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The role of pre-annealing in the sulfurization of Cu-Zn-Sn stacked metal layer prepared by magnetron sputtering

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ABSTRACT

Cu_2ZnSnS_4 (CZTS) films were fabricated by sulfurizing the stacked metal layer (SML) prepared by DC magnetron sputtering. The influence of pre-annealing treatment of the SML precursor on the sulfurization process and the crystal growth characteristics of the CZTS film were investigated. It was found that the crystallinity of the CZTS film was improved with the increase of the pre-annealing temperature and duration, indicating that the pre-annealing treatment promoted the sulfurization. The formation and distribution of the metal compounds in the SML dominated the sulfurization reaction. And, the microstructure and elemental composition of the CZTS film depended very much on the properties of the SML. The role of pre-annealing treatment in the sulfurization of metal stacked precursors is proposed. A highly crystalline p-type kesterite Cu_2ZnSnS_4 film with carrier concentration of 2.38×10^{17} cm^{-3}, mobility of 1.38 $cm^2/V\,s$ and optical bandgap of 1.46 eV was obtained. The CZTS layers are expected to fabricate high efficiency thin film solar cells.

1. Introduction

Cu_2ZnSnS_4 (CZTS), a p-type semiconductor with a closed-optimized band gap (1.35 eV) of about 1.5 eV and a high optical absorption efficient, has attracted considerable interests as a promising absorber material for photovoltaic devices and has shown potential as an alternative to CdTe and CIGS owing to the use of abundance and non-toxic raw material [1–3]. Although considerable progress has been made since the first CZTS solar cell with a conversion efficiency of 0.66% was successfully manufactured in 1996 [4], even to this day there remains an on-going debate about the growth mechanism of CZTS, and some challenges have not been solved yet. Above all, it is tough to prepare single-phase CZTS owing to the increased degrees of freedom of chemical composition and structure for quaternary semiconductor and small scope of the stable chemical potential of CZTS [5,6]. Therefore, it is tough to avoid introduction of secondary phases which cause negative affect the photoelectric properties and device performance of the film [4]. For instance, the open-circuit voltage of device will be reduced owing to the existence of secondary phase (Cu_2SnS_3, for example) with a lower bandgap. And if Cu_2S compound is residual in the film, the carrier concentration of the film will be higher than desired. In addition, the loss of constituent elements attributed to the evaporation of volatile elements (such as Zn, Sn) and compounds decomposition was revealed in the high temperature synthesis of CZTS procedure resulting in the difficulty in composition-control of CZTS [7,8]. What's more, the low tolerance of compositional deviations increases the difficulty in preparing CZTS with controlled structure and uniform distribution in the experiment.

Various vacuum [9,10] and non-vacuum [11–13] based technologies have been applied to the synthesis of CZTS, magnetron sputtering has been considered as a blooming technique which has the potential for mass production due to its high deposition rate, good uniformity and high reproducibility, besides it is flexible to tune the crystallinity and constituent composition [14]. To date, sputtering applied to prepare CZTS thin film solar cell has received much attention, and various post-treatment conditions have been investigated. Nevertheless, it is tough to guarantee uniformity and composition of the film in the procedure of converting stacked metal layer (SML) precursors to single-phase CZTS. It has been suggested that high efficiency CZTS solar cells have a Cu-poor and Zn-rich composition of absorber layer. Some authors pointed out that Cu/Sn ratio had a significant effect on device performance, and a CZTS solar cell with 9.2% efficiency was prepared by adjusting Cu/Sn ratio [15]. In addition, other authors demonstrated co-sputtering which can mix constituents uniformly from target and react faster in the sulfurization process [16,17]. Alternatively, the CZTS film can be prepared using a quaternary target which is more

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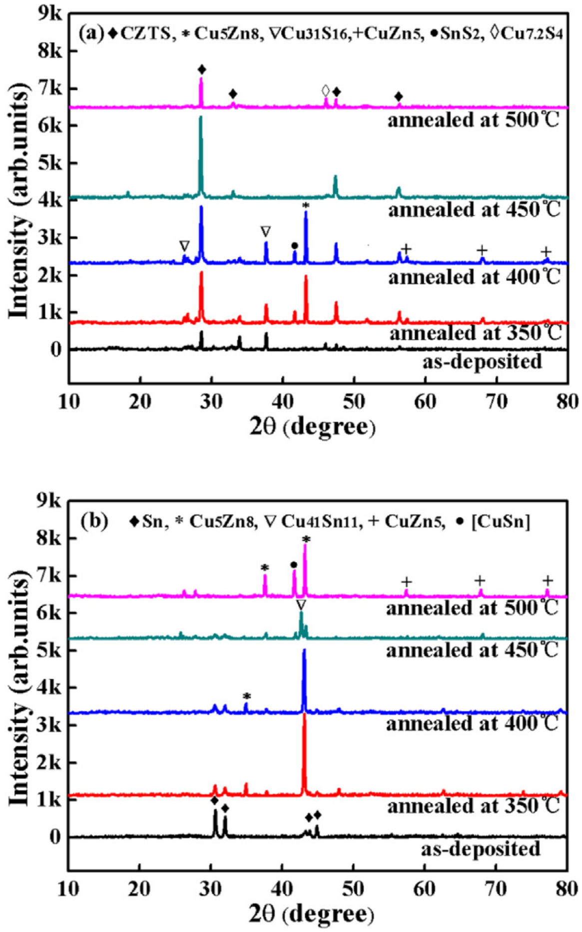

Fig. 1. XRD spectra of (a) post-sulfurized samples and (b) SML precursors annealed at various temperatures for 10 min.

convenient to control element proportion, especially it can be manufactured in one-step by adjusting the substrate temperature [18,19].

Furthermore, it was found that pre-annealing treatment applied to the precursors was equally beneficial to the post-sulfurization [20,21]. The optimum conditions of pre-annealing to achieve better device performance have been reported [12], but the influence of pre-annealing on the preparation of CZTS thin films is still matter of debate. In this study, the dependence of the crystallinity and composition of post-sulfurized thin films on various pre-annealing temperatures and durations are discussed on the basis of analysis of the phases and microstructure. In addition, the effect of temperature on the reaction order of the three metal elements is demonstrated as well.

2. Experimental

Three highly pure (4 N) Cu, Zn and Sn metal targets (75 mm diameter and 4 mm thickness) was used to deposit the Cu-Zn-Sn SML precursors. The layers of Cu, Zn and Sn were sequentially deposited on soda lime glass (SLG) substrates (2.5 cm × 3.0 cm) at room temperature via a DC magnetron sputtering process. The stacking order was SLG/Cu/Zn/Sn. The sputtering power for Cu, Zn, Sn targets were fixed at 100 W, 60 W and 30 W, and the deposition time were 20, 35, 45 min, and the thickness of each layer was approximately 245 nm, 118 nm and 125 nm respectively. The base pressure of the sputtering system was 6.0×10^{-4} Pa and the working pressure was kept at 1.0 Pa. Sulfurization was accomplished at 550 °C in a vacuum furnace without any protection atmosphere. The sulphur source was pure sulphur nanoparticle powder placed in a graphite crucible (the volume was about 2×10^{-4} m^3) along with the samples. The mass of sulphur powder was 150 mg. Prior to the sulfurization process, the SML precursors undergone pre-annealing at different temperatures (350 °C, 400 °C, 450 °C and 500 °C) and different annealing times (5, 10, 20 and 30 min) in the same furnace, as indicated in parentheses. The infrared lamp was used for heating. The heating current was 10 A (the rising-rate of temperature was approximately 1 °C/s). The samples were allowed to cool down naturally in the furnace.

3D optical profiler (Wyko 9100) was applied to detect thickness of films. X-ray diffraction (XRD, Empyrean) analysis using Cu Kα radiation (λ = 1.5405 Å), in the 2θ range of 10–80°, was used to analyse the phase composition of the samples. The microstructure and composition contents of the films were determined by scanning electron microscopy (SEM) with an energy dispersive X-ray spectroscopy (EDS) system (Quanta 400/INCA). A Hall effects measurement system (PhysTech RH2035) using the van-der-Pauw method was employed to character electrical properties such as carrier concentration, carrier mobility and resistivity of the CZTS. The measured error is < 2%. The optical transmittance spectra analysis were carried out with a UV–visible spectrophotometer (Hitachi U-4100).

3. Result and discussion

Fig. 1(a) depicts the XRD spectra of the post-sulfurized samples whose SML precursors were pre-annealed at various temperatures. The sulfurization temperature was 550 °C, and the duration time was 5 min. The sulfides $Cu_{31}S_{16}$ and $Cu_{7.2}S_4$ were observed besides the CZTS phase in the XRD patterns of the film without pre-annealing treatment. The weak and various phases' diffraction peaks of the sample indicated the poor crystallinity. In contrast, the crystallinity was improved after pre-annealing treatment was applied to the SML precursors. The structure characteristics of the samples strongly depended on the pre-annealing temperature. It can be noted that Cu_5Zn_8, $CuZn_5$ alloys and SnS_2 secondary phases were detected in the post-sulfurized films at the temperatures of 350 °C and 400 °C. This is due to the insufficient sulfurization. As the temperature was increased to 450 °C, improvement of the crystallinity of the sample was found. The diffraction peaks were sharp and intense, and no obvious impurity peak was detected. However, when the temperature was further increased to 500 °C, a weak $Cu_{7.2}S_4$ secondary phase was detected. It can be concluded that the crystallinity of post-sulfurized films was promoted when the SML precursors were annealed at a relative higher temperature. To further study the influence of pre-annealing, phase compositions of the SML pre-treated at different temperatures were investigated and the results are illuminated in Fig. 1(b). Significant different in the phase structure of SML was observed. The as-deposited sample consisted of metal Sn and Cu/Zn or alloy phase. The peak intensity of the Sn phase was gradually reduced with the increase of the annealing temperature, while the diffraction peak of Cu_5Zn_8 alloy phase was gradually enhanced. It can be confirmed that the metals transferred to metal alloys after the annealing treatment. However, it should be noted that Sn and Cu_5Zn_8 were predominate phases after the sample annealed at 350 °C and 400 °C. As the annealing temperature was increased to 450 °C, Cu_5Zn_8 transferred to $CuZn_5$, and Sn was consumed totally and transformed to $Cu_{41}Sn_{11}$ and CuSn alloys. Once the temperature was further

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