Current Applied Physics 12 (2012) 1052–1057

Contents lists available at SciVerse ScienceDirect

Current Applied Physics

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

Sulfurization temperature effects on the growth of Cu_2ZnSnS_4 thin film

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ARTICLE INFO

Article history:
Received 4 August 2011
Received in revised form
2 January 2012
Accepted 7 January 2012
Available online 25 January 2012

Keywords:
Cu_2ZnSnS_4
Sulfurization
Film growth
Raman spectroscopy
Secondary phase
Band gap

ABSTRACT

We made Cu_2ZnSnS_4 (CZTS) thin films by sulfurization of Cu/Sn/Cu/Zn metallic films. Sulfurizations were carried out under different thermal annealing conditions, where maximum temperatures were 440 °C (LT-CZTS) and 550 °C (HT-CZTS). For LT-CZTS films, secondary phases such as SnS_2 and $Cu_{2-x}S$ were observed, whereas for HT-CZTS films secondary impurities were not detected. Chemical composition of LT-CZTS film was observed to be very non-uniform. Highly Sn-rich and Zn-rich regions were found on the film surface of LT-CZTS. However, averaged chemical composition for larger area was close to stoichiometry. The HT-CZTS film showed homogeneous structural and chemical composition features. But, for HT-CZTS film, the Sn composition was observed to be decreased, which was due to the Sn-loss. By UV–Visible spectroscopy, optical band gaps of LT- and HT-CZTS films were measured to be ∼1.33 eV and ∼1.42 eV, respectively. The band gap of LT-CZTS film was also observed to be smaller by photoluminescence measurement. The depressed band gap of LT-CZTS film may be ascribed to some defects and low band gap impurities such as Cu_2SnS_3 and $Cu_{2-x}S$ in the LT-CZTS film.
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1. Introduction

CIGS solar cell has achieved ∼20% conversion efficiency in laboratory cell scale, which is one of the highest efficiency among various thin film solar cells. However, CIGS solar cells adopt rare earth materials, In and Ga, which are also used in the display industry. Thus, considering applications in large scale, alternative solar cell with earth abundant element is desirable. In terms of this view point, kesterite Cu_2ZnSnS_4 (CZTS) is very promising absorber material [1–4]. It includes earth abundant materials Sn, Zn, and less toxic S. In additions, CZTS exhibits excellent material properties such as direct band gap of 1.4–1.5 eV and large absorption coefficient of 10^4 cm^{-1} in visible spectrum range.

Recently, the conversion efficiency of CZTS solar cell was dramatically increased. For the record efficiency of CZTS, vacuum-based process yielded 6.77% [5], and hydrazine-adopted solution process showed 9.6% [6], and nanoparticle-based process gave 7.2% [7] conversion efficiency. However, although device performance was greatly improved, basic researches on CZTS material itself are insufficient. For example, fabrication of compositionally uniform CZTS film is still hard task due to Sn-loss during annealing process [8]. Considering that high efficiency CZTS solar cell can be realized just with Cu-poor and Zn-rich CZTS [9], well-adjustment of chemical composition of CZTS is prerequisite. Hence, systematic sulfurization experiments under controlled temperature and surrounding atmosphere come to be significant. On the other hand, for Cu2ZnSnSe2 (CZTSe) film the determination of exact band gap was controversial. Some reported band gap of CZTSe was observed to be 0.8–1 eV [10–12], while others claimed that it was measured to be 1.4–1.5 eV [13–15]. In this paper, we report that on the CZTS film the band gap can be affected by the sulfurization temperature of stacked metallic film. In additions, the detection of secondary phases in CZTS films by using X-ray diffraction (XRD) is very hard because lattice constants of the secondary phases are similar to those of CZTS. Here, we show experimental results that Raman spectroscopy can reveal possible secondary phases with higher sensitivity.

We report the impact of sulfurization condition on structural and optical properties of CZTS films. By sulfurization of Cu/Sn/Cu/Zn/glass stacked films, we made CZTS films under different sulfurization conditions. The fabricated films were characterized by XRD, Raman spectroscopy, UV–Visible spectroscopy, photoluminescence (PL), scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX). Based on these measurement results, growth properties of CZTS films will be discussed.

2. Experiments

We made precursor metallic films by rf sputtering method. The metallic films were sequentially deposited onto glass so as to

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doi:10.1016/j.cap.2012.01.006

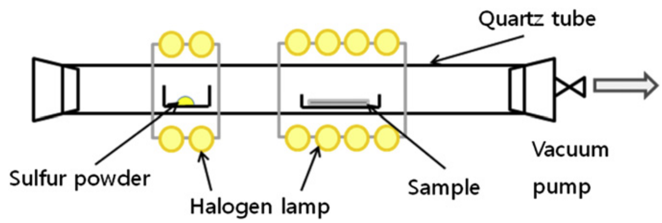

Fig. 1. Schematic diagram of sulfurization furnace. It consists of two heating zones, where sulfur is located at upstream and Cu/Sn/Cu/Zn/glass is placed at downstream.

be stacked Cu/Sn/Cu/Zn/glass. All films were sputtered in-situ with three different sputtering targets Cu, Sn and Zn without vacuum break. After base pressure was reached to 10^{-6} Torr, sputtering was performed with rf power of 60 W and Ar pressure of 6 mTorr. The composition of Cu, Sn and Zn can be adjusted by deposition time of Cu, Sn and Zn. The deposition time of upper-Cu, Sn, lower-Cu, and Zn were selected as 7, 12, 7 and 10 min, respectively. The composition ratio of the precursor metallic film was measured to be Cu:Zn:Sn = 1.76:1:1.37. According to our previous study, Cu-poor CZTS film is expected with this precursor film [16,17].

The fabricated Cu/Sn/Cu/Zn/glass films were sulfurized with a two-zone vacuum furnace. At one zone sulfur powder was located in alumina crucible, and at the other zone the Cu/Sn/Cu/Zn/glass film was placed. The schematic of vacuum furnace is shown in Fig. 1. We carried out sulfurization of Cu/Sn/Cu/Zn/glass films with two different thermal annealing profiles. The two thermal annealing profiles are depicted in Fig. 2, where one is treated at 440 °C for 20 min (LT-CZTS) and the other at 550 °C for 30 min (HT-CZTS). For all sulfurizations, sulfur zone was heated to be ~180 °C beforehand. Once sulfur vapor covered surface of Cu/Sn/Cu/Zn/glass, sulfurization was started. As the sample zone was cooled down, sulfur-supply was terminated by cooling down the sulfur zone.

Crystallinity of fabricated CZTS film was characterized by XRD θ-2θ scans. For XRD, Cu K_α line ($\lambda = 0.15406$ nm) was used as X-ray source, and scanning speed was 2°/min. To detect possible secondary phase, Raman spectroscopy was used with 514 nm laser as excitation light that penetrates into film to ~500 nm [18]. We also measured optical band gaps of CZTS films by using UV–Visible spectroscopy and PL measurements. PL measurement was done at 10 K with 352 nm laser.

3. Results and discussion

Fig. 3 shows results of XRD measurements of LT-CZTS and HT-CZTS films. Both films were grown well with polycrystalline structures with (112) dominant texture. The film thickness was measured to be ~1.3 μm for both films. For LT-CZTS film, secondary phase near ~15° is observed, which corresponds to SnS_2 (001) peak [19]. SnS_2 may be formed at lower temperature during sulfurization process for CZTS films. For HT-CZTS film, secondary phase was not observed. In the formation of CZTS phase, we can consider following reaction pathways.

$$Sn + S_2 \rightarrow SnS_2 \quad (1)$$

$$Zn + S \rightarrow ZnS \quad (2)$$

$$Cu_2 + S \rightarrow Cu_2S \quad (3)$$

$$Cu + S \rightarrow CuS \quad (4)$$

$$Cu_2S + SnS_2 \rightarrow Cu_2SnS_3 \quad (5)$$

$$Cu_2SnS_3 + ZnS \rightarrow Cu_2ZnSnS_4 \quad (6)$$

Binary and ternary compounds are formed at low temperature through reactions, (1), (2), (3), (4) and (5). The reaction (6) for formation of CZTS occurs at higher temperature during sulfurization [20]. In our experiments, LT-CZTS films may contain all binary and ternary compounds above. Except for SnS_2, the existence of the other compounds is not certain. We compare the (112) peaks of LT-and HT-CZTS films, which are shown in Fig. 3(b). The peak centers for LT- and HT-CZTS films are measured to be 28.47° and 28.45°, respectively. The (112) of CZTS ($2\theta_{CZTS} = 28.44$, ICDD : 04-005–0388) is very close to (112) of tetragonal Cu_2SnS_3 ($28.54 = 2\theta_{CZTS}+0.1$, ICDD: 01-089–4714), (111) of cubic Cu_2SnS_3 ($28.45 = 2\theta_{CZTS}+0.01$, ICDD: 01-089–2877) and (111) of cubic-ZnS ($28.50 = 2\theta_{CZTS}+0.06$, ICDD: 04-006–0807). When they co-exist in LT-CZTS film, it's difficult to discriminate each peak. But, the existence of Cu_2SnS_3 and ZnS may make (112) peak of CZTS broader and more asymmetric. This analysis is consistent with the inset of Fig. 3(b), which shows normalized (112) peaks of LT- and HT-CZTS films. The (112) peak of LT-CZTS film looks broader to higher angle, which implicates co-existence of another peaks such as Cu_2SnS_3 and ZnS. Although it is not shown here, same feature was observed in (204) peak of LT-CZTS.

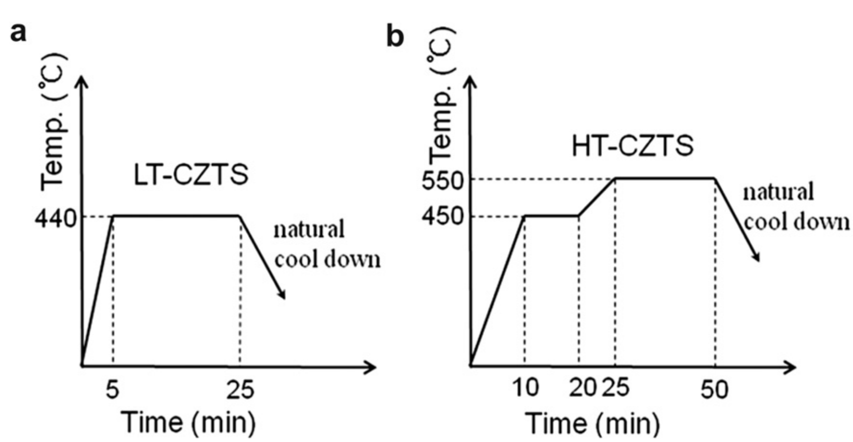

Fig. 2. Thermal annealing profiles of sample zone. Profiles of low temperature sulfurization for LT-CZTS film (a) and high temperature sulfurization for HT-CZTS (b).

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