Solar Energy Materials & Solar Cells 143 (2015) 128–134

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Deposition and characterization of Cu_2SnS_3 thin films by co-evaporation for photovoltaic application

T. Srinivasa Reddy, R. Amiruddin, M.C. Santhosh Kumar *

Optoelectronic Materials and Devices Laboratory, Department of Physics, National Institute of Technology, Tiruchirappalli, Tamil Nadu 620015, India

ARTICLE INFO

Article history:
Received 11 March 2015
Received in revised form
24 June 2015
Accepted 24 June 2015

Keywords:
Thin films
Co-evaporation
Copper tin sulfide
Electrical properties
Optical properties

ABSTRACT

Cu_2SnS_3 (CTS) is a p-type direct band gap ternary compound semiconductor. Its constituent elements are non-toxic, abundant in earth crust and low cost. We report the deposition of Cu_2SnS_3 thin films on soda-lime glass substrate by co-evaporation technique at different substrate temperatures. The effect of substrate temperature on the growth of CTS thin films has been investigated. X-ray diffraction study confirms the formation of tetragonal phase of Cu_2SnS_3. The Raman analysis confirms the ternary/binary phases of the CTS thin films. The surface morphology of the film is examined by atomic force microscopy (AFM) and Scanning electron microscopy (SEM). Energy dispersive spectroscopy (EDS) has been used for analyzing the film composition. The X-ray photoelectron spectroscopy (XPS) shows that Cu, Sn and S are in the oxidation states of $+1$, $+4$ and -2 respectively. The optical band gap of CTS thin films is 1.23 eV and the absorption coefficient is the order of $10^5\ cm^{-1}$. Hall measurements confirm the p-type nature of the as-prepared CTS films. The carrier concentration, resistivity and mobility are $2.81 \times 10^{21}\ cm^{-3}$, $1.31 \times 10^{-3}\ \Omega$ cm and $1.70\ cm^2\ V^{-1}\ S^{-1}$ respectively.

1. Introduction

The conventional thin film solar cell (TFSC) materials like CIGS and CdTe played a major role in the development of thin film solar cells. These thin film solar cells composed of rare elements like In, Ga, Te or heavy metals, which are toxic in nature. Cu_2ZnSnS_4 (CZTS) is an emerging absorber layer material, which can replace existing CdTe and CIGS absorbers. TFSCs with CZTS as absorber layer have yielded efficiency of 8.4% using vacuum evaporation [1]. The compound semiconductor CZTS has direct band gap energy in the range of 1.4–1.6 eV and have large absorption coefficient in the order of $10^4\ cm^{-1}$, which is suitable for photovoltaic absorber layer in solar cells. Despite these advantages the CZTS having uncontrollable growth condition leading to the formation of the binary and ternary phases along with the desired CZTS phase [2]. Some Cu–Sn–S ternary compounds are formed in the presence of CZTS thin films. These ternary compound exhibits a variety of phases like Cu_2SnS_3, Cu_3SnS_4 and Cu_4SnS_4 [3]. Another approach to overcome this problem is to go for a ternary material with similar structure and material properties to that of CZTS. The ternary compound Cu_2SnS_3 (CTS) is a promising absorber material for photovoltaic application. The ternary compound semiconductor Cu_2SnS_3 (CTS) is a p-type direct band gap material and its elements are non-toxic and earth abundant. It is a known fact that, CTS exhibits dimorphic or polymorphic phases with a phase transition occurring at 780 °C. The high temperature phases of CTS above 780 °C are reported as isomorphic with sphalerite structure (cubic) [2], and low temperature phases are reported as tetragonal [4], monoclinic [5] and triclinic [6]. CTS have been reported to have band gap energies in the range of 1.15 eV and an absorption coefficient greater than $10^4\ cm^{-1}$ [7]. The thin films of Cu_2SnS_3 (CTS) have been prepared using several techniques like direct liquid coating [8], spray pyrolysis technique [7], spin coating [4,6], sulfurization of stacked metal precursors [2] and successive ionic layer absorption and reaction (SILAR) [9].

In the present work copper tin sulfide (CTS) thin films have been prepared by co-evaporation technique. There are only a few reports available for deposition of ternary compound semiconductor thin films using co-evaporation technique [10,11]. In this investigation CTS films are deposited on soda-lime glass at different substrate temperature from 200 °C to 300 °C. The structural, morphological, optical and electrical properties of the co-evaporated CTS thin films are studied and reported for the first time.

2. Experimental

Copper tin sulfide (CTS) thin films have been deposited on soda-lime glass substrate using co-evaporation technique. A 12″

* Corresponding author.
E-mail addresses: santhoshmc@nitt.edu, Srinusolasa728@gmail.com (M.C. Santhosh Kumar).

http://dx.doi.org/10.1016/j.solmat.2015.06.049
0927-0248/

vacuum coater, which consists of oil diffusion pump coupled with rotary pump, was used for deposition of CTS thin films at a vacuum better than 7×10^{-6} mbar. Copper wire (Sigma-Aldrich, 99.999%), tin wire (Sigma-Aldrich, 99.999%) and sulfur powder (Sigma-Aldrich) were taken as source materials. Ultrasonically cleaned soda-lime glass was used as substrates. Copper and tin were evaporated from two separate molybdenum boats and the sulfur powder was evaporated from a glass crucible kept in a tungsten basket. The working pressure of the three-source vacuum coating unit was 5.5×10^{-5} mbar. After reaching the evaporation temperature of source materials, shutter over the boats was moved to sideway for the deposition the film on the substrate [10]. A 1 kW heater with PID controller was used as the substrate heater. CTS thin films were deposited at substrate temperature of 200 °C, 250 °C and 300 °C. The source to substrate distance was fixed at 22 cm. In the present study, thin films were deposited on optically flat soda-lime glass substrates. The glass slides were first cleaned with detergent solution and then thoroughly washed in running water. These slides were cleaned with double distilled water and followed by ultrasonic cleaning for 30 min. These substrates were cleaned with acetone, then dried with a hot-air dryer and loaded into the substrate holder of vacuum chamber. The substrates were further cleaned by ion-bombardment (HT) in vacuum chamber for 10 min, prior to the deposition of the film.

X-ray diffraction (XRD) was used to confirm the structure and phase of the CTS thin films. Cu K_α radiation ($\lambda = 1.54$ Å) was used to record the spectrum in the range of angle (2θ) 20–80°. The Raman analysis was carried out using Renishaw inVia micro-Raman spectrometer. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) was used to analyze the morphology and chemical composition of the films by using Zeiss Ultra 55 FESEM with Oxford EDX system. The atomic force microscopy (AFM-Park NX10) was used to study the surface roughness of the films. The X-ray photoelectron spectroscopy was used to study the binding energy for core level of the films using PHI 5000 Versa Probe-II. The optical band gap, absorption coefficient, extinction coefficient and refractive index of CTS films have been computed from optical absorbance and reflectance measurements. The optical absorbance spectra were recorded using UV–vis–NIR spectroscopy (JASCO V-670) in the range of wavelength 200–2500 nm. Hall measurement technique (ECOPIA HMS-5000) was employed for electrical measurements using vander pauw configuration.

3. Results and discussion

3.1. Structral and Raman study

Fig. 1 shows the X-ray diffraction patterns of the CTS thin films deposited at different substrate temperatures. The XRD patterns indicate the as-deposited films are polycrystalline in nature. The diffraction peaks for the samples prepared at 250 °C are $2\theta = 28.46°$, 29.84°, 38.26°, 44.52°, 47.45°, 64.78° and 71.91° could be assigned to (112), (103), (211), (213), (220), (314) and (413) planes respectively. The XRD patterns of the sample are in close agreement with standard tetragonal phase of Cu_2SnS_3 (JCPDS 89-4714). These results are in good agreement with those reported by Fernandes et al. [2]. The principal peak of the films deposited at 250 °C is 28.46°corresponding to the (112) plane, which indicates the preferred crystallization along this plane. The secondary phases Cu_2S are present for all deposited films at 31.69°. Similar binary phases are also reported by Fernandes et al. [2]. In addition to this, for all deposited films, there is a peak at 21.21°. This peak corresponds to (103) plane of binary phase Sn_2S_3 (JCPDS 75-21830). The lattice parameters corresponding to tetragonal phase

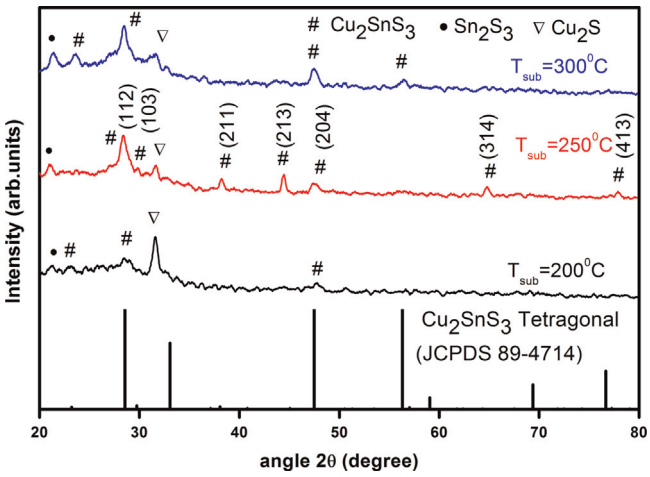

Fig. 1. XRD patterns of the Cu_2SnS_3 thin films at different substrate temperatures.

of the film deposited at substrate temperature of 250 °C were calculated using the relation:

$$\frac{1}{d^2_{(hkl)}} = \left[\frac{h^2 + k^2}{a^2}\right] + \frac{l^2}{c^2} \quad (1)$$

where d is the interplanar distance and (hkl) are the Miller indices. The evaluated lattice parameters are $a = 5.412$ Å, $b = 5.412$ Å and $c = 10.860$ Å. These values are very close to the tetragonal system of CTS film (JCPDS 89-4714). The average crystallite size of the samples was calculated from the full width at the half-maximum (FWHM) of the peak (β), using the Debye–Scherrer equation as follows:

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (2)$$

where λ is the wavelength of the X-ray radiation (1.54 Å) and θ is the Bragg angle of the peak. The average crystallite sizes of all deposited CTS thin films increases from 10.7 nm to 14 nm with increase of substrate temperature. Thus, the average crystallite size of the film deposited at 250 °C using the highest peak (112) is 12 nm, which is close to the value (11.4 nm) observed for CTS film grown by spray pyrolysis technique [12].

Raman spectroscopy is a standard characterization technique to reveal the exact phases of ternary semiconductor compound thin films. Fig. 2 shows the Raman spectra of the film deposited at the substrate temperature of 250 °C in the wavelength range 50–600 cm^{-1} with Gaussian fitting. The micro-Raman spectra contains modes at 71 cm^{-1}, 127 cm^{-1}, 285 cm^{-1}, 332 cm^{-1} and 472 cm^{-1}. The modes at 285 cm^{-1} and 332 cm^{-1} are characteristic vibration symmetry of the tetragonal phase of Cu_2SnS_3 thin films. The high intense mode at 332 cm^{-1} attributed to the tetragonal phase of Cu_2SnS_3, which is in close agreement with reported Raman data by Guan et al. [9]. The mode at 285 cm^{-1} is assigned to the tetragonal phase of Cu_2SnS_3 as reported earlier by Han et al. [6]. The slight difference in the frequency might be due to composition, growth condition and microstructure of the CTS thin films. The tetragonal (Cu_2SnS_3) and binary phases (Cu_2S, Sn_2S_3) of the film deposited at substrate temperature of 250 °C are reveled by XRD analysis. The mode at 472 cm^{-1} is a characteristic binary phases of Cu_2S [13]. The mode at 71 cm^{-1} is attributed to the binary phase of Sn_2S_3 phase [14]. The low intensity mode at 127 cm^{-1}, attributed to the binary phase of SnS [15].