Ceramics International ■ (■■■■) ■■■–■■■

Contents lists available at ScienceDirect

Ceramics International

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

CIGS absorbing layers prepared by RF magnetron sputtering from a single quaternary target

H.X. Zhang, R.J. Hong *

Institute for Solar Energy Systems, Guangdong Provincial Key Laboratory of Photovoltaic Technology, Sun Yat-sen University, Guangzhou 510006, China

ARTICLE INFO

Article history:
Received 28 April 2016
Received in revised form
9 June 2016
Accepted 10 June 2016

Keywords:
CIGS
Quaternary target
RF magnetron sputtering
Stoichiometric ratio
Thin film solar cell

ABSTRACT

$Cu(In_{1-x}Ga_x)Se_2$ (CIGS) thin films were prepared by RF magnetron sputtering from a single quaternary target at multiple processing parameters. The structural, compositional, and electrical properties of the as-deposited films were systematically investigated by XRD, Raman, SEM, and Hall effects analysis. The results demonstrate that by adjusting the processing parameters, the CIGS thin films with a preferential orientation along the (112) direction which exhibited single chalcopyrite phase were obtained. The films deposited at relatively higher substrate temperature, sputtering power, and Ar pressure exhibited favorable stoichiometric ratio (Cu/(In+Ga):0.8–0.9 and Ga/(In+Ga):0.25–0.36) with grain size of about 1–1.5 μm, and desirable electrical properties with p-type carrier concentration of $10^{16}-10^{17}$ cm^{-3} and carrier mobility of 10–60 cm^2/Vs. The CIGS layers are expected to fabricate high efficiency thin film solar cells.

1. Introduction

$Cu(In_{1-x}Ga_x)Se_2$ (CIGS) thin film solar cell is one of the most widely applied commercial thin film solar cells with a production about 1.7 GW in 2014 [1]. CIGS thin film material has the highest absorption coefficient among all the semiconductors for solar cell and a direct bandgap varying from 1.02 to 1.67 eV with the incorporation of gallium [2]. The highest conversion efficiency achieved in laboratory for CIGS thin film solar cells and modules measured under the global AM1.5 solar spectrum at 25 °C is $21.0 \pm 0.6\%$ [3] and $17.5 \pm 0.5\%$ [4] respectively. Multiple processing techniques have been studied for CIGS thin film deposition, while the most successful routes in both laboratory and commercial products are co-evaporation and selenization of the metallic precursor. Three stages co-evaporation is the most advanced technique for CIGS thin film growth for the precise control on Cu, In, Ga, Se elements to form a desired stoichiometry and uniformity which provides the highest conversion efficiency [5]. However, multiple sources co-evaporation has drawbacks in scaling up in industry-scale production because of the engineering challenges for equipment and the difficulty in controlling the uniformity of the films on large area which limits the solar cells production [6]. On the contrary, deposition of metallic precursors with Cu, In and Ga elements which are subsequently selenized by Se vapor or H_2Se gas is a stable and reproducible technique for mass production with the capability for large-area deposition [7], whereas the selenization process involves the highly toxic H_2Se which also increases the complexity in production process and costs. Several groups have tried to deposit CIGS thin film by magnetron sputtering with a ternary or quaternary targets followed by post-selenization which simplify the film growth processes, while the selenization process is still needed [8,9].

In this study, deposition of CIGS thin films was carried out by magnetron sputtering using a single quaternary target at multiple processing parameters. The optimum film performance was obtained by adjusting the processing parameters. By understanding the films characteristics deposited at different substrate temperature, sputtering power, and Ar pressure, we synthesized the CIGS thin films with relatively fine structural, compositional and electrical properties which were qualified for high performance CIGS thin film solar cells.

2. Experimental details

Soda-lime glasses (SLG) were used as substrates. Prior to deposition, the substrates were cleaned in ultrasonic bathes in ethanol, acetone, and DI water, respectively. About 1 μm thick Mo back contact layer was deposited on SLGs by DC magnetron sputtering. The resistivity of the Mo back contact was about 5–6×10^{-5} Ω cm which was achieved at the processing parameters of 180 W, 0.3 Pa, 250 °C. The deposition of CIGS thin films was subsequently conducted by RF sputtering using a 3-in. quaternary $Cu_{0.9}In_{0.75}Ga_{0.25}Se_{2.1}$ target which was bonded with a copper plate

* Corresponding author.
E-mail address: hongruij@mail.sysu.edu.cn (R.J. Hong).

http://dx.doi.org/10.1016/j.ceramint.2016.06.067
0272-8842/

by indium. Prior to the deposition, the chamber was first evacuated to a base pressure of 3×10^{-4} Pa by a turbo molecular pump, and then the pre-sputtering was carried out under the condition of an elevated RF power about 10 W once every 10 min to prevent the target from cracking. During the sputtering process, Ar pressure was varied from 0.3 Pa to 1.2 Pa with a fixed flow of 30 sccm, the substrate temperature was raised up from 200 °C to 550 °C and the RF sputtering power was varied between 90 W and 150 W while the substrate was rotated at 10 rpm and the substrate-to-target distance was kept at 7 cm. The circulating cooling water system was applied for the whole deposition process which kept the sputtering system at 10 °C.

3D Optical Profiler (Veeco NT9100) was applied to measure the thickness and surface roughness of the CIGS thin films. Crystallographic structures and phases of the CIGS thin films were examined by X-ray diffraction (XRD) analysis (PANalytical Empyrean). The impurity phases and crystallinity were further examined by Raman spectroscopy (Renishaw inVia plus Laser Micro-Raman Spectrometer). Surface morphologies and elemental composition of the CIGS thin films were investigated by thermal field emission scanning electron microscope (FESEM, Oxford Quanta 400 F) with an Energy dispersive X-ray spectroscopy (EDS). Electrical properties such as carrier concentration, carrier mobility and resistivity of the CIGS thin films were determined by a Hall effects measurement system (PhysTech RH2035) using the van-der-Pauw method. The measured error is $<2\%$. All the characterization measurements were conducted at room temperature, and all the CIGS thin films were deposited around 1.5 μm, which is generally the thickness for CIGS thin film solar cells.

3. Results and discussion

3.1. Phase identification

Fig. 1 shows the XRD patterns of CIGS thin films deposited at different processing parameters. All the thin films exhibited polycrystalline chalcopyrite structural CIGS phase with a preferential orientation along the (112) direction, no impurity phases except Mo were observed suggesting that single target sputtering is appropriate for CIGS deposition. Fig. 1(a) shows the effects of substrate temperature on the CIGS thin films deposition. The intensity of (112) peak increased with the increasing substrate temperature, the stronger intensity of (112) peak indicates better crystallinity of the thin films, which is attributed to the stronger kinetic energy that the particles obtained for migration and diffusion with the higher substrate temperature. Substrate temperature above 550 °C reaches the softening temperature of the SLGs leading to fusion and deformation which adversely affects the film growth. In Fig. 1(b), the effect of sputtering power on the CIGS thin films deposition is demonstrated. At higher sputtering power, the intensity of (112) diffraction was stronger as a result of the growth of more homogeneous and compacted films, which led to a better crystallinity. Fig. 1(c) shows the effect of Ar pressure on the deposition of CIGS thin films. The diffraction intensities increased with the increasing Ar pressure. At higher Ar pressure, the sputtered particles collided with Ar cations more frequently, as a result, the nucleation growth rate was slower and the grains size were larger leading to a stronger diffraction intensity.

According to Scherrer equation, $D = k\lambda/B\cos\theta$, the grain size of the thin film can be calculated by the full width at half maximum (FWHM). Fig. 2 shows the FWHM results of (112) diffraction peaks for CIGS thin films deposited at different processing parameters. The FWHM of CIGS thin film decreased as the substrate temperature, sputtering power, Ar pressure increased, indicating better crystallinity and larger grain size of the film. The minimum

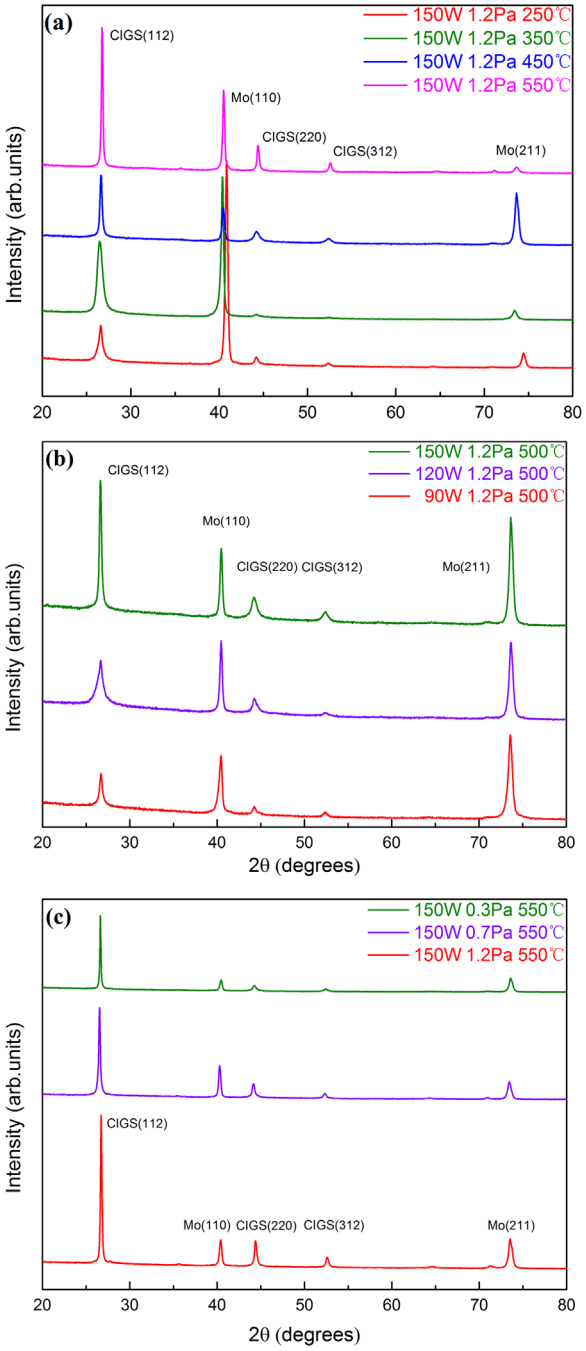

Fig. 1. XRD patterns of CIGS thin films deposited at different substrate temperatures (a), sputtering powers (b), and Ar pressures (c).

value emerged with films deposited at 150 W, 1.2 Pa, 500 °C, which obtained the best crystallinity.

3.2. Raman analysis

XRD analysis is an effective method to examine the crystallographic structures and phases of the as-deposited films. However, the XRD patterns of CIGS thin films are similar to the XRD patterns of Cu-poor phase which are chalcopyrite structural ordered vacancy compounds (OVC) such as $CuIn_3Se_5$ and $CuIn_2Se_{3.5}$ [10], and shifting of the peak positions caused by the stress in the films may overlap the XRD patterns of CIGS and OVC, making it difficult to identify the impurities in CIGS thin films. Raman spectra is based on the interatomic vibrations to determine the

Please cite this article as: H.X. Zhang, R.J. Hong, CIGS absorbing layers prepared by RF magnetron sputtering from a single quaternary target, Ceramics International (2016), http://dx.doi.org/10.1016/j.ceramint.2016.06.067