Journal of Alloys and Compounds 615 (2014) 461–468

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Conventional and rapid thermal annealing of spray pyrolyzed copper indium gallium sulfide thin films

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ARTICLE INFO

Article history:
Received 17 April 2014
Received in revised form 5 June 2014
Accepted 19 June 2014
Available online 7 July 2014

Keywords:
Spray pyrolysis
Copper gallium indium sulfide
Annealing
Absorber layer
Thin film solar cell

ABSTRACT

With this study for the first time effects of post annealing on morphological, structural, optical and electrical properties of spray pyrolyzed copper–indium–gallium–sulfide ($CuInGaS_2$) thin films have been investigated. Pros-and-cons of conventional (CA) and rapid thermal annealing (RTA) have been discussed to obtain the high quality thin film absorbers for solar cell applications. X-ray diffraction analysis revealed that all of the spray pyrolyzed $CuInGaS_2$ thin films have chalcopyrite structures with a highly (112) preferential orientation. Raman spectra also confirmed this structure. However, metal oxide secondary phases such as copper oxide and gallium oxide were detected when the temperature ramp rate was increased during RTA process. Energy dispersive X-ray measurements revealed that both copper and gallium diffused through the surface after annealing processes. Moreover, copper diffusion became pronounced especially at high annealing temperatures. Optical transmission measurements in the wavelength range between 600 and 1100 nm showed that band gap energy of $CuInGaS_2$ thin films was ranging between 1.36 and 1.51 eV depending on the annealing conditions. Very high mobility values have been observed for both processes. The maximum electrical mobility, 30.9 $cm^2/V\ s$, was observed for the films annealed at 600 °C via CA. This is the highest reported value among the $CuInGaS_2$ thin film absorbers deposited by both solution and vacuum based techniques. As a result, post-annealing of spray pyrolyzed $CuInGaS_2$ thin films without usage of highly toxic gases, reported in this study, is very promising and environmentally friendly method to produce solar cell quality absorber layers.

1. Introduction

Chalcopyrite semiconductors have a huge potential as absorber layer in thin film solar cell applications. Very high absorption coefficient in a broad spectral range, proper band gap energy value, excellent stability and radiation hardness are among the main advantages of these materials [1–5]. The reported record efficiency of 20.4% for $CuInGaSe_2$-based thin film solar cells on polymer foils indicates the potential of chalcopyrite semiconductors for efficient energy conversion [2]. Within the copper based family of chalcopyrite semiconductors, the sulfur compounds, such as $CuInS_2$, $CuGaS_2$ and $CuInGaS_2$, have been gaining more attention due to no need for selenium containing toxic precursor materials [3,4]. Numerous studies have been reported on the fabrication of $CuInGaS_2$ thin films via two-stage evaporation and/or co-sputtering followed by the reactive annealing using hydrogen sulfur (H_2S) gas [4,5]. Even though the efficiencies of the thin film solar cells produced by these methods exceeded the 10%, the module cost was very high because of the expensive vacuum based equipments used to fabricate these devices [6,7]. Moreover, H_2S gas is highly toxic and need extra care to use even at laboratory scale. In these respects, solution based methods can be a better alternative over vacuum deposition. Solution based manufacturing such as chemical bath and electrochemical deposition have already been industrialized to deposit both absorber and window layers of thin film solar cells [8]. However, there are very limited studies on wet chemical deposition of the $CuInGaS_2$ thin films [9–11]. Coughlan et al. have been reported a systematic study on the synthesis and shape development in colloidal $CuInGaS_2$ nanocrystals [9]. However, thin film formation and scalability of these nano materials have not been discussed in that study. In another study, Pan et al. reported the gallium doping of $CuInS_2$ thin films via chemical bath deposition method [10]. They have observed that the values of energy band gap and carrier densities of the Ga-doped samples were in the range of 1.50–1.51 eV and 2.07×10^{15}–4.50×10^{15} cm^{-3}, respectively. Recently, Kim and Kim deposited the $CuIn_xGa_{1-x}S_2$ thin film on molybdenum coated glass substrates by spray pyrolysis technique and converted them into $CuIn_xGa_{1-x}Se_2$ via post-selenization [11]. To our knowledge, no work about the effects of

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http://dx.doi.org/10.1016/j.jallcom.2014.06.140
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post annealing process on the film properties of the spray pyrolyzed $CuInGaS_2$ have been published yet. With this study for the first time, improvement of the structural, optical and electrical properties of the spray pyrolyzed $CuInGaS_2$ thin film to obtain high quality absorber layers for thin film solar cell applications have been reported.

2. Experimental

SonoTek flexicoat ultrasonic spray pyrolysis system has been used to form thin films on the molybdenum coated soda lime glass substrates. The experimental setup for the deposition has been described in our previous studies [12,13]. Aqueous precursor solutions were prepared using copper (II) chloride–dehydrate ($CuCl_2$, Sigma–Aldrich), indium (III) chloride ($InCl_3$, Acros Organics), gallium (III) chloride ($GaCl_3$, Sigma–Aldrich) and thiourea (NH_2CSNH_2, Sigma–Aldrich) as copper, indium, gallium and sulfur source, respectively. Table 1 summarizes the other experimental parameters used to build standard $CuInGaS_2$ thin films in this study. All samples have been deposited in two steps. First copper rich solution has been sprayed on molybdenum coated soda lime glass. Then indium rich solution has been sprayed on top of this layer. Post-annealing of the samples has been performed under nitrogen environment via Vaksis CVD-Handy/Tube RTA System. The surface morphology of the films was investigated by FEI, Quanta 200 FEG Scanning electron microscope (SEM). Energy dispersive X-ray (EDX) microanalysis has been used to evaluate the chemical compositions of the films. In order to increase the reliability of EDX results, we reported the average value of measurements of three distinct regions. EDX analysis was performed at 15 kV accelerating voltage over large areas ($300 \times 300\ \mu m^2$). The crystal structure of the films was confirmed using Panalytical X'pert Pro MPD X-ray) diffractometer (Cu Kα, = 1.5405 Å). Raman spectra were obtained by excitation using argon ion and diode lasers (Horiba Jobin Yvon Model: IHR550). Optical measurements have been performed in the wavelength range of 250–1100 nm using a Perkin Elmer Lambda 45 UV–VIS spectrophotometer. Hall Effect measurements were performed on Lake Shore Hall Effect system at room temperature. Samples, having square-shaped ($7 \times 7\ mm^2$) Van der Pauw geometry, were prepared with four contacts at the corners by silver sputtering. The ohmic behavior of the contacts was confirmed by the linear polarization of current–voltage characteristics. During Hall Effect measurements, the potential was applied to cross-contacts and current values were recorded.

3. Results and discussions

3.1. As-deposited and conventionally annealed (CA) films

One of the difficulties to build solar cell quality thin films via solution based manufacturing techniques is caused by the uncontrollability of the physical properties of these films during the fabrication. To build the chalcopyrite structure at least three elements are used and actually, each compositional atom has the possibility of occupying various lattice sites and even generating a vacancy and/or an interstitial during growth. This inevitably leads to difficulties in getting a micro-crystalline crystals. Also the temperatures higher than 300 °C are vital to obtain chalcopyrite structure with amenable crystal properties. However, films deposited at this temperature and under atmospheric conditions suffer from the formation of oxide phases. Moreover, highly diffusive elements such as copper and gallium may cause formation of secondary phases on the film surface. Therefore, it is very important to understand the effects of temperature-involved treatments on the physical properties of chalcopyrite thin films. For this purpose, we first deposited the $CuInGaS_2$ thin films on molybdenum coated glass at 300 °C under atmospheric conditions. Then films have been annealed at various temperatures. Fig. 1(a) shows the SEM images of the 2.1 μm thick $CuGaInS_2$ thin films deposited on molybdenum coated soda lime glass via spray pyrolysis at 300 °C. As can be seen in this figure large density of hillocks was observed. These hillock type structures, most probably were caused by the diffusion of highly mobile elements like copper through the surface during the heat-involved processes, which could result the copper based secondary phase formation. Similar morphologies have been reported in literature for absorber layers deposited via both chemical and vacuum based techniques [11–15].

Table 1
Experimental parameters to build standard CuInGaS2 thin films.

Deposition parameters	Values
Plate temperature	300 °C
Infuse rate	1.5 ml/min
Solvent	75% DDW + 25% MeOH
Carrier gas pressure	4 MPa
Solution loading for each deposition	$0.51\ ml/cm^2$
$CuCl_2/InCl_3/GaCl_3/NH_2CSNH_2$ molarities in the first spray solution	5.50/2.25/2.25/13.50 (mM)
$CuCl_2/InCl_3/GaCl_3/NH_2CSNH_2$ molarities in the second spray solution	4.50/2.75/1.75/13.50 (mM)

It has been known that the post annealing of the spray pyrolyzed thin films provides better crystallinity, and therefore, better electrical properties [16]. Besides deposition of the window and transparent conductive oxide (TCO) layers on top of the absorber layer may include high temperature processes. Therefore, it is important to have knowledge about the film properties of the spray pyrolyzed $CuInGaS_2$ absorber layers after post-annealing process. With these motivations we have annealed $CuInGaS_2$ thin films at 400, 500 and 600 °C for 30 min. These samples were named as As dep., S400, S500, S600 respectively in the text. Fig. 2 shows the temperature profile of both conventional and rapid thermal annealing processes used in this study. Smoother surfaces have been observed with increasing the annealing temperature (Fig. 1). In other words, the density of the hillocks decreased with increasing the annealing temperature and more homogenous surfaces have been obtained by post-annealing process. This could be an advantage to build homogenous window/absorber layers on top of the $CuInGaS_2$ absorber layer. Table 2 summarizes the composition of the as deposited and conventionally annealed samples determined via EDX analysis, which has also been used to calculate the atomic percent ratios of Ga/(In + Ga), Cu/(In + Ga) and S/(Cu + In + Ga). Typically quaternary compounds of copper indium gallium disulfide/diselenide have been characterized by the stoichiometry, which is the Ga/(In + Ga) ratio [17,18]. Also non-stoichiometric films, copper or indium rich, have been used in photovoltaic and electronic applications [19,20]. As can be seen in Table 2, while Ga/(In + Ga) and Cu/(In + Ga) ratios were increasing with annealing temperature, a slight decrease in S/(Cu + In + Ga) ratio has been observed as a general trend of the conventionally annealed $CuInGaS_2$ thin films. Moreover, the increase in the Cu/(In + Ga) ratio was greater than the increase in Ga/(Ga + In) ratio indicating the copper diffusion occurred faster than the gallium diffusion with raising the annealing temperature. Another important result obtained from the EDX analysis was the change in atomic percents of carbon, chlorine and oxygen, which were the undesired contaminants. Regardless of the annealing temperature, conventional annealing process resulted the decrease in atomic percents of both carbon and chlorine in the spray pyrolyzed $CuInGaS_2$ thin films. Additionally, amount of carbon and chlorine contaminants disappeared at 600 °C and 400 °C, respectively. On the other hand, oxygen atomic percent in the films have been raised with annealing temperature. Presence of oxygen in the spray pyrolyzed chalcopyrite semiconductors have been reported earlier [21,22]. Hence it is possible to conclude that oxygen atoms became mobile with increasing the annealing temperature and formed oxygen based secondary phases on the surface.

The effect of annealing on the structural properties and the formation of the secondary phases due to the contaminations observed in the EDX have been investigated via XRD and Raman analyses. Fig. 3 shows the XRD pattern of as-deposited and conventionally annealed samples. XRD peaks observed around 28.0°, 32.1°, 46.3°, and 54.1° (2θ) could be indexed to the (112), (004)/(002), (204)/(220) and (111)/(312)/(215) reflections of the