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Synthesis and characterization of thermally evaporated copper bismuth sulphide thin films

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ABSTRACT

Non-toxic copper containing chalcogenides are considered as promising alternate materials for the absorber layer in thin film solar cells and visible-light harvesting devices. In this paper, we reported synthesis of Cu_3BiS_3 thin films using a two-step thermal evaporation method for the first time. A Cu_2S layer of 0.4 μm thickness was firstly evaporated onto glass substrate at room temperature, followed by evaporation of a Bi_2S_3 layer of 0.8 μm thickness. The Cu_3BiS_3 thin films were formed by thermally annealing and diffusing the two evaporated layers in a vacuum furnace. This method resulted in the improved crystallinity and phase purity of the grown Cu_3BiS_3 films. Effects of annealing temperature on different properties of the fabricated samples were investigated. The obtained low band-gap (1.45 eV) and good optical properties such as low transmittance (10–30%) and reflectance (~10%) of the Cu_3BiS_3 films demonstrated it as a suitable material for the absorber layer of solar cells.

1. Introduction

The photovoltaic modules based on thin film solar cells such as CdTe and Cu(In,Ga)Se_2 have shown high efficiencies exceeding 22% [1,2], however, their toxicity has been a critical issue [3]. Moreover, large-scale manufacture of thin film solar panels requires cheap, earth-abundant and environment-friendly materials to be used as viable sources of green energy for the community. Among the newly developed, low cost and nontoxic materials, copper zinc tin sulphide (CZTS) is an emerging material with an efficiency of ~12%, however, there are still many complications associated with the CZTS. For example, its narrow single-phase region in the phase diagram and its multiple secondary phases within the material limit the further improvement in its cell efficiency [4,5].

In recent years investigations have begun to focus on another earth-abundant and less-toxic ternary semiconductor compound called copper bismuth sulphide (Cu_3BiS_3). It belongs to I-V-VI group and is naturally found in the Wittichenite mineral with an orthorhombic structure (a = 0.7725 nm, b = 1.0395 nm, and c = 0.6716 nm). It was reported to be one of the suitable materials for the solar cell absorber layer [6,7]. Fabrication of the Cu_3BiS_3 (CBS) thin films was reported by different research groups for solar cell applications using various techniques such as sputtering, evaporation, combined chemical and thermal approach, and solid state reactions [7–10]. It was reported that the CBS films have a stable structure at room temperature and an energy band gap of 1.4 eV, which is pretty close to the best region in the visible solar energy spectrum thus suitable for the photovoltaic applications [11]. The most common feature of the Cu_3BiS_3 is the presence of localized states due to inherent defects in the mobility gap, along with its polycrystalline nature [10]. P-type conductivity of the CBS samples was reported by Mesa et al. [12]. The same group also reported a Hall mobility of 4 cm^2/V s, a carrier concentration of 2×10^{16} cm^{-3} and a thermoelectric power output of ~0.73 mV/K for the thermally co-evaporated Cu_3BiS_3 thin films [13]. Cu_3BiS_3 thin films was also prepared by post-annealing the magnetron sputtered Cu and Bi layer with a thermally evaporated S layer, and the film was reported to have p-type conductivity, good lateral homogeneity, and Wittichenite orthorhombic structure with a direct band gap [14].

In this work, we report, for the first time, the fabrication of Cu_3BiS_3 thin films using a novel two-step thermal evaporation technique (i.e., successive deposition of Cu_2S and Bi_2S_3 layers) followed by post-annealing in vacuum. The structural, morphological, and optical properties of the annealed films are characterized.

2. Experimental

Soda lime glass substrates were cleaned with acetone and methanol, rinsed with deionized water, and then dried with nitrogen gas. A two-step thermal evaporation technique was employed for successively depositing Cu_2S and Bi_2S_3 pallets of 99.99% purity onto glass substrates.

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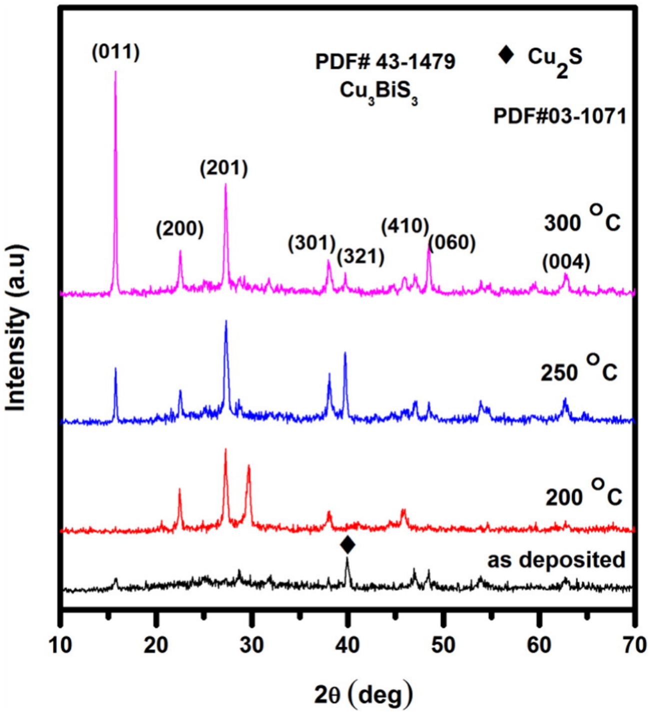

Fig. 1. XRD analysis of the as-deposited and annealed Cu_3BiS_3 films.

Both pallets were evaporated in a vacuum chamber at a pressure of 5×10^{-5} mbar from a tungsten crucible connected to a power supply. A Cu_2S layer of 400 nm thickness was firstly deposited by supplying a current of 95 A and then a Bi_2S_3 layer of 800 nm thickness was deposited on top of the Cu_2S layer, thus obtaining a film of 1.18 μm thickness. The Cu_3BiS_3 thin films were then obtained by thermally annealing the Cu_2S and Bi_2S_3 double layers at different temperatures of 200 °C, 250 °C and 300 °C for 60 min in a vacuum furnace to study the effect of thermal annealing on the structural and optical properties of the fabricated films. Structural characterization of the films was carried out using the X-ray D-8 Discover diffractometer with Cu radiation (k-α lines $\lambda = 1.54$ Å). Surface morphology of the as-deposited and annealed samples was investigated using a field emission scanning electron microscope (FESEM, SU8020 X-Max^N Oxford). Energy dispersive X-ray spectroscopy (EDX) with a probe current of 5.0 nA was used for elemental analysis. The UV–Vis spectroscopy was carried out for the optical characterization of the thin films using Shimadzu, UV 3101pc UV-VIS-NIR spectrometer. The four-probe technique using a programmable Keithly 2400 source meter was used for the electrical characterization of the thin films. The electrical contacts were made on the thin film surface using adhesive silver conductive paint and the measurement were performed with gradually increasing applied voltage up to 5 V. The photoluminescence (PL) spectra were obtained using a Perkin Elmer, LS5 photoluminescence spectrometer.

3. Results and discussion

Fig. 1 shows the XRD patterns for the as-deposited and annealed samples. The as-deposited film has a crystalline phase of Cu_2S based on the standard XRD card PDF#03-1071. Similarly, all the peaks observed in the annealed samples are well matched with the standard PDF#43-1479 (Using X'Pert HighScore software), for the Wittichenite Cu_3BiS_3 phase, and no secondary phases were observed. The crystallite size predicted using the Scherrer formula for the (011) peak at $2\theta = 15.75^{\circ}$ was ~44 nm for the film annealed at 300 °C.

Due to the low melting point of bismuth (271 °C), it is expected that the bismuth will be diffused throughout the thickness of the films. From

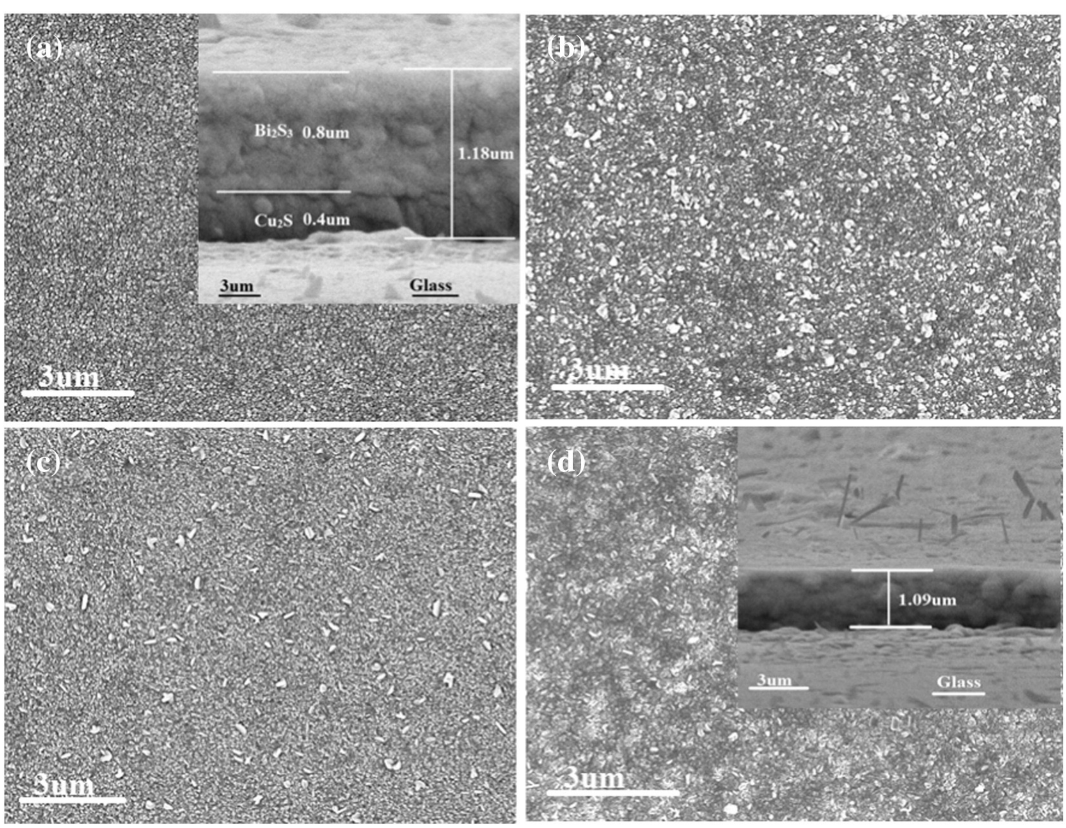

Fig. 2. Scanning electron micrographs of (a) as-deposited sample (b) 200 °C annealed sample (c) 250 °C annealed sample (d) 300 °C annealed sample and inset of (d) show the cross-sectional view of the sample.

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