



Optical Characterizations of $(\text{Sb}_2\text{S}_3)_{1-x}(\text{Bi}_2\text{S}_3)_x$ Thermally Evaporated Thin Films

Dr. Sr. Jessy Mathew .N¹, Dr. Rachel Oommen²

Assistant Professor¹, Professor²

Department of Physics

Mercy College, Palakkad, Kerala, India¹

Avinashilingam University for Women, Coimbatore (Rtd.), Tamil Nadu, India²

Abstract:

$(\text{Sb}_2\text{S}_3)_{1-x}(\text{Bi}_2\text{S}_3)_x$ ($x=0.1$) thin films were deposited on glass substrates by thermal evaporation technique. The optical properties of thin films were influenced by thermal treatment and thickness of the film. In this optical analysis, effect of both thickness and annealing temperatures (two temperatures 473K & 523K) on optical properties were investigated. Percentage of transmittance decreases with increase of film thickness and thermal treatment. Extinction coefficient increases with increase of annealing temperature and decreases with increase of film thickness. Band gap is in between 2.20 eV and 1.61 eV.

Keywords: Band gap, Optical properties, Semiconductors, Thermal evaporation, thin films

1. INTRODUCTION

The analysis of optical properties is very important in many scientific, technological and industrial applications of thin films such as photo-conductivity, solar energy, photography and numerous other applications. The band gap of the material determines what portion of the solar spectrum absorbs by the cells. Ultraviolet-visible spectroscopy (UV-Vis) involves the spectroscopy of photons in the UV-visible region. The absorption edge and energy band gap can be determined from the transmission measurements. The absorption in the visible region directly affects the colour of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that, fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state. The optical properties of amorphous and annealed chalcogenides have been observed and investigated by Tiguae et al. [1], Nicolae Tiguae [2] and R.S. Mane et al. [3]. The semiconductor properties of the materials are studied through the optical absorption. The applicability of a material can be determined by the estimation of its band gap. Therefore to choose the application level, tailoring of the band gap is an important factor. The band gap can be tailored by adjusting the composition of materials. By the measurement of transmission of incident photons is an important technique to measure the band gap energy of a semiconductor. In this case photons of selected wave length are directed at the sample, and relative transmission of the various photons is observed. Since photons with energies greater than the band gap energy ($h\nu \geq E_g$) are absorbed while photons with energies less than the band gap are transmitted. The type of optical transition can be explained by observing the dependence of absorption coefficient, α on the photon energy, $h\nu$. The electron excitation from valence band to conduction band is known as fundamental absorption and which can be used to determine the nature and value of the optical band gap. The plot of $(\alpha h\nu)^2$ or $(\alpha h\nu)^{1/2}$ against $(h\nu)$ provides the nature and E_g value of a particular film. Investigations on the optical properties of thin films became essential for their effective device oriented applications. The phenomenal growth of thin film research and development owes much to the stimulus provided by the utilitarian interest in the application of optical films in mirrors and interferometers [4]. This is a report of the optical studies of Sb-Bi-S as-deposited and annealed thin films.

Thin film samples of $(\text{Sb}_2\text{S}_3)_{0.90}(\text{Bi}_2\text{S}_3)_{0.1}$ were prepared from powder materials of Sb_2S_3 and Bi_2S_3 (99.999% purity, Sigma-aldrich) on chemically cleaned glass substrates by thermal vacuum evaporation technique. To prepare the compound, Sb_2S_3 and Bi_2S_3 were weighed and grinded for several hours and sintered. The newly prepared powder sample was used as the source material. Deposition rate and film thickness were controlled during deposition by quartz oscillator thickness monitor. The optical properties of the thermally deposited films of $(\text{Sb}_2\text{S}_3)_{0.90}(\text{Bi}_2\text{S}_3)_{0.1}$ were investigated from the transmission spectra by using a UV-VIS-NIR spectrometer (JASCO V-570). The optical transmittance of the as-deposited and annealed (for two temperatures 473K and 523K) samples was measured at room temperature with unpolarised light at normal incidence in the wavelength range 330 to 860nm. Absorption takes place only if the photon energy is greater

2. EXPERIMENTAL

Than the energy gap ($h\nu > E_g$). In this optical analysis, effect of both thickness and annealing temperatures on optical properties were investigated. Optical transmission spectra before and after heat treatment have been used to study the optical properties of these films. The optical transmittance was found to show different results with thickness and annealing. The optical band gap, E_g of the semiconductor is determined from the dependence of absorption coefficient values (α) on the photon energy, using Tauc's relation [1,5],

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

where B is a parameter that depend on the transition probability, E_g is the optical band gap energy of the material, $h\nu$ is the photon energy. The exact magnitude of absorption coefficient $\alpha(h\nu)$ for a given value of the incident photon energy is proportional to the probability for transition from

initial to the final electronic state and to density of electrons in the initial state as well as to the density of empty final state [6]. From the transmission spectra the extinction coefficient (k), absorption coefficient (α) and band gap of the three compound materials were observed by the following method of Swanepoel [7]. The absorption coefficient (α) is determined from transmittance values using the following relation [8].

$$\alpha = (1/t) * \ln (1/T), \text{ where } t \text{ is thickness and } T \text{ is the transmittance.}$$

The extinction coefficient (k) is calculated using the formula, $k = \alpha \lambda / 4\pi$

In this optical analysis, effect of both thickness (900nm, 1200nm) and annealing temperatures (two temperatures 473K & 523K) on optical properties were investigated for the thin films prepared by thermal evaporation technique from the compound $(Sb_2S_3)_{1-x}(Bi_2S_3)_x$ with $x = 0.1$.

3. RESULTS AND DISCUSSION

The optical measurements were taken for: (a) as-deposited films of two thickness (900nm, 1200nm) (b) films of the same thickness annealed in vacuum at 473 K for 1 hr and (c) films of the same thickness annealed in vacuum at 523 K for 1 hr. The transmission spectra of the as-deposited and annealed films of two thickness are shown in figure 1. The figures are exhibiting that the film transmittance in the spectral region 600-1000nm decreases with thermal treatment. Similar results have been

reported for thin film of Sb_2S_3 by N. Tigau et al., [9] and for Bi_2S_3 by Biljana Pejova and Ivan Grozdanov [6]. The combined transmission spectra of the as-deposited $(Sb_2S_3)_{0.90}(Bi_2S_3)_{0.1}$ films of two thickness is as shown in figure 2 which exhibits that thin film transmittance in the spectral region 500-1000nm decreases with increasing film thickness. The spectrum exhibits superimposed optical interference in the higher wavelength region. From this observation it is noted that the percentage of film transmittance decreases as thickness of the film increases which shows that the material is of highly absorbing nature. The decrease of transmittance may be due to the increase of crystallite size and an improvement of the film crystallinity and also the increased roughness of the heat-treated films. Increased roughness plays an important part in the drastic decrease of optical transmittance because the destructive interference of the light transmitted through the high and irregular grains of the samples which form non-levelled surfaces [1]. The low transmittance at higher annealing temperature is in principle attributed to increase of carrier concentration. The increase of optical transmittance in the higher wavelength region of all the as-deposited and annealed films is due to the shift of optical absorption edge to the higher wavelength side. Figure 3 shows the variation of the extinction coefficient, k as a function of photon energy of the as-deposited and annealed (two temperatures 473K & 523K) films of two thickness. The extinction coefficient, k increases with photon energy as well as with temperature

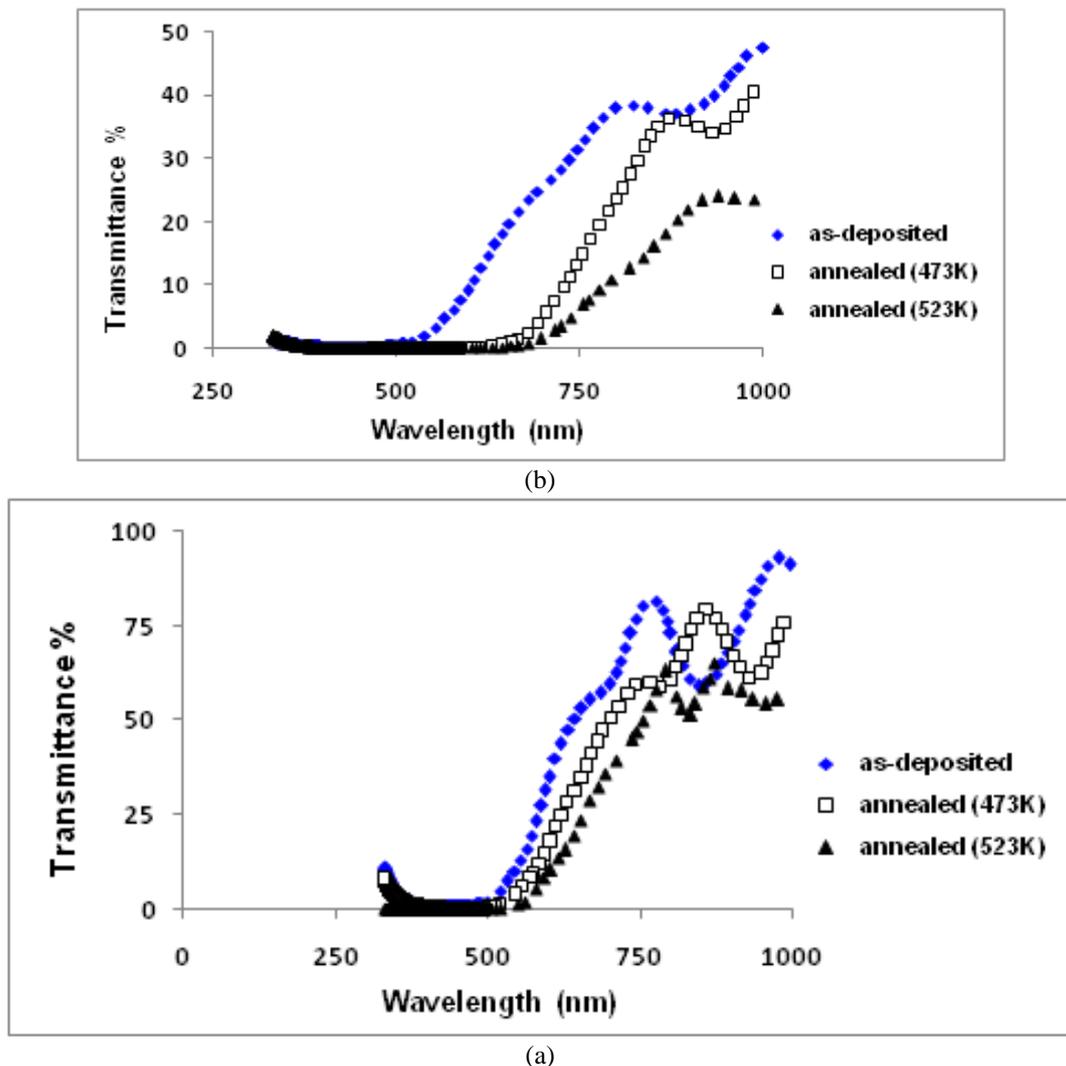


Figure.1. Transmission spectra of the as-deposited and annealed (473K & 523K) $(Sb_2S_3)_{0.90}(Bi_2S_3)_{0.1}$ films of thickness a) 900nm, b) 1200nm

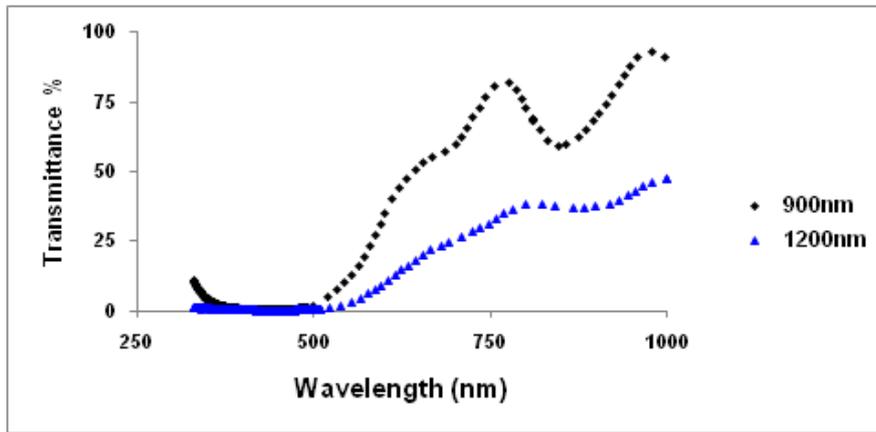
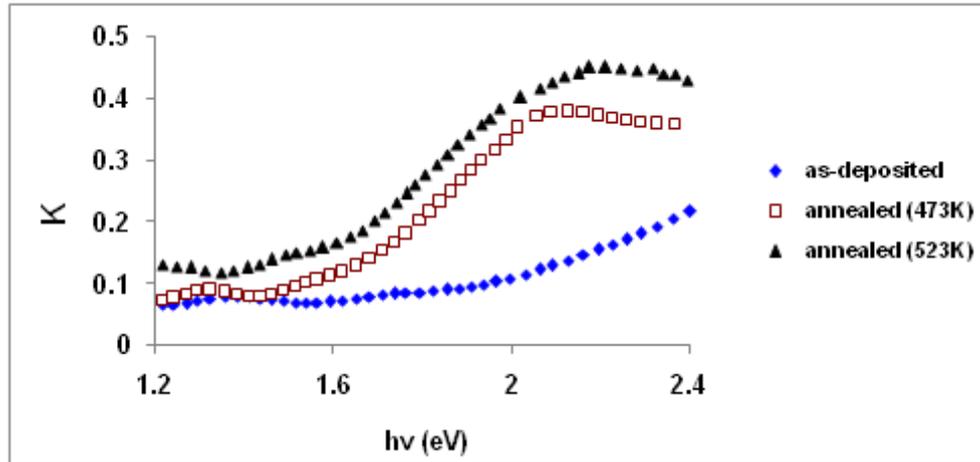
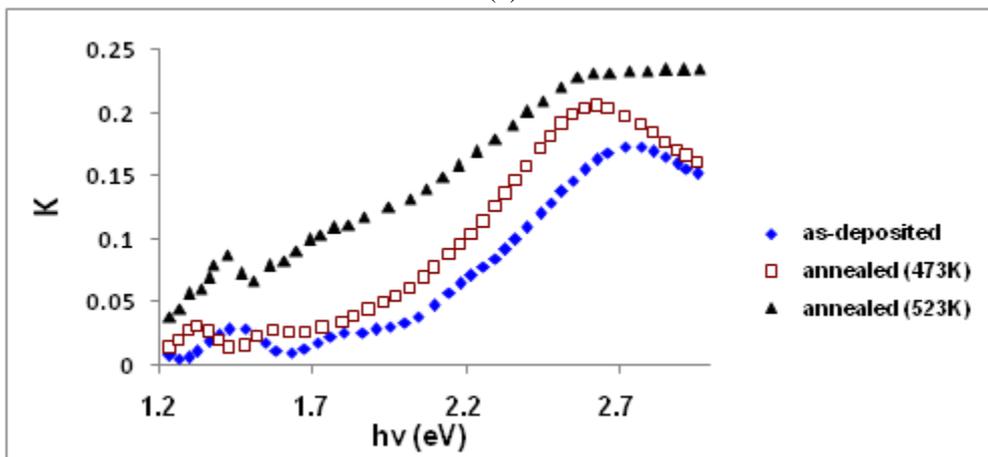


Figure.2. Transmission spectra of as-deposited $(\text{Sb}_2\text{S}_3)_{0.90}(\text{Bi}_2\text{S}_3)_{0.1}$ films of two thickness



(b)



(a)

Figure.3. Variation of extinction coefficient (k) with photon energy (hv) for $(\text{Sb}_2\text{S}_3)_{0.90}(\text{Bi}_2\text{S}_3)_{0.1}$ film of thickness a) 900nm, b) 1200nm

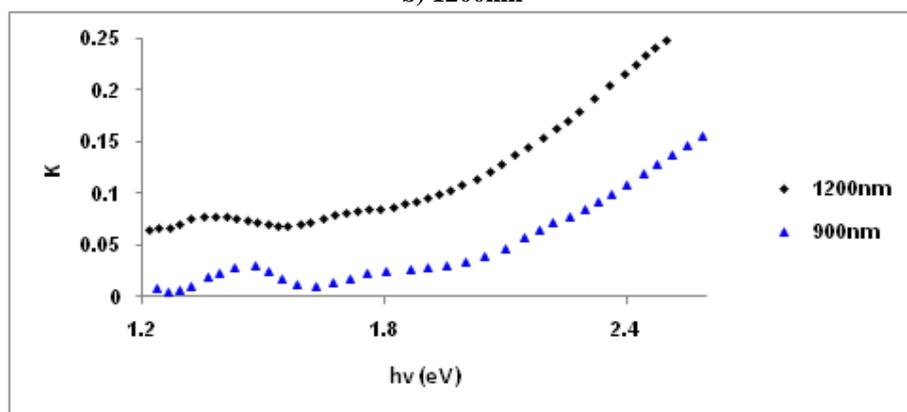
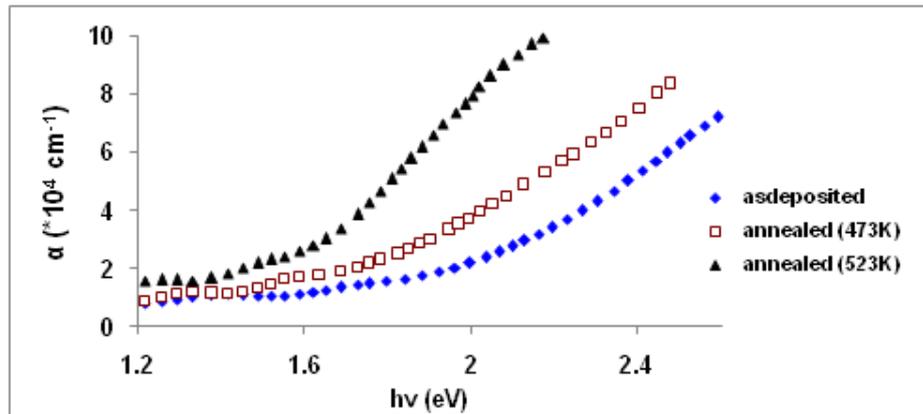


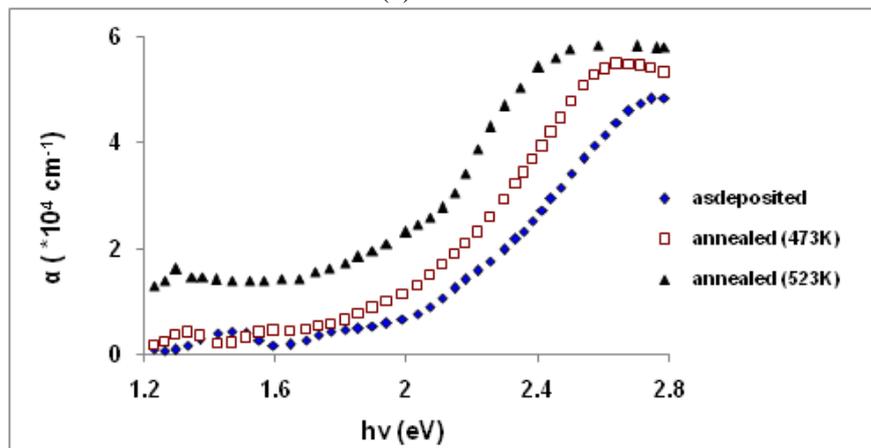
Figure.4. Variation of extinction coefficient (k) with photon energy (hv) for as-deposited $(\text{Sb}_2\text{S}_3)_{0.90}(\text{Bi}_2\text{S}_3)_{0.1}$ films

Figure 4 shows the combined spectra to explain the variation of the extinction coefficient, k as a function of photon energy of the as-deposited films of two thickness. The extinction coefficient increases with increasing film thickness and increases with the increase of photon energy. The value of k decreases with the increase of film thickness may be due to the improvement in crystallinity leading to the minimum imperfections. Figure 5 shows the variation of the absorption coefficient, α as a function of photon energy, $h\nu$ for as-deposited and annealed $(\text{Sb}_2\text{S}_3)_{0.90}(\text{Bi}_2\text{S}_3)_{0.1}$ films of same thickness. The value of absorption coefficient increases slowly at the long wavelength region whereas it increases fast at short wavelength region. This behaviour supports the assumption of using these thin films as antireflection coatings in the first

region while they are used for fabrication of photodetectors, solar cells, semiconductor lasers and light-emitting diodes in the second region [10]. Figure 6 shows the variation of $(\alpha h\nu)^2$ with photon energy ($h\nu$) for as-deposited and annealed $(\text{Sb}_2\text{S}_3)_{0.90}(\text{Bi}_2\text{S}_3)_{0.1}$ films of two thickness. For all the films there is a straight line portion. The straight-line portion is extrapolated to cut the x-axis, which gives the energy gap (E_g) and the energy gap values for as-deposited films of thickness 900nm and 1200nm are 2.20eV, 2.13eV and for annealed (473K, 523K) films of same thickness are 2.10eV, 2.06eV and 1.71eV, 1.61eV respectively. The band gap values for as-deposited and annealed films of the compound, $(\text{Sb}_2\text{S}_3)_{0.90}(\text{Bi}_2\text{S}_3)_{0.1}$ are shown in table 1.

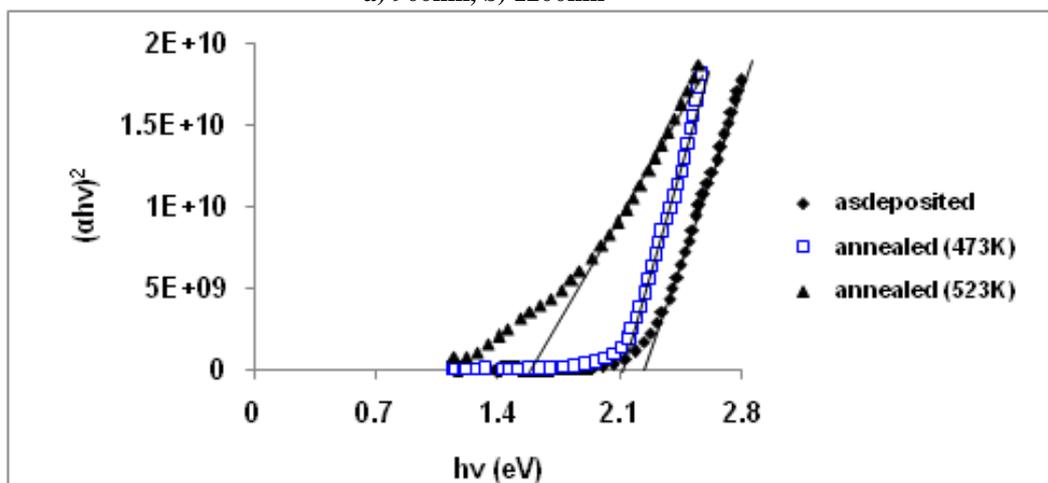


(b)

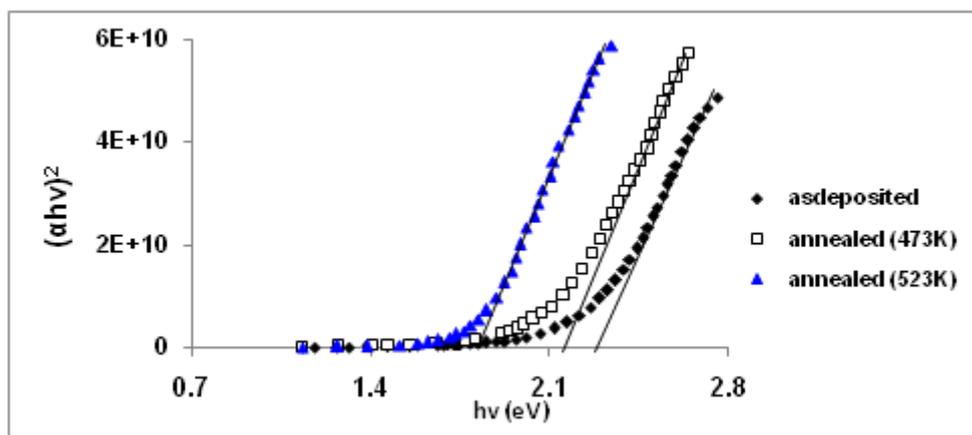


(a)

Figure 5. Variation of absorption coefficient, α as a function of photon energy, $h\nu$ for $(\text{Sb}_2\text{S}_3)_{0.90}(\text{Bi}_2\text{S}_3)_{0.1}$ film of thickness a) 900nm, b) 1200nm



(b)



(a)

Figure.6. Variation of $(ahv)^2$ with photon energy (hv) for $(Sb_2S_3)_{0.90}(Bi_2S_3)_{0.1}$ film of thickness a) 900nm, b) 1200nm

Table.1. The band gap values for as-deposited and annealed films

x	Thickness (nm)	Band gap, E_g (eV)		
		As-deposited	Annealed	
			473K	523K
0.1	900	2.20	2.10	1.71
	1200	2.13	2.06	1.61

4. CONCLUSION

Optical properties of thin films of $(Sb_2S_3)_{1-x}(Bi_2S_3)_x$ with $x = 0.1$ were studied. The estimated direct band gap energies of the compound with $x = 0.1$, for as-deposited films of thickness 900nm and 1200nm 2.20eV, 2.13eV and for annealed (473K, 523K) films of same thickness are 2.10eV, 2.06eV and 1.71eV, 1.61eV respectively. For all the films the plots were found to be straight-line which indicates that the transition is direct band to band transition and are dominant within the spectral range 400 to 750 nm .

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