Materials Science in Semiconductor Processing 80 (2018) 74–84

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Development of phase-pure $CuSbS_2$ thin films by annealing thermally evaporated CuS/Sb_2S_3 stacking layer for solar cell applications

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A R T I C L E I N F O

Keywords:
Copper antimony sulfide thin films
Thermal evaporation
Annealing treatment
Physical properties
Solar cells

A B S T R A C T

In this work, we report the preparation and study of phase-pure $CuSbS_2$ thin films fabricated by a two-stage process; 1) the growth of CuS/Sb_2S_3/glass by stacking layers through a sequential evaporation of Sb_2S_3 and CuS powders, 2) the annealing treatment to the stack layer at different temperatures. Under optimized conditions for the adequate thicknesses of the CuS and Sb_2S_3 layers, three scenarios with dependence on the annealing temperature were obtained. *i*) Annealing conditions below 350 °C are insufficient for the complete formation of $CuSbS_2$ because of its co-existence with $Cu_{12}Sb_4S_{13}$ and unreacted Sb_2S_3. *ii*) 350 °C is identified as the suitable temperature for accomplishment phase-pure $CuSbS_2$. *iii*) At 400 °C some percentage of $CuSbS_2$ decomposed in $Cu_{12}Sb_4S_{13}$. The quantification of phase content by Raman spectroscopy of $CuSbS_2$ and $Cu_{12}Sb_4S_{13}$ as a function of the annealing temperature is provided. In addition, differences in the compositional depth profile with the annealing condition were obtained, and chemical species such as Cu^+ and Cu^{2+} for the $Cu_{12}Sb_4S_{13}$ compound were distinguished by x-ray photoelectron spectroscopy analysis. It was found that photosensitivity of the $CuSbS_2$ film is affected by the presence of $Cu_{12}Sb_4S_{13}$ phase. Phase-pure $CuSbS_2$ thin films had an optical band gap of 1.55 eV and absorption coefficient around 10^4 cm^{-1}; the films showed *p*-type conductivity, electrical resistivity, carrier density and hole mobility of 37.6 Ω-cm, 4.9×10^{16} cm^{-3} and 4.0 cm^2/V s, respectively, and the presence of a dominant level with activation energy of 0.32 eV. Finally, the electrical parameters of the fabricated $CuSbS_2$ solar cell device are reported.

1. Introduction

Chalcostibite copper antimony sulfide ($CuSbS_2$) is an excellent absorber material as a simpler alternative to quaternaries chalcogenide materials such as copper indium gallium selenium (CIGS) and copper zinc tin sulfide (CZTS) for solar cell technologies. $CuSbS_2$ is a material consisting of earth-abundant, low-toxic and economic elements. It is a *p*-type semiconductor with a direct optical band gap from 1.4 to1.6 eV, an absorption coefficient above 10^4 cm^{-1} and moderate hole density ranging from 10^{15}–10^{18} cm^{-3}) [1–3]. Several fabrication methods are used for the preparation of $CuSbS_2$ thin films to be subsequently incorporated in a photovoltaic structure such as thermal co-evaporation [4], rf magnetron co-sputtering [5], chemical bath deposition [6,7], electrochemical deposition [8], hybrid ink method [9], atomic layer deposition [1], as well as combined methods [10]. Thermal evaporation has been one of the most employed methods for the preparation of copper antimony sulfide thin films. For example, $CuSbS_2$ thin films have been fabricated from a $CuSbS_2$ source [11,12], from co-evaporation of Cu, Sb and S sources [4] and CuS_2 and Sb_2S_3 binary sulfides [13], and from sequential evaporation of metallic Sb and Cu layers in a stacked configuration [14]. So far, the development of $CuSbS_2$ films from sequential evaporation of binary sulfides has not been reported. There is only one report on the preparation of Cu_3SbS_3 thin films from this route [15]. The preparation of $CuSbS_2$ thin films from stacked layers requires a two-step process, which consists of the sequential deposition of the precursor materials followed by annealing treatment under a specific atmosphere.

Despite the variety of approaches available for $CuSbS_2$ films preparation as reported in several articles, the presence of secondary phases such as Sb_2S_3 (stibnite), CuS (covellite), $Cu_{1.8}S$ (digenite), Cu_3SbS_3 (skinnerite) and $Cu_{12}Sb_4S_{13}$ (tetrahedrite) co-existing with this material remains as a challenge [4,14,16]. Among these compounds, $Cu_{12}Sb_4S_{13}$ is easily formed in a Cu-rich environment and phase-pure $Cu_{12}Sb_4S_{13}$ thin films have already been synthetized [1,17]. $Cu_{12}Sb_4S_{13}$

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https://doi.org/10.1016/j.mssp.2018.02.029
Received 25 November 2017; Received in revised form 5 February 2018; Accepted 18 February 2018
1369-8001/

is a *p*-type semiconductor with a direct band gap energy from 1.7 to 1.9 eV, absorption coefficient above 10^4 cm^{-1}, hole density ranging from 10^{18}–10^{20} cm^{-3} [18,19] and it is being studied as a thermoelectric material because of their low lattice thermal conductivity [20].

In this paper we report for the first time, the development of stoichiometric phase-pure $CuSbS_2$ thin films from sequential evaporation of binary sulfides, employing a two-step process. As a first step, Sb_2S_3 and CuS layers were sequentially deposited by thermal evaporation over glass substrate to obtain a stack in the order CuS/Sb_2S_3/glass. As a second step, this stack of binary precursors was annealed in a nitrogen atmosphere at different temperatures. The influence of annealing temperature on the evolution of the structural, morphological, chemical, compositional, optical, and electrical properties is discussed. The best conditions for the formation of phase-pure $CuSbS_2$ thin films, with satisfactory properties to be used as an absorber layer in solar cells have been identified. In addition, according to the background mentioned above, an important issue that has been considered in the present study, is the influence of secondary phases on the properties of $CuSbS_2$ thin films. The prepared thin films were characterized by XRD, Raman spectroscopy, ultraviolet-visible spectrophotometry, XPS, EDXS, SEM, AFM, Hall effect, photocurrent response and current versus temperature measurements. Finally, we report a first effort of assembly and testing of $CuSbS_2$ solar cells.

2. Experimental details

2.1. Preparation of Cu-Sb-S thin films

The development of copper antimony sulfide thin films was covered by a two-stage process. In the first step, antimony (III) sulfide (Sb_2S_3) and copper (II) sulfide (CuS) powders from Sigma Aldrich, were sequentially deposited by thermal evaporation on a glass substrate at room temperature. The stacking order that showed the best results was CuS/Sb_2S_3/glass-substrate. The vacuum base pressure was 6×10^{-5} mbar, the distance between source and substrate was 16 cm and the currents applied to the source were 120 and 210 A for Sb_2S_3 and CuS powders, respectively. Preliminary experiments involving various depositions were performed, in order to determine the adequate film thickness of each precursor material to obtain stoichiometric $CuSbS_2$ film without the formation of micro-phases. Once done this approach, the thickness of Sb_2S_3 film was adjusted to 400 nm and four thicknesses of CuS film were employed, 160, 180, 200 and 230 nm. The thicknesses ratios Sb_2S_3/CuS were 2.5, 2.2, 2.0 and 1.7. According to this, each stack layer was labeled as CuSbS_2.5, CuSbS_2.2, CuSbS_2.0 and CuSbS_1.7. In the second stage, the CuS/Sb_2S_3/glass stacks were thermally annealed in a quartz tubular furnace at atmospheric pressure employing N_2 gas for 2 h at different temperatures. The annealed temperatures for the CuSbS_2.5 stack were 250, 300, 350 and 400 °C; the other samples were only annealed at 350 °C. Table 1 summarizes the processing conditions of the fabricated samples in this work.

Table 1
Processing conditions of the stacked samples.

Sample	Film thickness [nm]		Annealing temperature [°C] / time [h]
	Sb_2S_3	CuS	
CuSbS_1.7	400	230	350 / 2
CuSbS_2.0	400	200	350 / 2
CuSbS_2.2	400	180	350 / 2
CuSbS_2.5	400	160	350 / 2
CuSbS_2.5	400	160	250 / 2
CuSbS_2.5	400	160	300 / 2
CuSbS_2.5	400	160	400 / 2

2.2. Fabrication of photovoltaic structures

Photovoltaic solar cells with the glass/FTO/CdS/$CuSbS_2$/C/Ag structure, were assembled to evaluate the $CuSbS_2$ thin film as absorber layer. First, a *n*-CdS film around 100 nm thickness was prepared by chemical bath deposition employing a previously reported method [21]. The as-deposited CdS film was annealed in N_2 at 350 °C for 30 min. Afterwards, the $CuSbS_2$ was grown on top of the annealed CdS film with the procedure described in Section 2.1. Finally, graphite and silver metallic contacts (C/Ag) were deposited on a surface of $CuSbS_2$, as a front contact of 10 mm^2 area, followed by annealing at 80 °C for 30 min.

2.3. Characterization techniques

The prepared thin films were investigated using several characterization techniques. The thickness was measured with an alpha step D-100 stylus profiler (KLA Tencor). The structure was determined by x-ray diffraction (XRD) with a X'Pert Pro diffractometer using a Cu Kα radiation (λ = 1.5406 Å); Raman spectra were acquired with a Dilor LabRam II micro-Raman system equipped with a 632 nm He-Ne laser as excitation source. Optical absorption spectra were measured using a Genesys 10 S UV–VIS spectrophotometer. X-ray photoelectron spectroscopy (XPS) spectra were registered with a Thermo Fisher Scientific K Alpha spectrometer using the Al Kα excitation line at 1487 eV. Surface morphology images were acquired by both atomic force microscopy (AFM) and scanning electron microscopy (SEM) using the DI-Veeco Nanoscope IV and Hitachi FESEM S-5500 systems. Elemental composition of the films was determined by energy dispersive x-ray spectroscopy, EDXS (Hitachi FESEM S-5500). Hall effect measurements were carried out in the dark at room temperature using an Ecopia HMS-3000 system. The photosensitivity of the films was assessed by current in dark and under illumination, using an automated Keithley 230 voltage source and a Keithley 619 electrometer. The samples were illuminated with a tungsten-halogen lamp at an incident power of ~ 100 mW/cm^2. The electrical current versus temperature measurements were carried out in the dark using a 4600 BIO-RAD, DLTS spectrometer. The films were heated at 0.15 K/s from 100 to 450 K with an applied bias voltage of 5 V. The dark-current signal was measured with a programmable 617 Keithley electrometer. Finally, current density versus voltage measurements of the solar cell device were performed with a LCS-100 Solar Simulator at standard compliant to ASTM &IEC for AM1.5 G, Newport, calibrated with a reference silicon solar cell.

3. Results and discussion

3.1. Optimization of the thickness of CuS and Sb_2S_3 precursor layers

3.1.1. XRD and Raman characterization

A schematic view of the stacking CuS and Sb_2S_3 layers, thermally evaporated on a glass substrate is shown in Fig. 1(a). The film thicknesses of the grown layers are also shown. The XRD and Raman measurements that were recorded for the CuSbS_2.5 sample before annealing (see Table 1) are displayed in Fig. 1(b)-(c), respectively. As observed in this figure, signals coming from the CuS layer are the only detected by both XRD pattern and Raman spectrum, because the as-deposited Sb_2S_3 thin film is amorphous in nature [22,23]. The XRD pattern reveals a diffraction plane at 2θ ≈ 46.3° which matches with the (110) plane of the Cu_9S_5 PDF-card#26–0476; the Raman spectrum shows two main bands at 262 and 470 cm^{-1}, corresponding to the A_{1g}TO and S-S bonding stretching vibration modes in copper sulfide [24–26].

As a first step in this study, it was to select an adequate thickness of the Sb_2S_3 and CuS layers with the aim to obtain a $CuSbS_2$ film without or with minor binary phases. For this purpose, the stacks labeled as CuSbS_1.7, CuSbS_2.0, CuSbS_2.2 and CuSbS_2.5 were subjected to the