Thin Solid Films 547 (2013) 86–90

Contents lists available at ScienceDirect

Thin Solid Films

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

Structural and electrical properties of radio frequency magnetron sputtered $Cu(In_xGa_{1-x})Se_2$ thin films with additional post-heat treatment

Sung Hee Jung [a], Rong Fan [a], Wan In Lee [b], Chee Won Chung [a,b,*]

[a] Department of Chemical Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Republic of Korea
[b] Department of Chemistry, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Republic of Korea

ARTICLE INFO

Available online 1 May 2013

Keywords:
$Cu(In_{1-x}Ga_x)Se_2$
thin film solar cell
absorber layer
rf magnetrons sputtering

ABSTRACT

$Cu(In_{1-x}Ga_x)(Se,S)_2$ (CIGSS) thin films were deposited using a single quaternary target of $Cu(In_{0.75}Ga_{0.25})Se_2$(CIGS) by rf magnetron sputtering, followed by sulfurization. The effects of substrate temperature and post-sulfurization on the properties of CIGSS films were investigated. As the substrate temperature increased, the crystallinity of the films increased significantly and the grain size also increased. Energy dispersive X-ray spectroscopy of CIGS films showed that Cu, Ga and Se contents approached the stoichiometry of CIGS films with increasing substrate temperature.

Post-sulfurization of as-deposited CIGS films was carried out to improve their properties. The resultant CIGSS thin films revealed a noticeable increase in (112) peak for films deposited under 200 °C, while the intensities of the (220)/(204) and (312)/(116) peaks increased as well. Grains with a size of approximately 100 nm were grown after sulfurization. The results of EDX of CIGSS thin films after sulfurization indicated that the Cu content increased slightly and the Ga and (Se + S) contents decreased significantly. The band gaps of the films were also noticeably reduced after sulfurization. The carrier concentrations of the films after sulfurization decreased greatly at substrate temperatures below 400 °C, while they showed little change at temperatures above 400 °C. The resistivity of the films after sulfurization increased with increasing substrate temperature and showed little change at temperatures above 400 °C. As a result, CIGS films were transformed to the chalcopyrite phase with well crystallized grains through sulfurization.

1. Introduction

$Cu(In_{1-x}Ga_x)(Se,S)_2$ (CIGSS) thin film solar cells are one of the most promising solar cells for the replacement of Si solar cells. CIGSS thin films which are used as an absorbing medium are a compound semiconductor material with a chalcopyrite structure [1]. These films are a direct band gap material with the capability to achieve high efficiency solar cells with a thickness of approximately 1–2 μm due to the high absorption coefficient of 10^{-5} cm which is the highest among currently available semiconductors [2,3].

The deposition of $Cu(In_{1-x}Ga_x)(Se)_2$ (CIGS) thin films has been known to be very difficult because of multi-component compounds with complicated structures. CIGS thin films have been prepared by a variety of deposition methods including co-evaporation, chemical spray pyrolysis (CSP), electrode position and sputtering [2,4–6]. CIGS thin films deposited by the co-evaporation method have been shown to have the highest efficiency (>20%); however, it is hard to meet the stoichiometry of CIGS thin films from various metal sources and run reliable processes with sources loaded in sequence for multiple-stage processes. It is also difficult to scale up for large-area deposition due to the complexity of the method [7,8]. The CSP method has primarily been used for $CuInSe_2$ and $CuInS_2$ films as a chalcopyrite semiconductor. This is expected to be a promising deposition method because large-area films with good uniformity can be grown at low cost. However, the efficiency of cells fabricated by CSP to date has not been good [9,10]. The electrode position method has emerged with various advantages such as low cost and large scale deposition with a non-vacuum system for CIGS deposition but has the disadvantages of poor uniformity and pinhole formation when thin films are prepared. Additionally, the films must be deposited very thickly and have not shown high efficiency [11–13]. The sputtering method, which is very effective for scale up to a large deposition area, has drawn a great deal of attention due to its ability for use in mass production and good reproducibility. This technique generally involves separate two-stage processes that involve the deposition of metallic precursors from the single, binary and ternary targets with Cu, In and Ga elements, and the selenization process [14–16]. The current popular sputtering method for deposition of CIGS films employs metal deposition from three single targets of Cu, In and Ga, and these deposited metal films are subsequently selenized by Se vapor from H_2Se gas or Se pellets [17,18].

* Corresponding author at: Department of Chemical Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Republic of Korea. Tel.: +82 32 860 7473; fax: +82 32 872 0959.
E-mail address: cwchung@inha.ac.kr (C.W. Chung).

0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.04.108

Among these deposition methods for CIGS thin films, the sputtering method has begun to receive a great deal of attention as a stable and reproducible technique for mass production with the capability of large-area deposition [19]. Recently, sputtering using a single quaternary target containing Cu, In, Ga and Se has been reported for preparation of CIGS films without an additional selenization process. This can provide a simple cost-effective deposition process for CIGS films when compared to other deposition methods. However, it is difficult to regulate the stoichiometry of the films and increase the grain size in the films when this sputtering method is used because of the low deposition rate of Se, which influences the efficiency of the absorber layer [19–24].

In this study, post-sulfurization after sputtering deposition was applied to reduce issues such as Se vacancy or grain control associated with the sputtering method using a single quaternary target without selenization. The effects of substrate temperature and post-sulfurization on the structural, optical and electrical characteristics of CIGS thin films were also examined.

2. Experimental details

CIGS thin films were prepared using a single quaternary target with an rf magnetron sputtering system (A-Tech system, Korea) on $15 \times 15 \times 2$ mm^3 soda lime glasses. The target was a 3 in. diameter material (Kojundo, Japan) composed of the quaternary components 25 at.% Cu, 18.8 at.% In, 6.2 at.% Ga and 50 at.% Se. Prior to deposition, the glass substrates were ultrasonically cleaned in acetone, ethanol, and deionized water in sequence.

The deposition chamber was evacuated to $0.93–1.20 \times 10^{-4}$ Pa using a turbomolecular pump backed by a mechanical pump. The substrate temperature in the chamber could be raised to 550 °C and Ar at 30 sccm was used as a sputtering gas. The rf power and process pressure used in this study were 80 W and 0.67 Pa, respectively. The distance between the target and the substrate was fixed at 5.5 cm and the substrate was rotated at 10 rpm. All deposited CIGS films were adjusted to a thickness of 500 nm. Prior to film deposition, pre-sputtering was carried out for 15 min to remove the contaminants on the target surface. The deposited thin films were then heat-treated at 525 °C for 1 h under an H_2S flow.

In this study, the influence of the substrate temperature and sulfurization process on the properties of CIGS thin films was investigated. The thickness and deposition rate of CIGS films were measured using a surface profiler (Tencor-P1). X-ray diffraction (XRD) analysis (Philips X'Pert PRO XRD system, Cu K_α irradiation, $\lambda = 1.50405$ Å) using 40 kV voltage and 30 mA current was employed to examine the crystalline structure of the films. Grazing incidence configuration with an incident angle of 1° was used for minimization diffraction peak from the substrate. The microstructure and surface morphology of the films were observed using field emission scanning electron microscopy (FESEM) (Hitachi S-4300) with the operating voltage of 15 kV. Energy dispersive x-ray spectroscopy (EDX) (INCA Energy) was utilized to investigate the contents of each element in the films with the accelerating voltage of 15 kV and collection time of 100 s. The band gaps of CIGS films were evaluated from the optical transmittance through the films using UV–Vis spectroscopy (Cary 300).The carrier concentration and resistivity of CIGS films were measured using the Van der Pauw method through the Hall effect measurement system (HMS-3000, ECOPIA) using a 0.1 μA current in a 0.55 T magnetic field at room temperature. Indium soldering in Hall effect measurement was applied onto the surface as the ohmic contact.

3. Results and discussion

CIGS thin films that were 500 nm thick were deposited using a single quaternary target by rf magnetron sputtering on soda lime glasses. The deposition condition was an rf power of 80 W, chamber pressure of 0.67 Pa and target–substrate distance of 5.5 cm. The substrate temperature was varied from room temperature (RT) to 550 °C and additional post-sulfurization was carried out at 525 °C for 1 h in a tube furnace.

Fig. 1 shows the XRD patterns of CIGS thin films deposited at different substrate temperatures. XRD patterns showed that most CIGS thin films have a strong preferential (112) plane of $Cu(In_{0.7}Ga_{0.3})Se_2$ (JCPDS 35-1102). Weak (220)/(204) and (312)/(116) planes of $Cu(In_{0.7}Ga_{0.3})Se_2$ were also observed. CIGS thin films were deposited as polycrystalline and had chalcopyrite structure. The (112) peak increased with increasing substrate temperature, with a noticeable increase occurring from 200 °C and the highest peak intensity was obtained for films deposited at 550 °C. A very weak peak around 25° was observed for films deposited at greater than 300 °C, and these corresponded to Cu-rich selenide phases Cu_3Se_2 (JCPDS 47-1745) [22].

Fig. 2 shows FESEM micrographs of CIGS films deposited at different substrate temperatures. Observable small grains were seen for films deposited at 200 °C. As the substrate temperature increased from 200 °C to 400 °C, circular grains grew and the grain size increased from 30 nm to 90 nm. Moreover, when the films were deposited at 550 °C, the grains were agglomerated and formed as large grains greater than 100 nm.

Table 1 presents the chemical composition of as-deposited CIGS thin films at various substrate temperatures using EDX system. CIGS films deposited at room temperature were Cu and Se deficient and had excessive Ga when compared to the stoichiometry of CIGS films. However, films deposited at 200 °C showed a slight increase in Cu/(In + Ga)and Se/(In + Ga), which indicated initiation of the formation of crystalline structures (Figs. 1 and 2). As the substrate temperature increased from 200 °C to 550 °C, the Cu/(In + Ga) and Se/(In + Ga) approached the stoichiometric composition of CIGS films. However, the film deposited at 550 °C showed a slight decrease in Cu/(In + Ga) and Ga/(In + Ga) ratios and a small increase in the Se/(In + Ga) ratio. These results are in good agreement with those shown in Figs. 1 and 2, which demonstrated the well grown grains of CIGS films at high substrate temperature. Since all films had Ga/(In + Ga) ratios above 0.39, preferential orientation of the (112) plane was obtained, as reported previously [21].

Post-sulfurization of as-deposited CIGS films was conducted to improve their properties by controlling the amounts of Ga and Se and adding S into the films. The post sulfurization process included heating the as-deposited films at different substrate temperatures in the tube furnace at 525 °C under a H_2S flow for 1 h. Fig. 3 shows the XRD patterns of $Cu(In_{1-x}Ga_x)(Se,S)_2$ (CIGSS) films after sulfurization. All

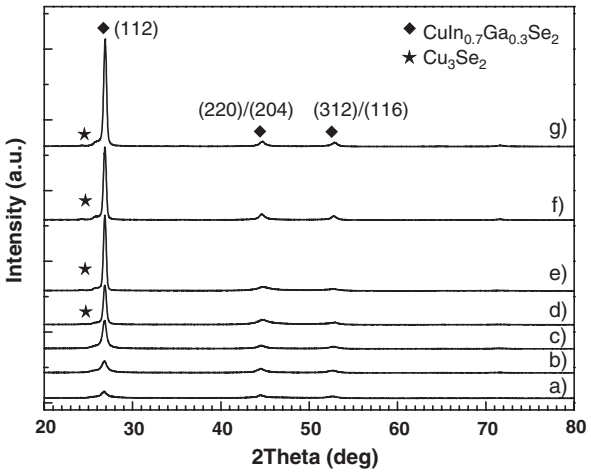

Fig. 1. XRD patterns of CIGS thin films deposited at different substrate temperatures: (a) room temperature, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C, (f) 500 °C, and (g) 550 °C.