Thin Solid Films 518 (2010) 7218–7221

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Single-step sputtered Cu_2SnSe_3 films using the targets composed of Cu_2Se and $SnSe_2$

Dong-Hau Kuo [a,*], Wei-Di Haung [b], Ying-Sheng Huang [c], Jiun-De Wu [c], Yan-Jih Lin [c]

[a] Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei, 10607, Taiwan
[b] Institute of Materials Science and Technology, National Taiwan University of Science and Technology, Taipei, 10607, Taiwan
[c] Department of Electrical Engineering, National Taiwan University of Science and Technology, Taipei, 10607, Taiwan

ARTICLE INFO

Available online 7 May 2010

Keywords:
Sputtering
Thin films
Cu_2SnSe_3
$SnSe_2$
Hall measurement

ABSTRACT

Cu_2SnSe_3 thin films were prepared by single-step D.C. sputtering at 100–400 °C for 3 h using targets composed of Cu_2Se and $SnSe_2$ in three different ratios of 2/1 (target A), 1.8/1 (target B), and 1.6/1 (target C). The advantages of self-synthesized $SnSe_2$ instead of commercially available SnSe for depositing Cu_2SnSe_3 thin films were demonstrated. Effects of target composition and substrate temperature on the properties of Cu_2SnSe_3 thin films were investigated. Structure, surface morphology, composition, electrical and optical properties at different process conditions were measured. The 400 °C-sputtered films obtained from target B display with direct band gap of 0.76 eV, electrical resistivity of 0.12 Ω cm, absorption coefficient of 10^4–10^5 cm^{-1}, carrier concentration of ~1.8×10^{19} cm^{-3}, and electrical mobility of 2.9 cm^2/V s.

1. Introduction

Chalcopyrite compounds based upon $CuInSe_2$ (CISe) have been the major candidates for absorber layer in the thin-film solar cells. Cu(In, Ga)Se_2 (CIGS) and Cu(In,Ga)S_2 (CIGSe) systems have high efficiency in converting solar energy into electricity [1]. However, this system needs to use the expensive and limited metal source of indium. The substitution of indium in CISe with abundant zinc and tin to form $CuZn_{1-x}Sn_xSe_2$ (CZTSe) for thin film solar cells has been investigated [2,3].

The preparation of the CISe- or CZTSe-based absorber layer needs to be cautious about the loss of easily vaporized elements including Se and S. To overcome the above-mentioned problem, metal elements of CISe or CZTSe were deposited, followed by the post annealing under the Se or S atmosphere [4]. The thin-film deposition is also conducted under multiple sputtering targets or multiple evaporating sources with the Se or S source independently operated [5,6]. Single-step sputtering with a single target had suffered the composition deviation above 150 °C [7,8]. SnSe has been used for preparing the CZTSe targets [8]. However, $SnSe_2$ is not commercially available in the powder form. For the Cu_2SnSe_3 work, Babu et al. deposited Cu_2SnSe_3 films by three-source evaporation at 400 °C, followed by annealing at 450 °C under Se vapor. [9]

It is the purpose of this study to grow Cu_2SnSe_3 films by the single-step sputtering with a single target formed by sintering the mixed powders of Cu_2Se and $SnSe_2$. The effects of $SnSe_2$ on the growth and performance of sputtered Cu_2SnSe_3 films are investigated in this study.

2. Experimental

Cu_2SnSe_3 films were prepared by single-step D. C. sputtering at 100–400 °C for 3 h with three different targets having the molar ratios of Cu_2Se and $SnSe_2$ at 2/1, 1.8/1, and 1.6/1, which were abbreviated as targets A, B, and C, respectively. The film thicknesses of all the sputtered films were ~1 μm. Cu_2Se and $SnSe_2$ powders were synthesized by ball-milled mixing of Cu and Se and Sn and Se in the required ratios, respectively, followed by firing at 200 °C for 3 h under vacuum. The three kinds of 2-in. targets having the mixed Cu_2Se and $SnSe_2$ powders in the ratios of 2/1, 1.8/1, and 1.6/1 were hot pressed at 650 °C for 30 min under argon with a hydraulic pressure of 400 psi. The composition and growth morphology of Cu_2SnSe_3 films were characterized by field-emission scanning electron microscopy (FE-SEM, JSM 6500F, JEOL, Japan). Crystal structure was analyzed by the X-ray diffractometry (XRD, D/Max-RC, Rigaku, Japan). Resistivity, carrier type, carrier concentration, and mobility were performed by a home-built Hall-effect measurement system. Absorption coefficient and energy gap were determined by absorption spectroscopy.

3. Results and discussion

Fig. 1 shows surface morphologies of sputtered Cu_2SnSe_3 films with (a, b) target A, (c, d) target B, and (e, f) target C at growth temperatures of (a, c, e) 100 °C and (b, d, f) 400 °C for 3 h. The target A–sputtered films had a grain size of ~100 nm at 100 °C. The grain size slightly increased with the deposited temperature. When deposition temperature was higher than 100 °C, the micrograph of sputtered film

* Corresponding author.
E-mail address: dhkuo@mail.ntust.edu.tw (D.-H. Kuo).

0040-6090/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2010.04.077

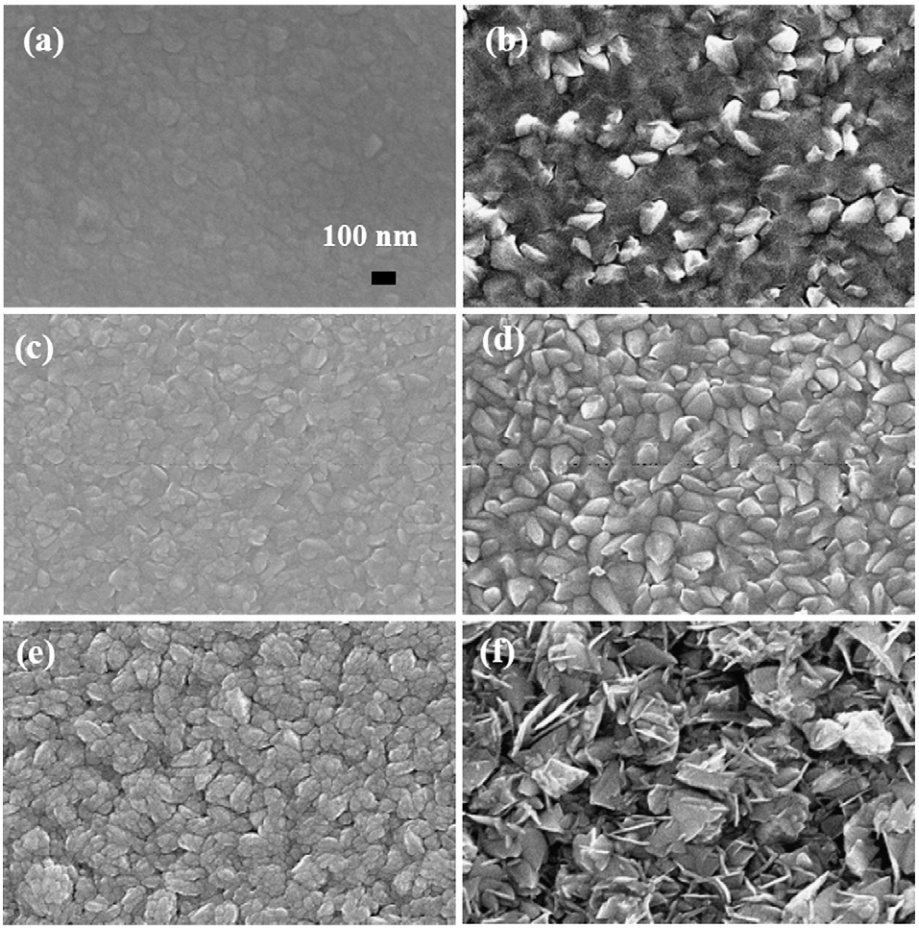

Fig. 1. Surface morphologies of sputtered Cu_2SnSe_3 films with (a, b) target A, (c, d) target B, and (e, f) target C at growth temperatures of (a, c, e) 100 °C and (b, d, f) 400 °C for 3 h.

shows two kinds of phase contrasts, which indicated the co-existence of a second phase (Fig. 1(b)). The target B–sputtered films had a grain size of 50–150 nm at 100 °C. The films deposited at 200 °C and 300 °C did not have apparent grain growth but slightly changed the grains to a round shape. The 400 °C-sputtered films had a grain size of 150–250 nm. This film had well-crystallized grains with sharp ends at the tips. The target C–sputtered films showed granular aggregates at 100 °C, which were composed of many nano-sized grains. When growth temperature increased, the films showed an increase in grain size. The 200 °C-sputtered films did not have granular aggregates but showed a grain size of 50–150 nm. The 300 °C-sputtered films had larger grains at ~200 nm. The 400 °C-sputtered films had a loose microstructure with flaky grains. The loose microstructure indicated the deposition suffered the loss of chemical species *via* vaporization. The target A–, target B–, and target C–sputtered films had quite different film compositions due to the different target compositions. The deposition condition under the target C should favor the formation of the easy-vaporized second phase on substrates and lead to the loose microstructure.

Fig. 2 shows the (a) Cu/Sn and (b) Se/(Cu+Sn) atomic ratios of Cu_2SnSe_3 films sputtered at 100–400 °C for 3 h with targets A, B, and C. All the films obtained from three different targets had high Se/(Cu+Sn) ratios above 0.85. By reducing the $Cu_2Se/SnSe_2$ ratios from target A to target C, the Cu content decreased and the Se content increased. The compositions of target A– and target B–sputtered films were Cu-rich and Sn- and Se-deficient. The target C–sputtered films had the Se/(Cu+Sn) ratio above 1.0 and were Se-rich. The Cu-rich absorber layer is preferred for the p-type semiconductor due to the occupation of Cu on the Sn lattice site to form the antisites p-type defects. However, target C–sputtered films with a Cu/Sn ratio less than 2.0 were Cu-deficient and were an un-favored p-type semiconductor with the formation of the acceptor level of Cu vacancy. At the higher deposition temperature of 400 °C, the target C–sputtered films quickly lost its Se content. This lost in Se resulted in the change in surface morphology, as shown in Fig. 1(f). Based upon the composition analyses, the changes of film composition with target composition were apparent. The consistency in the linear variation of film composition with target composition is advantageous for the process development. Seol et al. reported that the growth of quaternary CZTS films with sulfur concentration above 40 at.% could be succeeded by employing Cu_2S powder in the sputtering target [10]. Wibowo et al. found Cu_2Se partially replacing CuSe in sputtering targets improved the Se content leading to a Se/metals ratio of 1.135 for CZTSe films [8]. However, the Se/metals ratio dropped to 0.613 at a substrate temperature of 175 °C. The higher binding energy of Cu in Cu_2Se than in CuSe indicates the more Se supplied to deposition. For $SnSe_2$, it can provide more Se than SnSe does. Therefore, our targets sintered with Cu_2Se and $SnSe_2$ powders can sustain higher growth temperatures at the single-step sputtering.

Fig. 3 shows XRD spectra of the sputtered-Cu_2SnSe_3 films deposited with target A, target B, and target C at substrate temperatures of (a) 100 °C and (b) 400 °C for 3 h. Because the data in crystal structure of Cu_2SnSe_3 were not complete [11,12], we cannot determine the crystal orientations in Fig. 3. Although the XRD structural analyses were similar for target A– and target B–sputtered films in Fig. 3, the second phase observed in SEM images (Fig. 1(b)) and the compositional deviation detected by EDS analyses (Fig. 2) indicate that the second phases in target A–sputtered films had a very similar crystal parameters with the main phase of Cu_2SnSe_3. The peak splitting was distinguishable for target A–sputtered films grown