STRUCTURAL AND OPTICAL INVESTIGATION OF COBALT DOPED $SnSb_2S_4$ THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS

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$SnSb_2S_4$ thin film was deposited on a soda lime glass substrate by thermal evaporation technique, under high vacuum of 10^{-4} torr. The thin-film was further divided into three equal parts; two pieces out of them were dipped into cobalt nitrate solution ($CoNO_3$) for 20 minutes at room temperature, while the remaining piece was kept as deposited. The Co-doped samples were annealed in argon atmosphere for one hour at two different temperatures of 200ºC and 300ºC. The XRD pattern confirms the as-deposited thin film as amorphous. The crystallinity appeared after doping and further improved after annealing. The Optical properties including optical band gap, absorption coefficient, extinction coefficient, refractive index were investigated. Optical analysis shows that band gap decreases with cobalt doping and further decreases with annealing temperature. The resistivity decreases on the incorporation of cobalt content, which may be due to shift in Fermi level.

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Keywords: Chalcogenide material, Cobalt doping, Physical properties, Environment friendly Photovoltaics

1. Introduction

The most prominent semiconductor material for photovoltaic systems is silicon; however, the researchers are always looked for new and more efficient materials. Some of these materials used in photovoltaic are expansive as well as toxic [1-3] . There is always a need of such materials, which are environment friendly and low cost with higher efficiency [4]. Environmental friendly II–VI chalcogenide semiconductors have recently come under the scientific investigation because of their potential applications in photovoltaic [5-11] . Comparing to other ternary II–VI semiconductors, chalcogenide materials are more flexible and able to change their optical and electrical properties [12-14]. Ternary materials provide a possibility of tailoring structural, optical and electrical properties [15,16].

Cobalt doped tin antimony sulfide thin film is environmental friendly, good efficiency and low cost ternary material. It is beneficial and can be easily used for photovoltaic applications. In addition, this material has large absorbance from ultraviolet to NIR regions of the solar spectrum which is the first requirement of photovoltaic system.

Different techniques are used for the preparation of thin films such as thermal evaporation technique, chemical bath deposition, chemical vapor deposition and rf/dc sputtering etc [17-20]. The properties mostly depend on the preparation and deposition techniques. In the present paper, we have reported the structural, optical and electrical properties of cobalt doped $SnSb_2S_4$ alloy annealed at two different temperatures.

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2. Experimental

Thin film of tin antimony sulfide was fabricated on soda lime glass substrate by thermal evaporation technique. The SnS and Sb_2S_3 powders were used as initial source materials. High purity (99.99%) Sb_2S_3 was obtained from Sigma Aldrich, while SnS was prepared by grinding tin and sulfur powders with mortar and pestle. The mixture was annealed at 600°C in the presence of argon gas for 24 hours.

The source materials, both SnS and Sb_2S_3 were placed in the molybdenum boats for thermal evaporation. The glass substrate was placed in the closed doom at the distance of 10 cm from source materials covered with shutter. High vacuum in the evaporation chamber was achieved by using rotary and diffusion pumps. The precursors were heated by applying gradually increasing voltage. The shutters were removed for about 10 seconds to allow the evaporated species of precursor to condense on target substrate. Finally, a 1.2-micron thick layer of $SnSb_2S_4$ was deposited.

The next task was cobalt doping in the synthesized tin antimony sulfide thin film by ion-exchange method. For this purpose, one molar solution of cobalt nitrate was prepared by dissolving 2.415 g of $CoNO_3$ powder in 20 ml of distilled water at temperature of 26°C. The thin films were dipped into the solution for 20 minutes and annealed in argon environment for one hour; one of the samples was annealed at 200°C, while the other one was at 300°C.

3. Results and discussion

The structural, optical and electrical properties were investigated by using XRD, UV-visible and Four Probe method respectively.

X-ray diffraction pattern of as deposited and cobalt doped $SnSb_2S_4$ thin films annealed at 200℃ and 300ºC are shown in Fig. 1, while the crystallinity of the films increased as films were subjected to the annealing regime. Some other peaks of $SnSb_2S_4$ were also appeared in the pattern with varying intensities with annealing temperature. The crystallinity of the films has maximum value at 200ºC. From X-ray diffraction, the as deposited $SnSb_2S_4$ thin film is confirmed as amorphous in nature. On doping of cobalt, the thin films translated into crystalline structure and the diffraction peak is observed at glancing angle of 32.02° with miller indices (621) matched with reference pattern 00-035-1496. The cobalt doped thin film annealed at 200°C has much finer crystallinity than that of the film annealed at 300°C and another peak is observed at 66.4° with miller indices (417) matched with rreference code 01-083-2315. The intensity and sharp peak in XRD reveals good crystallinity, confirming the stoichiometric nature of cobalt doped $SnSb_2S_4$ thin films. The spectrum analysis confirms the orthorhombic structure of the thin film which were well matched with literature. These films are found to in nanoscale region having crystalline nature.

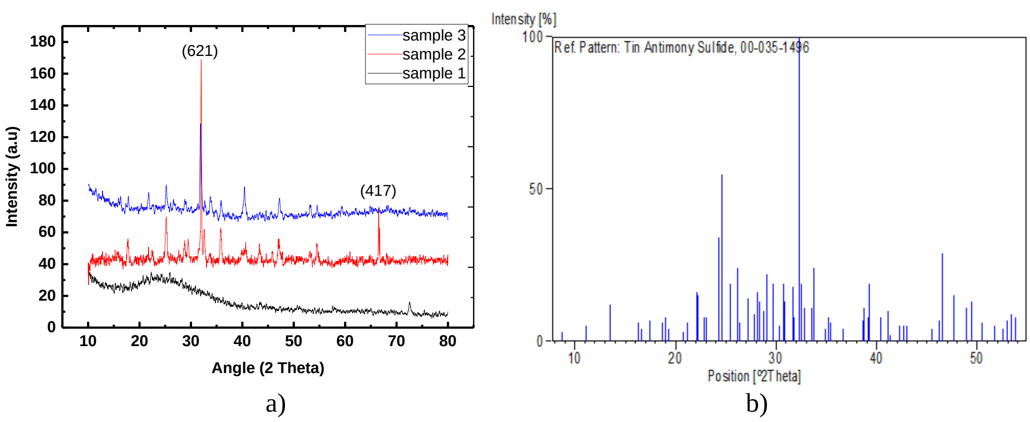

Fig. 1. a) Diffraction pattern of $SnSb_2S_4$ Thin Films, b) reference pattern of $SnSb_2S_4$

The optical properties were studied to determine optical constants such as absorption coefficient (α), optical band gap (E_g), refractive index (n) and extinction coefficient (k). UV-VIS spectroscopy was carried out for the measurements of transmission and absorption coefficient of $SnSb_2S_4$ thin films, consequently the band gap of thin film was determined.

The transmittance spectra of cobalt doped $SnSb_2S_4$ thin films annealed at different temperature is shown in Fig. 2. For UV region, transmittance of $SnSb_2S_4$ thin films is at its minimum, which is significantly increased in the visible and NIR regions. The transmittance of cobalt doped $SnSb_2S_4$ thin film annealed at 200°C is much lower as compared to remaining samples, which is useful for photovoltaic system. For photovoltaic applications, material with high absorption coefficient and a little transmittance are preferred. The absorption coefficient of the synthesized samples has been obtained simply as ratio of absorbance with the thickness of the thin film [21-23].

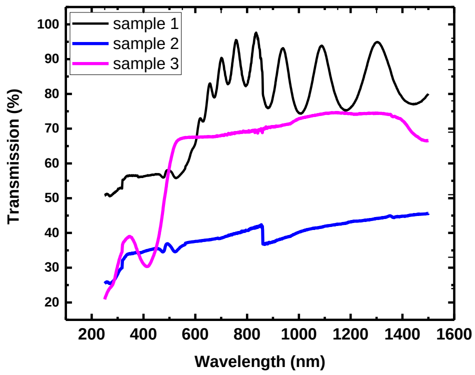

Fig. 2. Transmittance spectra of $SnSb_2S_4$ Thin Films

The plot of absorption coefficient as a function of photon energy for different annealing temperatures is presented in Fig. 3. The absorption coefficient increases with increasing photon energy for all the samples of $SnSb_2S_4$, which is due to the structural rearrangement. All the samples have comparatively high absorption coefficient that increases with increasing temperatures at the same photon energy. The sample 2 shows higher absorption spectra as compared to other samples. This result is very important because the spectral dependence of the absorption coefficient is one of the important factors that influence the solar conversion efficiency. For infrared region, the absorption coefficient of $SnSb_2S_4$ thin films is near zero except the thin film annealed at 200°C, where the absorption coefficient started rising comparatively much earlier. Fig. 4 shows the spectral dependence of the extinction coefficient (k) for $SnSb_2S_4$ thin films.

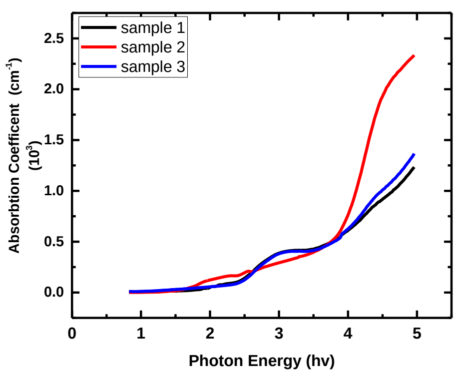

Fig. 3. Absorption coefficient as a function of photon energy

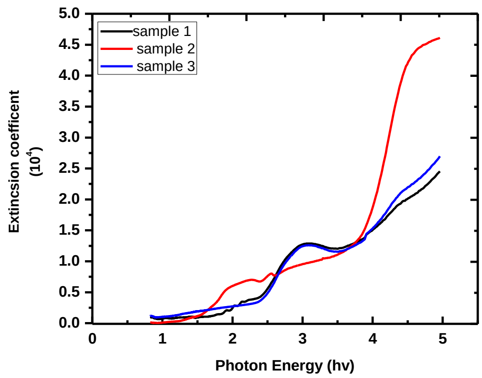

Fig. 4. Comparison of extension coefficient

The refractive index of samples was determined with Swanepoel envelope method [24].

$$n = \frac{[N+(N^2-4s^2)^{\frac{1}{2}}]}{2} \tag{1}$$

Where "s" is the refractive index of the substrate, "N" is the number of oscillations and obtained by the following relation.

$$N = 1 + s^2 + 4s\left(\frac{T_M - T_m}{T_M T_m}\right) \tag{2}$$

Where "T_M and T_m are the transmission maxima and transmission minima respectively. The average refractive index calculated (Fig. 5.) for as deposited and annealed sample at 200ºC and 300ºC was 2.34, 2.33 and 2.39 respectively. By correlating absorption coefficient and energy band gap, one can calculate the band gap by using equation[25].

$$\alpha h\upsilon = A(E_g - h\upsilon)^n \tag{3}$$

Where A is a constant, h and E_g are Planck's constant and energy band gap respectively. n is a number equal to ½ for a direct band gap and 2 for an indirect band gap semiconductor and decides the type of transition. The samples of $SnSb_2S_4$ follow the rule of direct transition for the measurement of optical band gap. The energy band gap can be determined by extrapolating the linear part of $(\alpha h\upsilon)^2$ versus hν curve to the horizontal photon energy axis [26], and shown in Fig. 6. The estimated energy band gap of the as-deposited film is 3.65 eV, while the band gaps of the films annealed at 200°C and 300°C was calculated 4.02 and 3.77 eV respectively. It means that the annealing process is helpful and enhance the optoelectronic properties of the thin films. This is attributed to the improved crystalline quality, increase in grain size and lack of oxygen succeeding to annealing, but still the effect of these procedures is not fully understood yet [20,21]. The crystalline size has been increased for the sample annealed at higher temperature and due to this; the radius of the particle is increased. There is an inverse relation between change in band gap energy and radius of the particle [27, 28]. The Fig. 6 shows that band gap of cobalt doped $SnSb_2S_4$ thin film, annealed at 200°C is 4.02 eV. The band gap increases with the level of doping and subsequent annealing of sample.

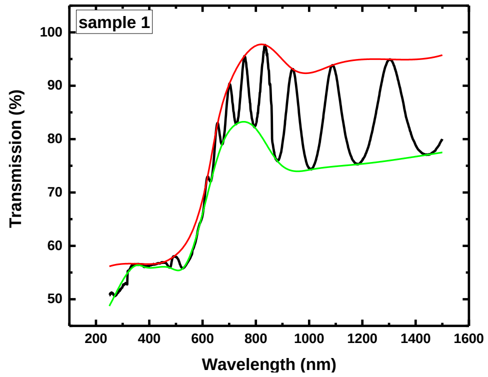

Fig. 5. Swanepoel envelope for the calculation of refractive index

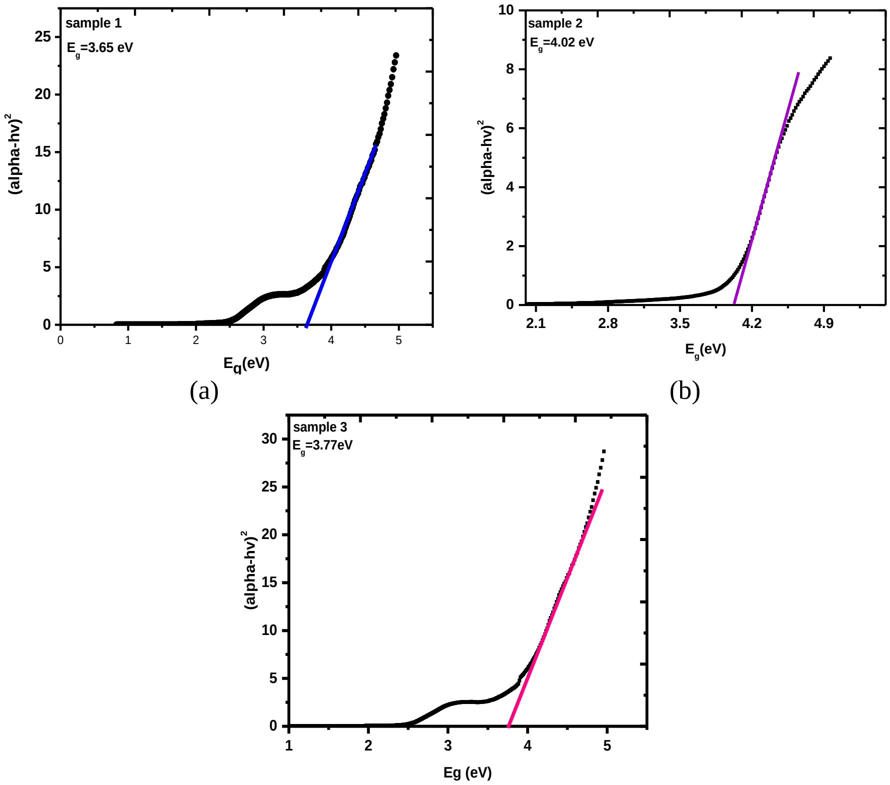

Fig. 6. Plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ of $SnSb_2S_4$ film for band gap calculations: (a) as deposited (3.65 eV), (b) annealed at 200°C (4.02 eV) (c) annealed at 300°C (3.766eV)

The increase in optical band gap on annealing at higher temperature in $SnSb_2S_4$ films may be due to little disorder of the system and decrease in density of localized states. It is also reported that the addition of cobalt into chalcogenide material may increase the optical band gap, which may be due to shift of Fermi level [29-31]. According to the Mott model of density states [32], the width of the localized states near mobility edge depends on the defects and degree of disorder present in amorphous material. It is known that unsaturated bonds together with some saturated bonds are produced resulting an insufficient number of atoms deposited in the amorphous film [33]. These unsaturated bonds are responsible for increasing the disorder in the films producing localized states. The high concentrated localized states are responsible for low value of optical band gap. Chalcogenide thin films always contain high number of defects states or unsaturated bonds. The addition of cobalt in $SnSb_2S_4$ system, decreases unsaturated defects which produced a number of saturated bonds, responsible for the increase in optical band gap.

Table 1: Electrical properties of $SnSb_2S_4$ thin films by four probe method

Sample. Name	Sheet Resistivity Ωm
As deposited	61.4
Annealed at 200^{o}C (cobalt doped)	10.9
Annealed at 300^{o}C (cobalt doped)	3.9

The four probe measurement was used to find the sheet resistance $SnSb_2S_4$ thin films. Each probe is kept at equal distance of 1 mm and constant temperature of 300 K. The sheet resistivity of the synthesized samples is shown in Table 1.

4. Conclusions

Thin film of SnS and Sb_2S_3 were deposited by thermal evaporation technique on clean glass substrate at room temperature. XRD results reveal that the as-deposited $SnSb_2S_4$ thin film are amorphous in nature while annealing at 200ºC and 300ºC transformed to polycrystalline with preferred orientation along the (621) plane with orthorhombic structure. The optical absorption measurement shows the direct band transition, which increase with increase of annealing temperature. Increase in optical band gap was due to decrease in disorder of the system and density of localized states. The optical constants i.e. absorption coefficient, extinction coefficient and refractive index significantly changes with photon energy and annealing temperature Cobalt doped $SnSb_2S_4$ is essential material for photovoltaic application as it has high absorption in visible and a little transmittance in UV-Visible region. The resistivity of $SnSb_2S_4$ thin film is decreased by doping of cobalt as well as with increasing annealing temperature. On the basis of these results, it can be accepted that cobalt doped $SnSb_2S_4$thin films absorb most part of the radiation and they are good candidate as an absorber layer in photovoltaic devices like thin film solar cells.

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