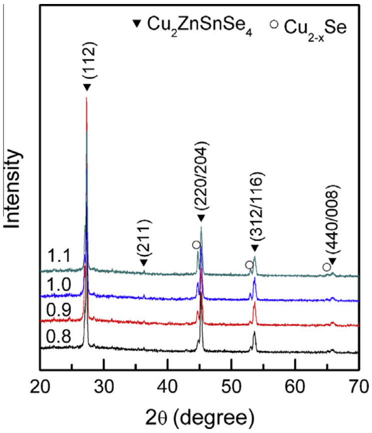

Fig. 2. XRD patterns of thin films selenized at 530 °C from the Cu–Zn–Sn precursor films having different Cu/(Zn + Sn) ratios of 0.8, 0.9, 1.0 and 1.1.

Fig. 3 represents surface microstructures and cross sectional images (as insets) of the CZTSe films processed with different ratios of Cu/(Zn + Sn) but selenized at the same temperature of 530 °C. Grain size tended to increase substantially with increasing the ratio. Distinguishable particulates over the surface became more evident at Cu-rich ratios of 1.0 and 1.1. According to the EDS analysis (not shown here), the particulates were identified as Cu-rich phase having the average Cu:Se ratio of 55.1:37.8, which is close to binary Cu–Se phase. It is known that the Cu–Se binary secondary phase is preferably located on high surface energy regions, such as surface and/or grain boundary, in the CZTSe absorbers [14]. Yoo and Kim [16] reported that Cu-rich films led to the formation of $Cu_{2-x}S$ whereas Cu-poor films favored a smoother film surface in the sputtered CZTS study. It suggests that the post selenization process prefers Cu deficient absorbers to achieve dense microstructure with least surface segregation and smoother surface.

3.2. Effect of sulfurization of the selenized CZTSe absorbers

Fig. 4 shows the XRD patterns of thin films after sulfurization of the 530 °C-selenized CZTSe films at 530 °C or 570 °C with different ratios of Cu/(Zn + Sn). The CZTSe phase completely disappeared resulting in $Cu_2ZnSn(S,Se)_4$ (CZTSSe) phase regardless of sulfurization temperature and Cu/(Zn + Sn) ratio. Smaller S^{-2} (170 pm) is assumed to be partially substituted into the Se^{-2} (184 pm) site during the sulfurization process. This complete phase transformation is similar to the sputtered $CuIn(Se,S)_2$ result where the transition into $CuIn(Se,S)_2$ phase was achieved depending on the degree of S incorporation that was determined by sulfurization conditions [17].

At 530 °C (Fig. 4a), increasing the Cu/(Zn + Sn) ratio caused the degree of crystallization of CZTSSe to increase with higher intensity peaks. A secondary phase close to the peaks of Cu_2S was found after sulfurization at the temperature. The peak position of the Cu_2S phase shifted distinctively toward the lower angle with increasing the ratio. At 570 °C, on the other hand, pure CZTSSe phase with sharper peaks were observed with no second phase even with increasing the Cu/(Zn + Sn) ratio. A higher sulfurization temperature seemed to prevent the formation of metallic impurity phase as reported elsewhere [18,19].