Superlattices and Microstructures xxx (2017) 1–7

Contents lists available at ScienceDirect

Superlattices and Microstructures

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

Effect of annealing atmosphere on properties of $Cu_2ZnSn(S,Se)_4$ thin films[☆]

Yuming Xue [a,*], Bingbing Yu [a,b], Wei Li [a], Shaojun Feng [a], Yukun Wang [a], Shengming Huang [a], Chao Zhang [b], Zaixiang Qiao [b,**]

[a] Tianjin Key Laboratory of Film Electronic & Communication Devices, School of Electrical and Electronic Engineering, Tianjin University of Technology, Tianjin, 300384, China
[b] Tianjin Institute of Power Sources, Tianjin, 300384, China

ARTICLE INFO

Article history:
Received 14 August 2017
Received in revised form 15 September 2017
Accepted 17 September 2017
Available online xxx

Keywords:
CZTSSe
Co-evaporated
Annealing
Atmospheres
Band gaps

ABSTRACT

Earth-abundant $Cu_2ZnSn(S,Se)_4$(CZTSSe) thin film photovoltaic absorber layers were fabricated by co-evaporated Cu, ZnS, SnS and Se sources in a vacuum chamber followed by annealing at tubular furnace for 30 min at 550 °C. In this paper, we investigated the metal elements with stoichiometric ratio film to study the effect of annealing conditions of Se, SnS + Se, S and SnS + S atmosphere on the structure, surface morphological, optical and electrical properties of $Cu_2ZnSn(S,Se)_4$ thin films respectively. These films were characterized by Inductively Coupled Plasma-Mass Spectrometer, scanning electron microscopy, X-ray diffraction to investigate the composition, morphological and crystal structural properties. The grain size of samples were found to increase after annealing. XRD patterns confirmed the formation of pure polycrystalline CZTSSe thin films at S atmosphere, the optical band gaps are 1.02, 1.05, 1.23, 1.35 eV for Se, SnS + Se, SnS + S and S atmosphere respectively.

1. Introduction

$Cu_2ZnSn(S,Se)_4$(CZTSSe) thin film absorber was considered to be a promising substitution of $Cu(In,Ga)Se_2$ as its abundant elements, large absorption coefficient [1] and more appropriate band gap varying 1.0–1.5 eV depending on Se/S ratio [2], and the band-gap of kesterite film can be tailored as a function of annealing temperature and pressure [3].

To date, the cells with the highest power conversion efficiency (PCE) (approximately 12.7%) have used the hybrid CZTSSe [4]. Lots of work focused on stacked metal or binary sulfide precursor prepared by sputtering [5,6]. $Cu_2ZnSn(S_{1-y}Se_y)_4(0 \leq y \leq 1)$ kesterite based solar cells are currently developing fast and have achieved a great improvement, 9.2% efficiency for Cu_2ZnSnS_4(CZTS) solar cells [7], 11.6% efficiency for $Cu_2ZnSnSe_4$(CZTSe) solar cells [8] and 12.6% efficiency for solid solution CZTSSe solar cells [9] were demonstrated. Until now, Se-rich solid solution CZTSSe solar cells show the best results (S/(S + Se) = 0.3), which is similar to the case of $Cu(In,Ga)Se_2$ (CIGS) based solar cells, in which the partial substitution of indium by gallium allows for the highest performance of 23.3% by now [10].

☆ Project supported by Innovation and entrepreneurship training program for college students in Tianjin (Grant No. 201510060006) and Tianjin Science & Technology Council (Grant No.15JCZDJC30900).

* Corresponding author.
** Corresponding author.
E-mail addresses: orwell.x@163.com (Y. Xue), zxqiao@sina.cn (Z. Qiao).

https://doi.org/10.1016/j.spmi.2017.09.036
0749-6036/© 2017 Published by Elsevier Ltd.

Jiang et al. [11] performed spin-coating technique and CZTS thin films were annealed at 550 °Cin N_2 environment, CZTS thin films exhibited kesterite structure, optical absorption coefficient of 10^4 cm^{-1} and efficiency of 0.63%. Rajesh et al. [12]. One potential method of preparing the CZTSSe compound from selenizing as-deposited Cu-Zn-Sn-S film, the incorporation of selenium into CZTS is rapid during heat treatment [13], while this method is hard to obtain high S CZTSSe with optimal band gap [14]. An initial work on secondary phases research using XRD with quantitative Rietveld refinement for solid solution CZTSSe thin films with broad metallic composition variation in precursors was presented by Wibowo et al. [15].

It is well-known that, the structural, optical, surface morphological, electrical properties of the poly-crystalline CZTS depend upon its annealing temperature and atmosphere [16]. However, there is a lack of sufficient information on the effect of the annealing atmosphere on the physical, chemical and electrical properties and grain size of the co-evaporated CZTSSe. Most work on air annealing(AA) has been performed on CZTSSe or CZTSe, while only one study mentions the pure sulfide CZTS [17]. Our study is to investigate the effect of annealing conditions of Se, SnS + Se, S and SnS + S atmosphere on the structural and morphological properties of metal elements with stoichiometric ratio CZTSSe thin films for 30 min at 550 °C in a tubular furnace. Consequently, we find annealed at S atmosphere can form high quality CZTSSe thin film.

2. Experimental details

CZTSSe thin films were deposited on soda lime glass using thermal co-evaporation technique. Equipment and procedures like CIGS processing, the difference is that we use ZnS and SnS instead of Ga and In in vacuum chamber under high temperature. Redinger et al. showed that SnS losses from CZTS films were reversible, with films of Cu_2S and ZnS being converted to CZTS in the presence of sulfur and SnS vapor [18], so it is very important to control the equilibrium point.

The pressure of the chamber during deposition was around 1.2×10^{-3}Pa. The substrate was heated up to 500 °C before Cu, ZnS, SnS and Se sources were open simultaneously for 10min. Subsequently, close Cu source, continue to evaporate the rest of sources for 10min. At last, close ZnS source, continue evaporate SnS and Se source for 5min so that the film turns from copper rich to copper poor. The overall cooling rate is similar to that used for CIGS, as is the choice to turn off Se and terminate temperature control around 300 °C [19]. A plateau in the cooling rate at 450 °C was included to replenish possible Sn vacancies just below the temperature at which significant Sn loss from the kesterite in vacuum has been observed [20].

Deposition process profiles for CZTSSe film growth are shown in Figs. 1 and 2. First, a Cu-rich film is prepared under all sources open to obtain large grains for liquid $Cu_{2-x}Se$ phase may benefit to deposited large-grained CZTSSe thin film in 10 min (see Fig. 3).

Second, close Cu source and continue to evaporate the remaining sources so that the liquid $Cu_{2-x}Se$ was consumed and initially formed CZTSSe precursor layer in 10 min and the surface of film is smooth furthermore have a good adhesion at the appropriate temperature in case of anti evaporation on substrate in this stage. At last, co-evaporate Se and SnS for 5 min to supply the loss of element at high temperature.

Here, a sufficient amount of SnS and Se can prevent the decomposition of CZTSSe in this chemical equilibrium.

$$2Cu(s)+ZnS(s)+SnS(s)+2Se \leftrightharpoons CZTSSe(s) \quad (1)$$

$$SnS(s) \leftrightharpoons SnS(g) \quad (2)$$

It is well-known that, the structural, optical, surface morphological, electrical properties of the poly-crystalline CZTS depend upon its annealing temperature and atmosphere [21]. Furthermore, the annealing process contributes to the diffusion of atoms adsorbed on the substrate and accelerates the migration of atoms to energetically favorable positions, resulting in an enhancement of the crystallinity [22]. To find the appropriate annealing atmosphere, we study the effect of atmosphere on CZTSSe films include Se, SnS + Se, SnS + S and S respectively.

The components of these samples were analyzed using Inductively Coupled Plasma-Mass Spectrometer(ICPMS) Thermo X Series. The surface and cross section were analyzed by scanning electron microscopy(SEM, Hitachi S4800). The crystalline structure of the samples were analyzed by X-ray diffraction(XRD), using the nickel-filtered Ka1 emission line of

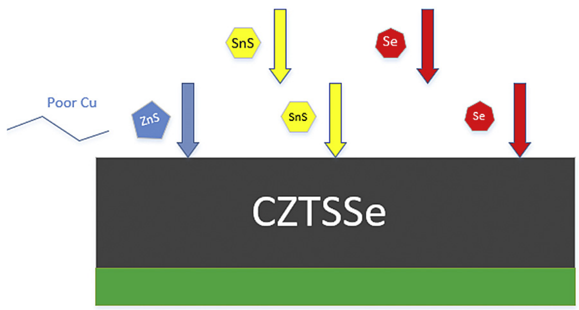

Fig. 1. Shematic diagram of sequential evaporation.

Please cite this article in press as: Y. Xue et al., Effect of annealing atmosphere on properties of $Cu_2ZnSn(S,Se)_4$ thin films, Superlattices and Microstructures (2017), https://doi.org/10.1016/j.spmi.2017.09.036