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Morphological evolution and structural properties of $Cu_2ZnSn(S,Se)_4$ thin films deposited from single ceramic target by a one-step sputtering process and selenization without H_2Se

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$Cu_2ZnSn(SSe)_4$ (CZTSSe) thin films were successfully deposited on TiN/Mo-coated glass substrate using RF-sputtering from single ceramic CZTSSe target, followed by annealing at 400–600 °C for 1 h in Se atmosphere. The influence of substrate heating (RT–300 °C) and post-selenization on the morphological, structural, and compositional properties of the films were investigated using X-ray diffraction, scanning electron microscopy, and energy dispersive X-ray spectroscopy, as well as by Raman scattering and X-ray photoelectron spectroscopy. The crystallinity with preferential (1 1 2) orientation of the as-sputtered precursor films increased with increasing the substrate temperature and the selenization temperature. Compared with the thin films as deposited, post-selenization (400–600 °C) further improved the microstructure features and elemental compositions. The thin films selenized at 600 °C got dense microstructure and large grain size of 2 μm, nearly stoichiometric Cu-poor and Zn-rich compositions with Cu/(Zn + Sn + Sb) ~0.78 and Zn/Sn ~1.24, and tetragonal structure with lattice parameters $a = 5.663$ Å, $c = 11.234$ Å. This study provides an insight into the use of single ceramic CZTSSe target sputtering method to demonstrate the selenization conditions, such as substrate temperature and selenium partial pressure, for improving the film crystallinity, stoichiometry and grain growth.

1. Introduction

$Cu_2ZnSn(S,Se)_4$ (CZTSSe) compound is a potential candidate for absorber layers to replace $Cu(In,Ga)Se_2$ (CIGS) in thin film solar cell applications due to its high absorption coefficient higher than 10^4 cm^{-1} and its band gap range from 1 to 1.5 eV [1,2]. Being mainly constituent of naturally abundant elements with low toxicity, CZTSSe kesterites have emerged as promising low cost and high efficiency materials for thin film solar cell technologies. A variety of processing techniques, such as thermal evaporation [3], solution-based process [4], electrodeposition [5] and sputtering [6], have been investigated to prepare high quality CZTSSe thin films. CZTSSe solar cells processed from a hydrazine-based precursor solution have achieved a record efficiency of 12.7% [4], exhibiting the capability of this still poorly understood material. Yet, the hazards associated with hydrazine may inhibit the adaptation of this particular method for large-scale industrial production. In this regard, sputtering is one of the promising methods which are viable for large-scale production of CZTSSe thin films with demonstrable productivity and easy adjustment. The best CZTSSe cells are made by respectively co-evaporation and sputtering processes and reach an efficiency of 9.15% [7] and 11% [8]. All the good performance of CZTSSe solar cells is related to a Cu-deficient and Zn-rich conditions with the Cu/(Zn + Sn) ratio at 0.8–0.95 and Zn/Sn ratio at 1.10–1.25 [9,10].

Post-selenization of precursor layers is one of the leading methods to fabricate the CZTSSe absorber layers. The precursor layers are typically prepared by sputtering or evaporation to sequentially deposit metallic elements and/or alloys with or without selenium or sulfur [5,11,12]. However, the major issue of these multi-source processes is inhomogeneity in compositions of the precursor layers. A post-selenization process at temperatures of typically 450–600 °C under a controlled inert or reactive atmosphere such as H_2Se is then followed, converting the precursor layers into CZTSe absorber layers [13,14]. But, H_2Se is known to have toxicity problem. For an alternative use of H_2Se vapor, Se or $SnSe_2$ sources have been used [15–18]. The selenization process by utilizing Se element above 500 °C easily led to porous and rough CZTSe films. The utilization of $(SnSe_2 + Se)$ pellets for selenizing sputtered

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Cu–Zn–Sn films has been also reported [19]. The control of Se/S flux is actually important to hold CZTSSe in stoichiometry, to allow grain growth, and to avoid the Se/S vaporization and phase transformation by reduction.

Compared with other fabrication technologies, sputtering directly from a single target overweighs others in terms of cost effectiveness through the use of one power source, easily adjustable compositions, and simplicity to produce films with good uniformity and surface morphology. The use of Cu–Zn–Sn single target to prepare CZTSe thin films by sputtering method with a need of additional selenization has been reported [19]. On the other report, $Cu_2ZnSnSe_4$ thin films were prepared by selenization of one-step electroplating deposited Cu–Zn–Sn–Se precursors [20]. However, to the best of our knowledge, a study on the use of single CZTSSe target sputtering in achieving good grain growth, morphology and compositional homogeneity in the films has not been reported. A simple single-target approach can avoid the complex sequential deposition process. The selenization parameters, such as substrate temperature and selenium partial pressure play a key role to control film composition. Hence suitable growth and selenization strategies need to be explored to arrive at optimal growth/selenization conditions while simultaneously achieving the desired micron sized grains with compositional and morphological homogeneity. The aim of this work is to optimize the process conditions to grow CZTSSe films from single ceramic target sputtering without the extra control of deposition sequence in achieving large grains, uniform composition and better structural quality suitable for solar cells applications. The study only dealt with the growth and characterization of CZTSSe thin films without the fabrication of CZTSSe solar cells.

In this report, CZTSSe thin films were prepared on TiN/Mo-coated glass substrate with a cost-effective single ceramic target, one-step radio frequency (RF) magnetron sputtering process. The deposition of TiN thin layer can be used to obtain dense and void-free films, and also to reduce the formation of $MoSe_2$ interface, which may suppress the injecting of the majority carriers [21,22]. In order to optimize the synthesis conditions, CZTSSe precursor films were performed at different substrate temperatures followed by post-selenization. The selenization was done with Se vapor from the ($SnSe_2$ + Se) pellet thus avoiding the use of toxic H_2Se. We also investigated the connection between the precursor deposition temperatures and the post-selenized film properties. Furthermore, influences of selenization temperature on the compositional, morphological and structural properties of the grown CZTSSe films are discussed.

2. Experimental details

CZTSSe thin films were deposited on TiN/Mo-coated glass substrates by radio frequency (RF) balanced magnetron sputtering system using Cu–Zn–Sn–S–Se single ceramic target (130 mm diameter and 2 mm thick) with a power of 70 W for 90 min. The CZTSSe target was made by the hot pressing method at 450 °C for 30 min under a pressure of 45 psi (pound per square inch) in a graphite die from self-prepared (Cu_2Se, $SnSe_2$) and commercially purchased (ZnSe, Sb_2S_3, Te) powders. Sb2S3 and Te were added for densification purpose and anionic S and Te sources. The constituent weights were actually based upon the actual formula of $Cu_{1.8}[(ZnSn)_{0.9}Sb_{0.2}](Se_{3.3}S_{0.3}Te_{0.4})$. Prior to film deposition, the sputter chamber was evacuated to approximately 6×10^{-4} torr using oil-based high vacuum pump. The distance between target and substrate was about 120 mm. Argon was introduced as working gas during the sputter deposition with a flow of 40 sccm, and the sputtering pressure was controlled to 1.1×10^{-2} torr. The substrates were ultrasonically and chemically cleaned in organic solvents. The Mo back electrode (~1.0 μm) was deposited on glass by direct current (DC) sputtering at 100 W with a substrate temperature of 400 °C for 2 h. TiN thin layer (~200 nm) onto Mo-glass substrate was also deposited by DC sputtering (50 W) at 200 °C for 20 min. In order to investigate the effect of substrate temperature (T_{sub}) on the growth of CZTSSe films, the films were deposited at T_{sub} = RT (room temperature), 100 °C, 200 °C, and 300 °C. During selenizaion, the as-deposited precursor was inserted into a ceramic boat containing single ($SnSe_2$ + Se) pellet in order to supply selenium vapor during the selenization process. This tube was then placed inside a stainless steel tube furnace and the selenization process executed with a step-heating procedure at atmospheric pressure under a constant flow of Ar gas. In the first stage, the sample was kept at 300 °C for 30 min, then the temperature was increased to 400–600 °C and the sample was kept for 1 h at the second stage.

The composition and growth morphology of the as-sputtered Cu–Zn–Sn–S–Se precursor and selenized $Cu_2ZnSn(S,Se)_4$ films were characterized by a scanning electron microscope (SEM; JEOL JSM-6390LV) equipped with an energy dispersive spectrometer (EDS). The structural properties of the precursor and selenized CZTSSe films were investigated using X-ray diffractometry (XRD; Bruker D2). The phase components of the selenized CZTSSe films are characterized by Raman spectroscopy equipped with a 514.5 nm Ar laser. X-ray photoelectron spectroscopy (XPS; VG Scientific) with an Al Kα radiation source was used to determine the chemical bonding. All measurements were performed at room temperature.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of CZTSSe precursor films deposited at different substrate temperatures (T_{sub}) for 90 min. At room temperature, the (1 1 2)-oriented reflection is suppressed, and the film is almost amorphous except very weak orientation of (332/316) plane. When the substrate temperature increased to 100 °C, additional broad peak appeared which can be assigned to CZTSSe (1 1 2). This indicates that the formation of (1 1 2) preferential orientation had started. With an increase in substrate temperature from 200 to 300 °C, the XRD patterns exhibited three peaks, which could be perfectly indexed to (1 1 2), (220/204), and (332/316) of kesterite CZTSSe. No distinct peaks of secondary phases are observed in the XRD pattern. The intensity of (1 1 2) preferred orientation increased with increasing the deposition temperature to 200 °C. XRD pattern of films deposited at T_{sub} = 300 °C clearly shows that there is a slightly decrease in the intensity of (1 1 2) peak of CZTSSe when compared to the pattern of T_{sub} = 200 °C. At higher T_{sub}, probably due to loss of volatile constituents through re-evaporation, the formation of crystalline CZTSSe might have been hindered [23]. So the intensity of the diffraction peaks became weak. The full width at half maximum (FWHM) of a diffraction peak from the 112 plane is shown in Fig. 1(b) as a function of substrate temperature (T_{sub} = 100–300 °C). It could be observed that the FWHM value varies from 0.60° to 0.31°. It was found that the FWHMs of deposited films were significantly narrower with increasing substrate temperature, indicating better crystallinity.

Fig. 2(a)–(d) shows the plane FESEM images obtained for the as-sputtered CZTSSe precursor films on TiN/Mo/glass substrate at different substrate temperatures. All the obtained precursor films are dense, smooth, and homogeneous. The as-sputtered film at room temperature has well-defined grain structures and large grain size about 200 nm (Fig. 2(a)). However, grain size becomes smaller with increasing the substrate temperature from 100 °C to 300 °C. The grain sizes for thin films at the substrate temperature of 100 and 200 °C were 100 and 50 nm, respectively (Fig. 2(b) and (c)), while small grains about 30 nm and unclear grain boundaries were obtained at the substrate temperature of 300 °C (Fig. 2(d)). The small grains at higher substrate temperature may due to re-evaporation of non-metal precursors (S, Se or Te) from the substrate. This result was consistent with the reduced (1 1 2) peak intensity from XRD study (Fig. 1(d)). The SEM result demonstrates better grain growth at a substrate temperature up to 200 °C unlike for 300 °C.

In order to investigate the connection between the precursor deposition temperatures and the selenized film properties, each precursor film deposited at different temperatures was selenized at 600 °C for 1 h. This selenization temperature was kept constant for each precursor sample. Fig. 3 shows FESEM images of the selenized films at 600 °C for 1 h from as-sputtered precursor films at (a) RT, (b) 100 °C, (c) 200 °C, and (d) 300 °C. After annealing in Se vapor, the morphology is drastically changed. The selenized films from low substrate temperatures of RT and 100 °C got an