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Synthesis and characterization of Sn-Sb-S thin films for solar cell applications by sputtering techniques

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Abstract

Tin antimony metallic films were deposited by the sputtering technique. Sulfurization of these metallic films was carried out in thermal vacuum coating unit. Furthermore, the samples were annealed in argon atmosphere at different temperatures ranges from 425 to 525 °C for one hour inside quartz ampoules. The effects of the thermal annealing on the structural, optical and electrical properties on the sulfosalt Sn-Sb-S films have been investigated. The estimation of elemental composition was carried out with Energy Dispersive X-ray Spectroscopy. Molybdenum contacts were deposited for electrical measurement through sputtered coater by using mask arrangement. The photoconductivity measurements suggest that the obtained films show semiconducting behavior with band gap of 1.3 eV.

Key words: sputtering, photoconductivity, band gap, sulfurization, annealing

1. Introduction

Tin antimony sulfide (TAS) is an abundant and cheap material and is a new type of absorber layer recently reported for thin film solar cells. This semiconductor thin film can be achieved by exchanging indium atoms in chalcopyrite mineral, $CuInS_2$ with antimony, and by copper with tin. The abundance of indium and tin in the earth crust is 0.049 and 2.2 ppm, correspondingly [1]. Therefore, all constituents in TAS thin film are abundant and are also nontoxic. Due to their potential applications in solar cell technology, the metal based chalcogenide thin films have attracted much attention of the scientific community [2]. Sn-Sb-S thin films are being pursued with increasing interest on account of their proven and potential applications in many semiconductor devices, in particular with the photovoltaic applications. For a quality scientific research in thin film applications, a close and precise thin film growth is necessary [3]. Many deposition techniques are consistently being used for thin films fabrication such as thermal evaporation, electron beam evaporation, chemical bath deposition, and many more chemical deposition techniques [4]. Among many metallic deposition techniques for thin films, sputtering technique is one of the sound techniques in terms of quality of films and controlling different parameters [5]. The knowledge about the electronic properties is scarce due to marginal publications in the relevant field. The Sn-Sb-S ternary compound has been reported as a good candidate for photovoltaic applications [6, 7]. This paper mainly concerns with the elemental composition, structural, electrical and morphological properties of Sn-Sb-S thin films annealed under argon atmosphere for the applications in particular with the solar cell technology.

2. Experimental

2.1. Fabrication, sulfurization and annealing of SnSb thin films

SnSb thin films were deposited by using sputtering coating unit. Argon gas at 2×10^{-5} mbar pressure is used as sputtering gas. The top layer of the machine was replaced by an aligned target layer for the growth of the libraries of SnSb thin films. The targets were

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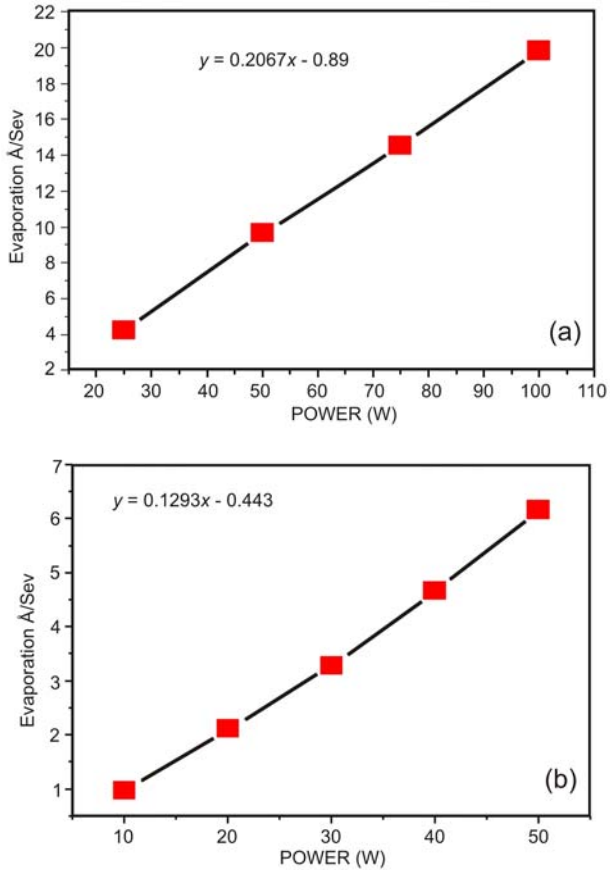

Fig. 1. Antimony (Sb) target calibration, density = 6.62 g cm^{-3}, purity = 99.999 % (a), tin (Sn) target calibration, density = 7.2 g cm^{-3}, purity = 99.998–99.999 % (b).

calibrated with the help of quartz crystal and balancing techniques. Calibration of the target is presented in Fig. 1. The distance between target and substrate was fixed at 10 cm and quartz crystal was inserted in the chamber to calibrate the target [8], after these calibrations the thin films of SnSb were deposited by the sputtering coating unit.

The as-deposited SnSb sputtered films on glass substrates were sulfurized by thermal evaporation techniques in vacuum chamber. The sulfurized SnSb thin films were placed in closed quartz ampoule enclosing argon gas at a pressure below atmospheric for 1 h annealing at a temperature of 425, 450, 475, 500 till 525 ℃ in tube furnace. Abrupt cooling of the heated quartz tubes containing thin films leads to crack the films due to thermal contraction. In order to avoid such cracking, the tube was cooled down to room temperature with slow cooling rate (1/2 ℃ min^{-1}).

The temperature was monitored by the thermocouple inserted inside the furnace and interfaced with the computer.

Table 1. Elemental composition of Sn-Sb-S thin films (at.%)

S	Sn	Sb
61.63	21.53	17.11

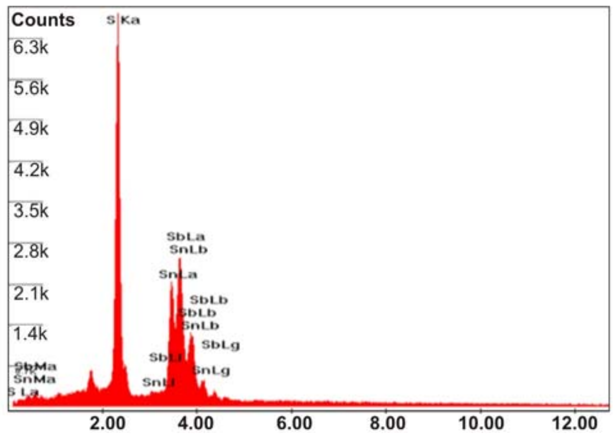

Fig. 2. Elemental analysis: EDS plot of Sn-Sb-S thin films.

2.2. Characterization of thin films

Since the physical, optical and mechanical properties of a material are strongly influenced by their structure, their studies are essential to cognize the correlation among the processing parameters and material behavior while used in practical applications. The structural properties were determined by X-ray diffraction (XRD) using Cu Kα (λ = 1.5406 Å) radiation. The photoconductive response in the visible and NIR range up to 1200 nm was determined by photoconductivity spectrometer. SEM equipped with EDX was employed to examine the micro-structural features such as grains, porosity and elemental composition. The band gap of Sn-Sb-S thin films was calculated from the photoconductivity measurement by plotting the photoconductivity response with the energy (eV).

3. Results and discussion

Table 1 shows the results of the compositional analysis in atomic percentage for the fabricated thin films. The elemental study (Fig. 2) of the deposited films was confirmed by the EDS.

The XRD pattern of Sn-Sb-S is presented in Fig. 3. With the help of the XRD results of the libraries, it was confirmed that alloys were not formed as no peak shift was observed for Sn and Sb, instead this is gen-

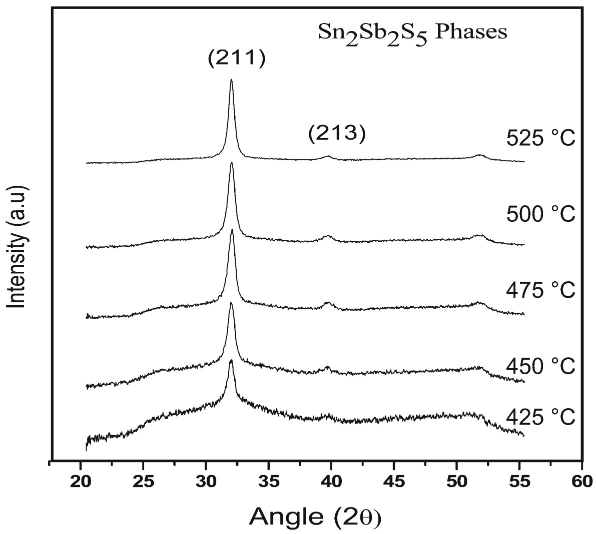

Fig. 3. XRD pattern of Sn-Sb-S thin films at different annealing temperatures.

erally an indication that the solid state solution was formed [9–11]. The $Sn_2Sb_2S_5$ phase is distinctly found in the samples at all annealing temperatures.

The sample annealed at 425 ℃ is taken as the starting sample, e.g., as deposited, which is in amorphous phase, while the samples annealed at high temperature (450–525 ℃) are polycrystalline.

It is also confirmed from the XRD, that the crystallinity seemed increasing with the increase in annealing temperature. The crystalline size for the films was calculated by using Debye-Scherer's formula:

$$D = 0.9\lambda/\beta\cos\theta, \quad (1)$$

where D, λ and β are the average crystallite size, the wavelength and the full-width at half maximum, respectively [9, 10]. The average grain size of our crystalline sample was 110 Å.

The photoconductivity response of the library is plotted in Fig. 4. It is noted that the samples annealed at 425 ℃ have poor photoconductivity, while the photoconductivity response increases for the samples annealed at higher temperatures. At low annealing temperature some of the sulfur still remains in elemental form and all the sulfur does not take part in reaction with SnSb, which causes poor photoconductivity. At higher annealing temperatures sulfur reacts as whole with Sn-Sb-S, and the photoconductivity of the thin film increases [12]. This is also clear in the SEM images shown in Fig. 5. All the films were enclosed in quartz ampoules while annealing, and therefore retained their stoichiometry. As SnS and Sb_2S_3 are already reported as absorber layers in solar cells [13–19], therefore we measured the photoconductivity of Sn-Sb-S thin films and found it a good photo active material. At high annealing temperature, SnS dissolved into Sb_2S_3 by forming a stable SnSbS compound in the form of thin film which shows good photoconductivity. The photoconductivity response for this material lies in the visible and near infrared region. Figure 5 shows the SEM images of selected points of Sn-Sb-S thin film sputtered library at different annealing temperatures. It is evident from SEM images that the sample annealed at 425 ℃ shows the presence of sulfur in boiled condition (Fig. 5a), however, as the annealing tem-

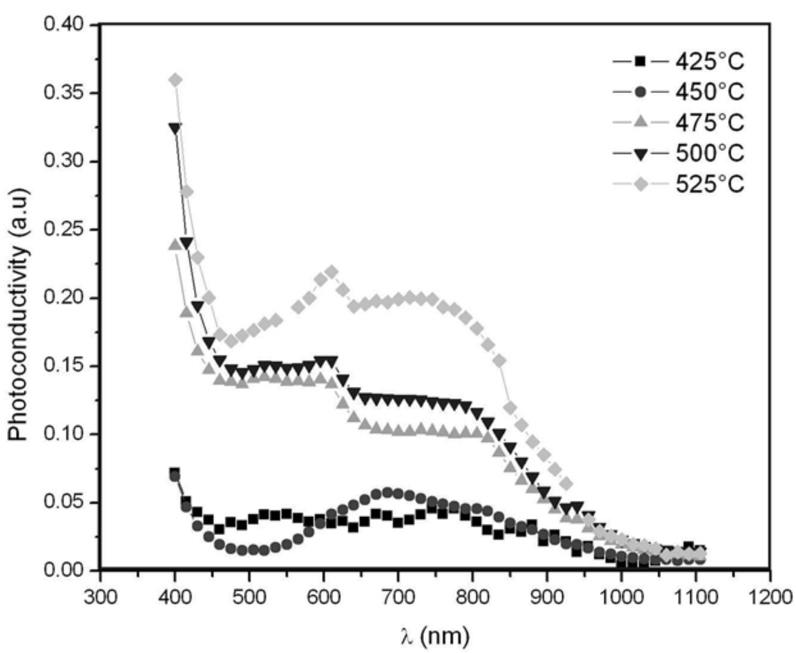

Fig. 4. Photoconductivity response of the as-deposited and annealed films.

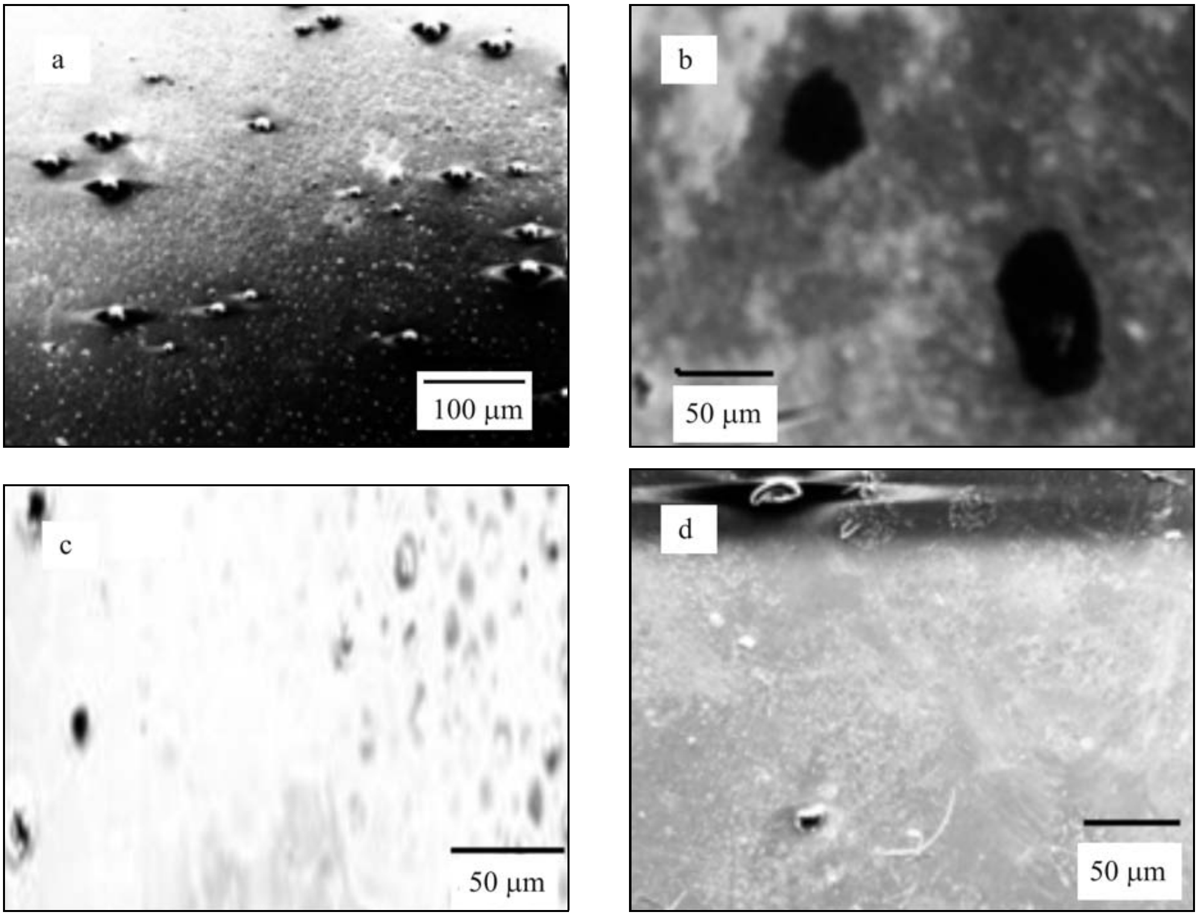

Fig. 5. SEM images of SnSbS library of selected points at different annealing temperatures: 425 ℃ (a), 475 ℃ (b), 500 ℃ (c), 525 ℃ (d).

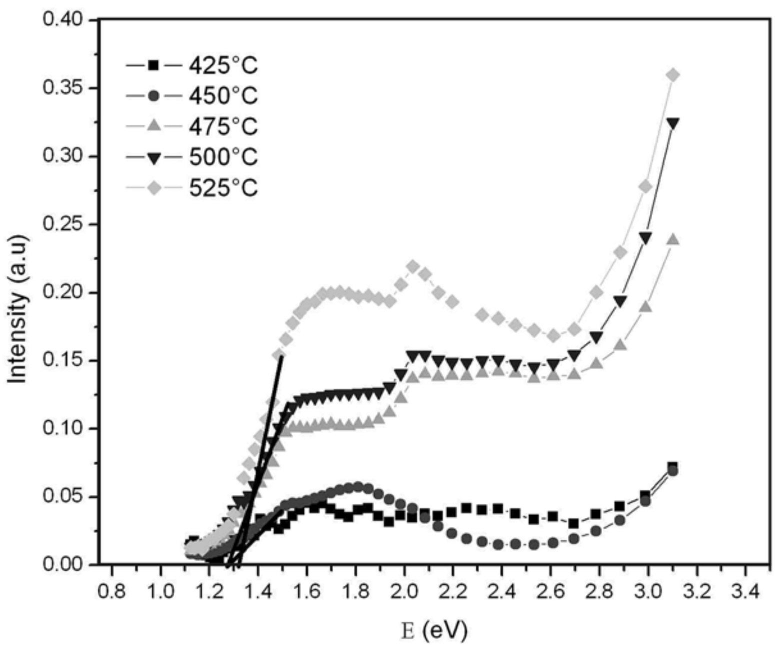

Fig. 6. Energy band gap calculations for the samples annealed at different temperatures.

perature increases, the sulfur is adsorbed and reacted with Sn and Sb to make the required phases. This is more evident from the samples annealed at 500 and 525 °C (Fig. 5c,d) that the sulfur is adsorbed and reacted with SnSb.

Figure 6 shows the measurements of the optical band gap for all the thin films. The band gap for Sn-Sb-S thin films is in good agreement and consistent with the literature [20–22]. The band gap calculated from the photoconductivity measurement by plotting the photoconductivity response with the energy (eV) is found to be 1.3 eV for all the samples; an optimal value for band gap to be used in solar cells. The lower band gap is attributed to the opaque nature of antimony present in the ternary compound.

4. Conclusions

We have discussed the role of Sn-Sb-S thin film as a low cost and non toxic material deposited by sputtering coating unit for the applications in solar cells. The metallic thin films of SnSb were sputtered from Sn and Sb tilted targets on glass substrates. The films were then sulfurized by thermal evaporation techniques. The films were then annealed at 425, 450, 475, 500 and 525 °C inside sealed quartz ampoules containing argon gas. The elemental compositional study was carried out with EDS techniques. The XRD shows that the peaks of different compounds have no shift at different annealing temperatures, which suggests that no solid state solution is formed. XRD also confirms that $Sn_2Sb_2S_5$ phase is very stable. The photoconductivity measurement confirms that the material is highly photoconductive. The band gap was calculated by the method of "fitting curve" from photoconductivity data through horizontal axis. We found the band gap to be 1.3 eV for $Sn_2Sb_2S_5$ phase which would cover the visible as well as near infrared solar spectrum and could be used for device fabrication.

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