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EFFECT OF ANTIMONY VARIATION ON THE PHYSICAL PROPERTIES OF THERMALLY DEPOSITED SnS THIN FILMS

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Antimony doped tin sulphide thin films were prepared on glass substrate from SnS and Sb_2S_3 powder by thermal evaporation techniques. The thin films were annealed in argon gas at 250°C for 30 minutes. The films were characterized by X-ray diffraction (XRD), optical microscopy, optical absorption, photoconductivity, and hot-probe techniques. The XRD studies revealed that the annealed films are polycrystalline. The band gap was found to be in the range 2.2-2.6eV along with p-type conductivity. The value of the absorption coefficient is found to be higher than 10^5 cm^{-1}.

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1. Introduction

Recently, sulfosalts have attracted the researchers because of its low cost, nontoxicity and high potential in many technological applications such as photovoltaics, thermoelectric applications, phase change memory devices etc. [1]. More than 220 sulfosalts species have been defined either from structural considerations or formal chemistry definition (bond-valence concepts) [2]. Many sulfosalts are ternary sulfides, quaternary compounds or multinary compounds with complex chemistry [3]. The systematic studies of different mineralogical compounds indicate that the band gap energy of many of them are suitable for production of thin film solar cells [4]. Indeed, sulfosalts have direct band gaps in the range of 1.78 - 2.5eV, which are very close to the theoretical value for conversion of light energy into electrical energy for photovoltaics [5, 6]. Moreover, sulfosalts with high absorption coefficient make them suitable candidates for photovoltaics [7]. The early scientific research on sulfosalts have been focused on their crystal structures and thermodynamic properties, but the research work on their electronic properties is extremely rare [3]. Dittrich et al. reported the first sulfosalt solar cell by using tin antimony sulphide (TAS) as an absorber layer [4]. The idea of Dittrich et al. was further promoted by various groups, reported the optoelectronic properties of the sulfosalt compounds with pronouncing results applicable for photovoltaics [8-10]. In our previous work, we reported the variation of Sn on Sb_2S_3 and found remarkable results in the field of photovoltaics [11]. In this work we are exploring the properties of Sb variation on SnS thin films by thermal evaporation techniques.

2. Experimental

Thin films (1.2μm, quartz crystal monitor) of Sn-Sb-S were deposited via thermal coater by using 99.999% pure tin (Sn), sulphur (S), and antimony sulphide Sb_2S_3 (sigma Aldrich) at a chamber pressure~2×10^{-4} mbar on soda lime glass substrate.

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All the films were annealed inside glass ampoule at 250°C for 30 minutes. Elemental composition was analyzed by Energy Dispersive X-ray Spectroscopy with beam current of 200μA. The structural properties were determined by X-ray diffractometer system JDX-3532, JEOL Japan. The optical properties were examined by making use of J. A. Woollam variable angle ellipsometry (VASE). Photoconductivity spectrophotometer in the wavelength range 300-1100 nm was used for photoconductivity measurement. Molybdenum contacts were deposited on the films via dc sputtering coater for electrical characterization.

3. Results and discussion

Energy Dispersive X-ray Spectroscopy was used for the determination of elemental composition of the films. The variation of antimony is tabulated in table 1.

Table 1. Elemental composition of Sn-Sb-S thin films

Points	S%	Sn%	Sb%
1	50	45	0.87
2	50	45	1.21
3	50	45	1.7
4	50	45	2.05
5	50	45	2.35

Fig. 1 shows the XRD pattern of tin antimony sulfide thin films. The $Sn_2Sb_2S_5$ phase was identified by comparing XRD data with the standard pattern. The increase in the concentration of antimony (Sb) influenced on the peaks width as well as slight displacement of the peaks, is an indication of the Sb varying concentration [12]. The grain size "D" of the films is calculated using the Scherer's formula [13] i.e.

$$D = 0.9\,\lambda/\beta cos\theta$$

K_α radiation are used in XRD analysis while β is the full-width at half-maximum in the equation used. The average grain size was found to be 120nm, calculated by Debye Scherer formula corresponding to the main peak (402). Other impurity phases (i.e., Sn_2S_3 and SnS_2) were not detected in the annealed films. It is assumed that the concentration of Sb in this sample exceeded the solid solubility at deposition temperature and the resulting super saturation was relieved via precipitation of a secondary phase [14].

The variation of antimony in SnS films not only influence the photoconductivity but also have a prominent effect on the optical properties. With the same annealing temperature, the average grain size appear to be the same. Therefore the grain size will not be responsible for the change in optoelectronic properties. So the change in photoconductivity is connected with the population of energy levels as well as position of the Fermi level. The probability of electron in conduction band will be high if the Fermi level is closer to the conduction band [15, 16]. It is therefore expected that the antimony will change the position of Fermi level, resulting in the photoconductivity variation. The curves (Fig. 2.a) show that the maximum photoconductivity of the material is found at 850nm. The photoconductivity decreases with the increase in antimony content. The curves also show that when the concentration of antimony is 1.7% or below, no appreciable change in the photoconductivity is anticipated.

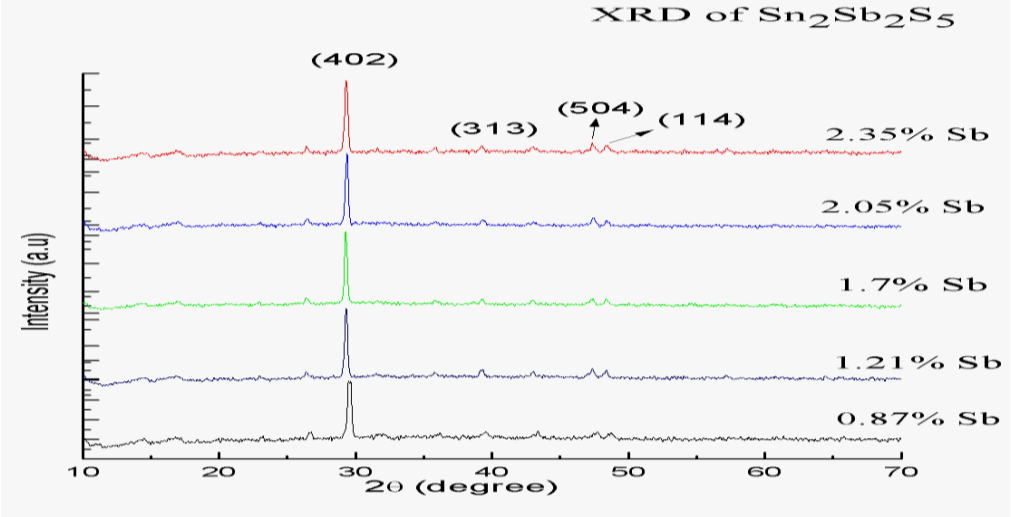

Fig. 1. X-ray diffraction pattern of Sn-Sb-S thin Films with variable amount of Sb

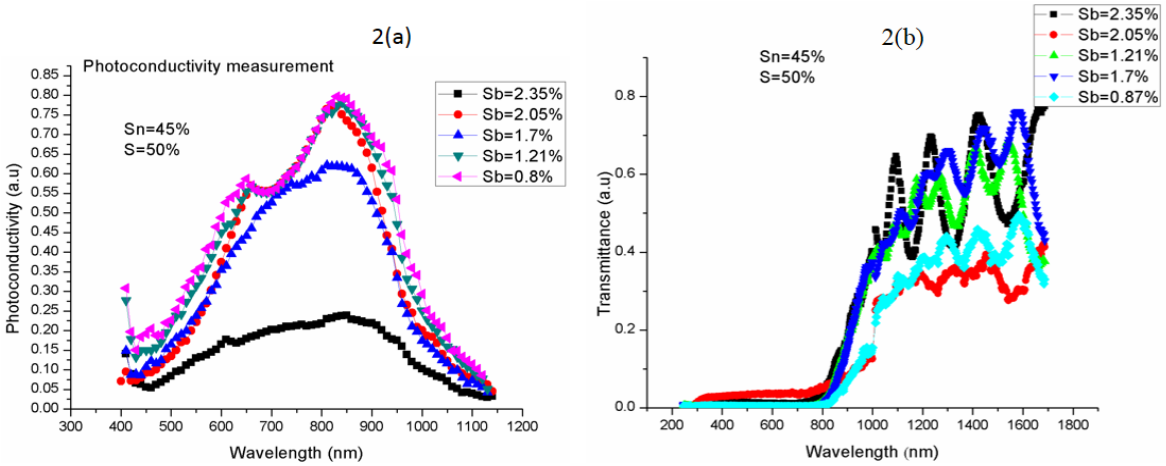

Fig. 2. (a) Photoconductivity response of SnS thin films with varying Sb content. (b) Transmittance spectra of SnS thin films with Sb variation

Fig. 2(b) shows the transmission spectra of Sn-Sb-S thin films. The films show transmittance in visible and NIR region. The transmittance of the films decreases with increasing antimony (Sb) concentration [17]. As the Sb contents is increasing, the interference phenomena is more favorable in the film which support the idea of an increase in absorption. The reason of decreasing transmittance with antimony content is the absorbing nature of antimony.

The refractive indices (n) of Sn-Sb-S thin films were calculated by modeling ellipsometric data and are found to be in the range 1.6 to 3.5 (Fig. 3a). Increasing the amount of antimony enhances the refractive index, which, in turn shows the opacity aspect of antimony [18].

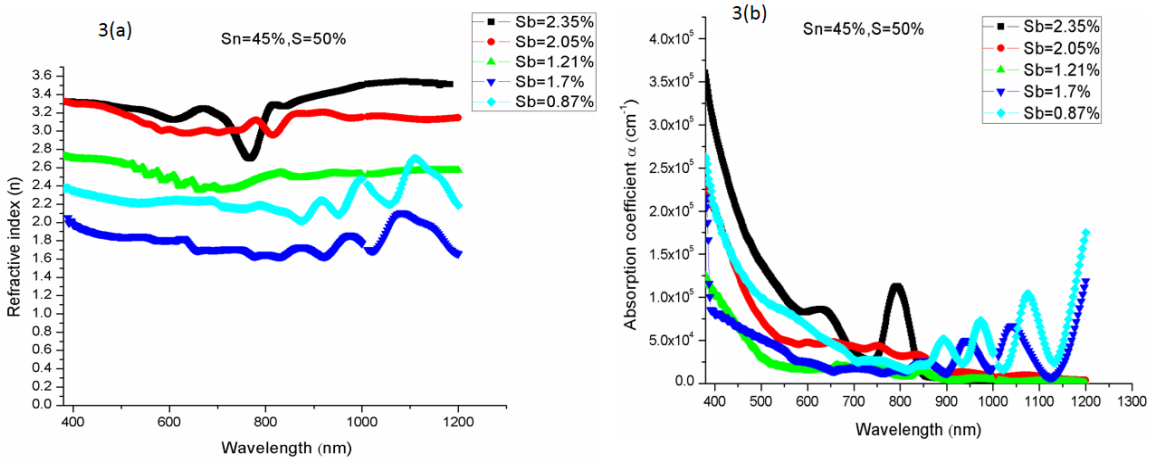

Fig.3. (a) Refractive indices of SnS thin films with Sb variation annealed at 250°C (b) Absorption coefficient of SnS thin films with Sb variation annealed at 250°C.

Absorption coefficient (α) of Sn-Sb-S thin films was calculated by [19]

$$\alpha = \frac{4\pi k}{\lambda}$$

Where k is the extinction coefficient of the material and is determined from variable angle ellipsometry. The films show high absorption coefficients in the range 10^4-$10^5 cm^{-1}$ in visible and NIR region (Fig. 3b). The absorption coefficients decrease from visible to NIR region with the increase in wavelength. The curve shows that the absorption coefficient is high at high Sb content. The relation between absorption coefficient α and band gap energy is found using [20];

$$\alpha h\nu = A(E_g - h\nu)^n$$

Where A is a constant, h is the Planck constant and n is equal to 2 for a direct band gap and 1/2 for an indirect band gap semiconductor. Band gap energy was calculated from extrapolation of the straight section of the $(\alpha h\nu)^2$ vs. hν curve to the horizontal axis, as displayed in Fig. 4(a) and table 2. Energy band gap is found to be in the range from 2.2 to 2.6 eV. Presumably, increase in Sb concentration tends to change crystalline phase into amorphous and thus increases the band gap energies of the films [21].

Table 2. Band gap values for SnSb-S thin films

No	Sb concentration	Band gap
1	0.87%	2.2 eV
2	1.21%	2.4 eV
3	1.7%	2.4 eV
4	2.05%	2.5 eV
5	2.35%	2.6 eV

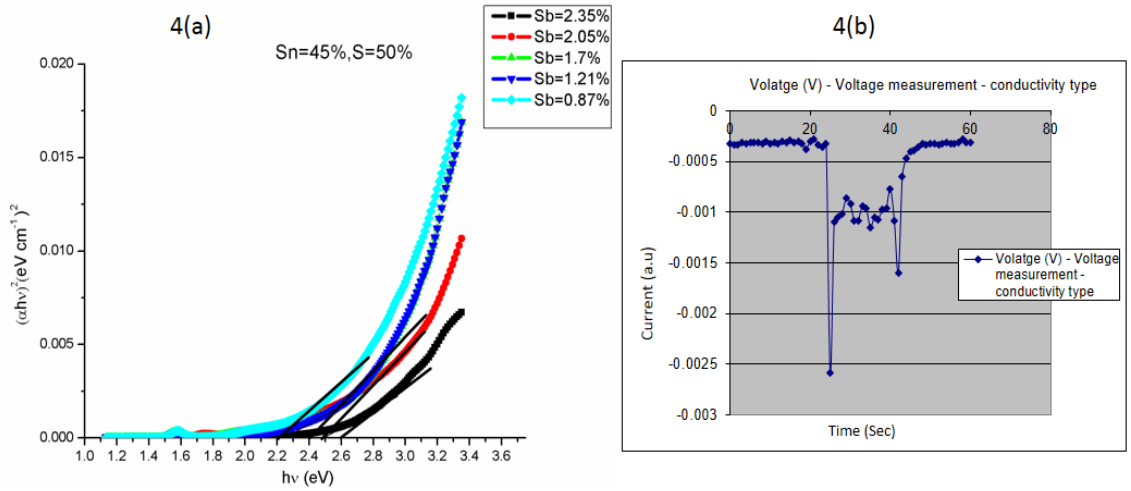

Fig. 4. (a) Plots of $(\alpha h\nu)^2$ vs. hν for the Sn-Sb-S thin films (b) Conductivity type measurement

The conductivity type of the material is checked with hot point probe method. The conductivity type of known material (p-type silicon) was checked initially on the device and then used for Sn-Sb-S thin films [22]. From Fig. 4(b), having the same spectrum as p-type silicon, it is observed that the films show p-type conductivity.

4. Conclusion

It was concluded in the study that the increase of Sb content in SnS thin films increase the absorbance but reduces the electrical properties and band gap of the material. It was also concluded that the lower concentration (up to 2.35%) of antimony don't change the conductivity of SnS from p-type to n-type. The band gap variation occurs due to change in the position of the Fermi level between the energy levels. Keeping in view these properties of TAS, it can serve as alternative material in photovoltaics.

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