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Band gap tunable and improved microstructure characteristics of $Cu_2ZnSn(S_{1-x},Se_x)_4$ thin films by annealing under atmosphere containing S and Se

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A B S T R A C T

$Cu_2ZnSn(S_xS_{1-x})_4$ (CZTSSe) thin films were prepared by annealing a stacked precursor prepared on Mo coated glass substrates by the sputtering technique. The stacked precursor thin films were prepared from Cu, SnS_2, and ZnS targets at room temperature with stacking orders of Cu/SnS_2/ZnS. The stacked precursor thin films were annealed using a tubular two zone furnace system under a mixed N_2 (95%) + H_2S (5%) + Se vaporization atmosphere at 580 °C for 2 h. The effects of different Se vaporization temperature from 250 °C to 500 °C on the structural, morphological, chemical, and optical properties of the CZTSSe thin films were investigated. X-ray diffraction patterns, Raman spectroscopy, and X-ray photoelectron spectroscopy results showed that the annealed thin films had a single kesterite crystal structure without a secondary phase. The 2θ angle position for the peaks from the (112) plane in the annealed thin films decreased with increasing Se vaporization temperature. Energy dispersive X-ray results showed that the presence of Se in annealed thin films increased from 0 at% to 42.7 at% with increasing Se vaporization temperatures. UV–VIS spectroscopy results showed that the absorption coefficient of all the annealed thin films was over 10^4 cm^{-1} and that the optical band gap energy decreased from 1.5 eV to 1.05 eV with increasing Se vaporization temperature.

1. Introduction

Recently, chalcogenide-based materials, in particular CdTe- and $Cu(In,Ga)Se_2$ (CIGS), have become commercialized candidates for large scale photovoltaic (PV) manufacture, having already achieved stable and high power conversion efficiency (PCE) [1]. Unfortunately, they have some drawbacks such as scarcity of In, Ga, and Te and the potential environmental issue resulting from Cd, indicating limitation for commercialization of low cost and high PCE thin film solar cells (TFSCs) [2]. Even though TFSCs containing earth abundant elements can be achieved, similar to PCE for CdTe or CIGS, they may be a long term solution for the realization of cost-effective TFSCs [3]. The kesterite $Cu_2ZnSn(S_x,Se_{1-x})_4$ (CZTSSe)-based materials, which are promising candidates for In- and Ga-free absorber layers, have recently attracted interest for PV applications due to their suitable optical band gap energy from 1 eV to 1.5 eV, high absorption coefficient over 10^4 cm^{-1} in the visible wavelength region, and high stability characteristic compared to CdTe- and CIGS-based TFSCs [2,3]. In addition, W. Hillhouse et al. show the maximum efficiency for single junction Cu_2ZnSnS_4 and $Cu_2ZnSnSe$ TFSCs devices and use photon balance calculations (Shockley–Queisser style detailed balances, CZTSe, η = 31.0%, and CZTS, η = 32.4%) [4,5]. Previous literature surveys for CZTSSe-based TFSCs indicate the best efficiency of 11.1% is achieved using a solution-based hybrid slurry process [6], while vacuum-based processes

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provide a lower efficiency of 9.15% using the CZTSe absorber layer by the co-evaporation method [7]. Even though a wide band gap energy of 1.5 eV from the CZTS absorber material is expected, the high theoretical efficiency, practicality, and band gap energy of the highest PCE for CZTS-based TFSCs is about 1.0 eV ∼ 1.15 eV due to the requirement of controlling the conduction band offset between the absorber and buffer layers. Therefore, it is necessary to precisely control the band gap engineering of CZTSSe-based absorber materials without secondary phases and substituted element segregation to improve the PCE. Several studies report the band gap engineering of CZTSSe-based absorber materials using Se, Ti, Pb, and Ge in the CZTS absorber compounds [6,8–12]. J. Krustok, J. He, and other researchers have reported the band gap engineering of CZTS-based absorber compounds by introducing Se elements, and the band gap energy of CZTSSe decreased from 1.5 eV to 0.95 eV with increasing Se concentrations [8,10,13,14]. S. M. Lee et al. reported the systemic phase development and characterization of $(Cu_{2-x},Pb_x)ZnSnSe_4$ and $Cu_2Zn(Sn_{1-y},Ti_y)Se_4$ compounds by introducing Pb and Ti elements in the CZTSe. The band gap energy of these compounds increased from 1.43 eV to 1.81 eV (Pb substitution) and from 1.43 eV to 2.1 eV (Ti substitution), respectively [12]. S.B. Bag et al. reported the synthesis of $Cu_2Zn(Sn_{1-x},Ge_x)(S_{1-y},Se_y)_4$ (CZTGSSe) nanocrystals (NCs) formed using a hydrazine-based mixed particle-solution approach method. The band gap energy of CZTGSSe NCs increased from 1.0 eV to 2.0 eV with increasing S and Ge concentrations and 9.14% PCE of CZTGSSe-based TFSCs ($x = 0.4$, $y = 0$) has been achieved at a band gap energy of 1.15 eV [15]. Although previous researches have confirmed the effective and systematic band gap engineering of CZTS-based absorber materials, more detailed research on fine tunable band gap engineering and controlling microstructure, through the addition of Se in the CZTS absorber materials, is required in order to improve the PCE of CZTSSe-based TFSCs.

In this manuscript, we report the systematic synthesis and band gap engineering of CZTSSe thin films prepared by annealing of a sputtering deposited stacked precursor with a $Cu/SnS_2/ZnS$ order in a Se vapor + N_2 + H_2S atmosphere. The effects of different Se vaporization temperatures from 250 °C to 500 °C on the structural, morphological, compositional and optical properties of CZTS thin films were investigated.

2. Experimental details

The CZTSSe thin films were prepared on Mo coated glass substrates by annealing the stacked precursor under atmospheres containing Se and S. The stacked precursor thin films were sequentially deposited by sputtering method from Cu (99.999%), SnS_2 (99.99%), and ZnS (99.99%) targets at room temperature with stacking orders of $Cu/SnS_2/ZnS/Mo$/glass. One micrometer thick Mo back contact thin film with bi-layered structure was prepared by DC sputtering technique at room temperature. After Mo back contact thin film deposition, the films were introduced into the sputtering chamber. The chamber was evacuated to 2×10^{-6} Torr base pressure and the substrates were then cleaned using a plasma treatment. High purity Ar gas (99.999%) was used as the plasma source and the gas flow rate was controlled by using MFC (mass flow controller) at a 30 sccm. The RF power was fixed at 150 W for the ZnS and SnS_2 targets and the DC power was fixed at 40 W for the Cu target. The working pressure was fixed at 5 mTorr. The thicknesses of ZnS, SnS2, Cu layers were 500 nm, 700 nm and 200 nm, respectively. The Se pellets and precursor thin films were placed in the left and right zones, respectively, in a tubular furnace system. The stacked precursor thin films were annealed under the mixed N_2 (95%) + H_2S (5%) + Se vapor atmosphere. The Se vaporization temperature was varied from 250 °C to 500 °C at an interval °C, while the precursor thin films were fixed at 580 °C for 2 h. The pressure during selenization process was kept at 780 mTorr. After the annealing process, the annealed thin films were cooled naturally for 4 h.

The structural properties of thin films were measured by using high-resolution X-ray diffraction (XRD, X'pert PRO, Philips, Eindhoven, Netherlands) operated at 40 kV and 30 mA and analyzed through Raman scattering spectroscopy using a Jobin-Yvon T64000 Raman scattering system with an Olympus microscope equipped with a 100× magnification lens and in the backscattering configuration. The excitation source was an Ar ion laser operating at a 514 nm wavelength and at 220 mW output powers. The chemical binding energies of the annealed thin films were examined using high-resolution X-ray photoelectron spectroscopy (HR-XPS, VG Multilab 2000, ThermoVG Scientific, UK). The surface morphology of the thin films was characterized by using field emission scanning electron microscopy (FE-SEM, Model: JSM-6701F). The compositional property of thin films was examined using energy-dispersive X-ray spectra (EDS) attached to the FE-SEM. The optical properties of thin films were measured using UV–visible spectroscopy (Cary 100, Varian, Mulgrave, Australia) at room temperature.

3. Results and discussion

Fig. 1 shows XRD patterns (a) and peak positions for the 112 plane (b) of the stacked precursor and annealed thin films prepared

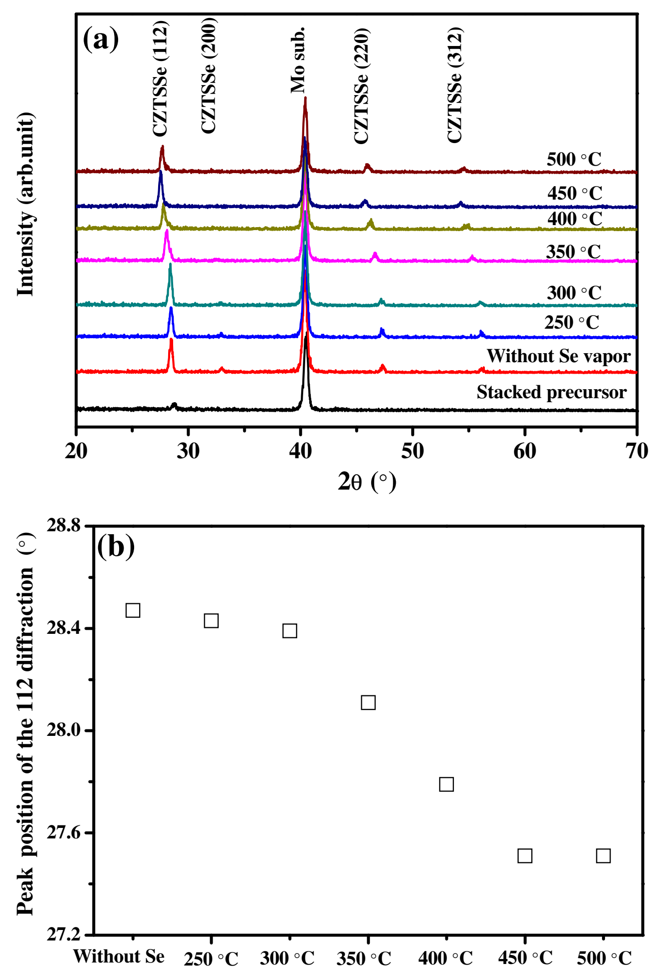

Fig. 1. X-ray diffraction patterns (a) and (112) peak position of the annealed CZTSSe thin films prepared with different Se vaporization temperatures.