



Effect of post-deposition annealing on the performance of D.C. sputtered Cu_2SnSe_3 thin films

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ABSTRACT

Cost-effective Cu_2SnSe_3 thin films for the absorption layer of solar cells were prepared by D.C. sputtering. Different sputtering targets were fabricated by sintering the different mixtures of Cu_2Se and SnSe_2 powders. SnSe_2 instead of commercially available SnSe was self-synthesized and used for thin-film solar cells for the first time. With our approach, Cu_2SnSe_3 thin films can be treated at higher temperatures for the benefit of larger grain size, which is an important factor for the performance of solar cells. The effects of target composition and annealing temperature on the properties of Cu_2SnSe_3 thin films were investigated. Structure, surface morphology, composition, and electrical and optical properties at different process conditions were measured. After 500 °C annealing, 400 °C-sputtered films can display with the direct band gap of 0.84 eV and has an electrical resistivity of $\sim 0.18 \Omega \text{ cm}$, absorption coefficient of $10^4\text{--}10^5 \text{ cm}^{-1}$, carrier concentration of $\sim 10^{19} \text{ cm}^{-3}$, and electrical mobility of $3\text{--}10 \text{ cm}^2/\text{V s}$.

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1. Introduction

Polycrystalline thin-film solar cells have been developed for saving the utilization of silicon wafer. Chalcopyrite compounds based upon CuInS_2 (CIS) or CuInSe_2 (CISE) are the major candidates for absorber layer. These thin-film solar cell systems, $\text{Cu}_2(\text{In,Ga})\text{Se}_4$ (CIGSe) or $\text{Cu}_2(\text{In,Ga})\text{S}_4$ (CIGS), or the systems alloying gallium and sulphur with CIS have shown the most promising performance in converting solar energy into electricity [1,2]. Although it is recognized that a CIS-based system has achieved the best efficiency, it further develops and has been concerned for the expansive and limited resource of metal indium. The research and development of the solar cell that composes abundant materials without using any rare metals are extremely important. CIS-derived $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) and $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) solar cell systems have the potentials to be the CIGS replacements for the considerations of the supply of the rare metal indium [3–5]. CZTSe thin-film solar cells over 6.7% efficiency were obtained by soaking the CZTS layer on the Mo-coated glasses in deionized water after forming the CZTSe layer, which eliminated selectively metal oxide particles in the CZTSe layer [4,6].

The preparation of the CIS-, CISE-, CZTS-, or CZTSe-based absorber layer, limited by the easy loss of Se or S due to their higher vapor pressure, needs to be performed by individually controlling the element vapor flux with the methods of co-evaporation, co-sputtering, and molecular beam epitaxy [2,7–12]. To ensure the right stoichiometry in composition, the

grown absorber layer annealed under H_2S or H_2Se had shown better performance. The components used for co-depositing CZTSe layers contain Cu_2Se , CuSe , ZnSe , Sn , Se , and SnSe [5,10,13]. Wibowo et al. grew CZTSe films below 200 °C and found that the sputtering targets should contain a Cu_2Se component in order to have the Se content above 40% [13]. SnSe is the only commercially available tin selenide compound and all the sputtering research in CZTSe films utilizes SnSe . The other tin selenide compound is SnSe_2 . This compound is expected to provide more Se during deposition, as compared with SnSe . The effects of SnSe_2 being used as the target composition on the sputtering growth and performance of CZTSe films remain unclear.

CZTS-related solar cell systems have the potentials to be the CIGS or CIGSe replacements for the considerations of the supply of the rare metals indium and gallium. There are no reports yet for Cu_2SnSe_3 films prepared by sputtering technique. As $\text{Cu}_2\text{ZnSnSe}_4$ can be easily synthesized by mixing Cu_2SnSe_3 and ZnSe , it is the purpose of this study to firstly investigate and understand the growth and characterizations of Cu_2SnSe_3 films before we conduct the study of $\text{Cu}_2\text{ZnSnSe}_4$ films at the next step. To take the advantage of SnSe_2 , this Cu_2SnSe_3 thin-film study utilizes the targets obtained by sintering the powders of Cu_2Se and SnSe_2 .

2. Experimental

Cu_2SnSe_3 films were prepared by single-source D.C. sputtering at 400 °C for 3 h with three different targets having the compositions in the molar ratios of Cu_2Se and SnSe_2 at 2/1, 1.8/1, and 1.6/1, abbreviated as targets A, B, and C, respectively. Cu_2Se and SnSe_2 powders were

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synthesized by ball-milled mixing of Cu and Se and Sn and Se, respectively, followed by firing at 200 °C for 3 h under vacuum. The 2-inch targets were hot pressed at 650 °C for 30 min under argon with a hydraulic pressure of 400 psi. The 400 °C-sputtered films were annealed at 450–600 °C for 1 h under SnSe₂ and Se pellets for the purpose of compensating the loss of Se in Cu₂SnSe₃ films during annealing. Growth morphology of Cu₂SnSe₃ films was characterized by field-emission scanning electron microscopy (FE-SEM, JSM 6500F, JEOL, Japan). Energy dispersive spectroscopy (EDS) equipped on SEM was used to semiquantitatively analyze the phase composition. Crystal structure was analyzed by X-ray diffractometry (XRD, D/Max-RC, Rigaku, Japan). Resistivity, carrier type, carrier concentration, and mobility were performed by a Hall measurement system. Absorption coefficient and energy gap were determined by absorption spectroscopy.

3. Results and discussion

Fig. 1 shows surface morphologies of Cu₂SnSe₃ films obtained with (a) target A, (b) target B, and (c) target C sputtered at 400 °C for 3 h. The

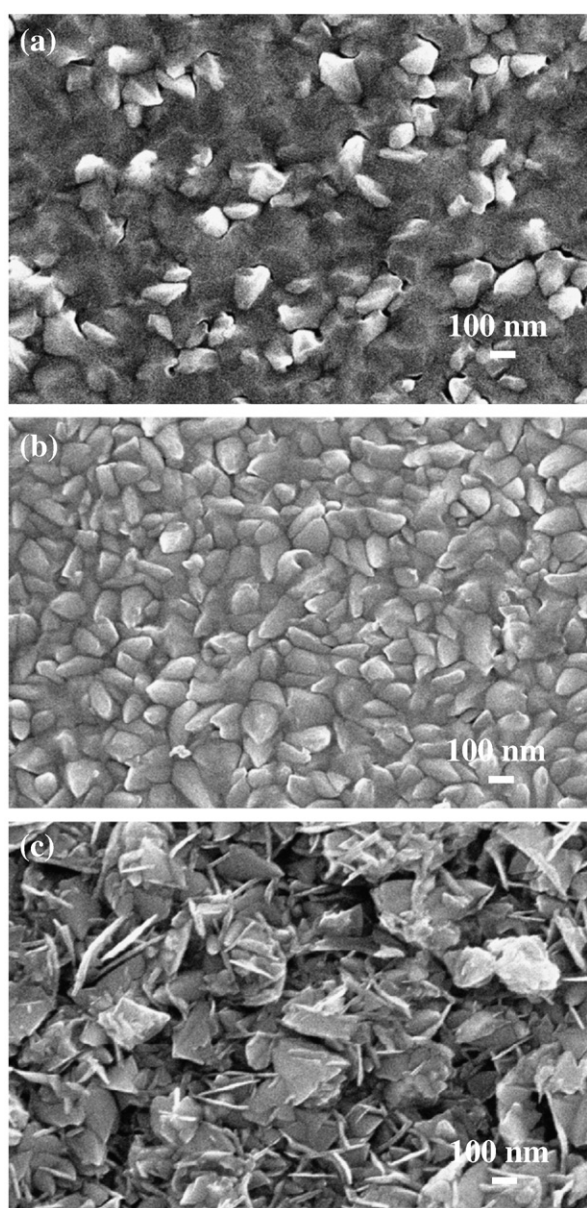


Fig. 1. Surface morphologies of Cu₂SnSe₃ films obtained with (a) target A, (b) target B, and (c) target C sputtered at 400 °C for 3 h.

films obtained from target B (Fig. 1(b)) had the dense and uniform microstructure with a grain size in the range of 0.1–0.4 μm. Target A-sputtered films had grains in different contrasts (Fig. 1(a)), which indicated the existence of different phases. These films did not display a clear grain structure. Target C-sputtered films had a loose microstructure with flaky grains. Obviously, the changes in target composition led to very different microstructures in sputtered films.

Fig. 2 demonstrates the compositional analyses of sputtered Cu₂SnSe₃ films obtained at 400 °C from targets A, B, and C. With the increase in the SnSe₂ content from target A to target C, the obtained films had the increased Sn and Se contents but the decreased Cu content. With the stoichiometric ratios at 33.3%, 16.7%, and 50% for Cu, Sn, and Se, respectively, the target A- and target B-sputtered films were Cu-rich and Sn- and Se-deficient, while the target C-sputtered films were Sn-rich and Cu- and Se-deficient. Although all sputtered films were Se-deficient, the Se content reached above 48%. Few sputtered CZTSe-related films can be deposited above 200 °C without severe Se loss. The second phase shown in Fig. 1(a) is expected to be Cu_xSe and will be discussed in the next XRD paragraph. For target C-sputtered films, the existence of a second phase of SnSe or SnSe₂ along with the major phase of Cu₂SnSe₃ is possible. Sputtering at higher temperatures and obtaining films with higher Se content are two process achievements, which make the sputtering preparation of thin-film solar cells easier.

Fig. 3 displays the XRD spectra of the Cu₂SnSe₃ films obtained with targets A, B, and C sputtered at 400 °C for 3 h. Target C-sputtered films showed the coexistence of the Cu₂SnSe₃ and SnSe phases. The favor of SnSe instead of SnSe₂ as the second phase is due to the Se-deficient composition in target C-sputtered films and the high bonding strength of SnSe, as indicated by its higher melting point. The expected Cu_xSe in the target A-sputtered films was distinguished by analyzing its XRD spectrum. Because of the close crystal structure of Cu_xSe and Cu₂SnSe₃, their diffractions resulted in broad peaks for the target A-sputtered films. Actually, Cu_xSe with different structures at different x values is difficult to identify. The target B-sputtered films showed a preferred orientation at 2θ–27°, as evidenced by its single strong peak. Without the phase contrast observed from the SEM image (Fig. 1(b)), the major phase in the target B-sputtered films was Cu₂SnSe₃ with the second phase of Cu_xSe in a small content.

Fig. 4 shows the SEM images of the target B-sputtered Cu₂SnSe₃ films after annealing at (a,d) 450 °C, (b,e) 500 °C, and (c,f) 550 °C under the presence of (a,b,c) SnSe₂ pellets and (d,e,f) Se pellets. The annealing at 600 °C led to the film cracking. The SnSe₂-pellet annealing is quite sensitive to the annealing temperature. The grains quickly grew at the annealing temperature of 550 °C with a grain size of 1–4 μm (Fig. 4(c)), while there was no grain growth at the annealing temperature of 400 °C. The annealing process under the Se pellets

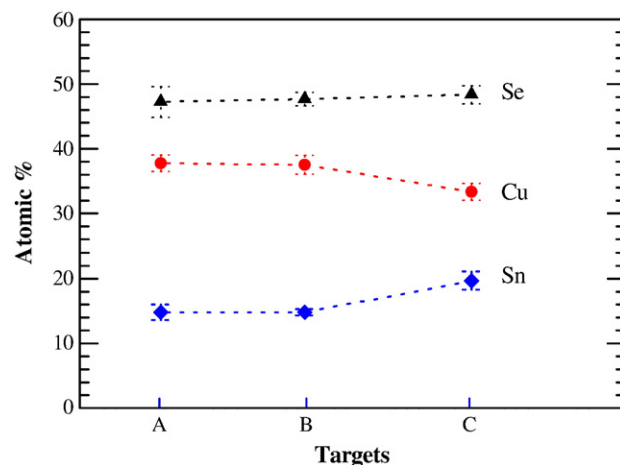


Fig. 2. Compositional analyses of sputtered Cu₂SnSe₃ films obtained at 400 °C from targets A, B, and C.

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