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Effect of temperature on the optical parameter of amorphous Sb-Se thin films

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Thin films of a-Sb_xSe_{1-x} (x = 0.4, 0.5, 0.6) are prepared by vacuum evaporation technique onto glass substrates. The amorphous nature of as deposited thin films has been checked by XRD technique. The transmittances of the films are measured at various temperature ranges 100-400K in the wavelength range 400-1100 nm. Optical absorption obeyed the indirect transition process. The temperature dependence of the optical energy gaps in this range are fitted with four equations beginning with linear, non linear, Varshni and Bose Einstein equations. The results are best fitted with the Varshni equation. We have found that the energy gap decreases with the increase in Sb percentage in these thin films and an increase in energy gap with the decrease of temperature.

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1. Introduction

Se–Sb glasses have been proved to be attractive candidate in optical and electronic communications, switching and memory devices and photovoltaic applications. Antimony selenide is a semiconducting chalcogenide of the VB and VIB groups of elements. It has been of considerable interest due to its good photoconducting properties and has wide range of applications in optical thermoelectric cooling devices [1,2]. Polycrystalline antimony selenide (Sb_2Se_3) has received a great deal of attention in the last few years, due to the demonstrated switching effects and its good photovoltaic properties and high thermoelectric power. The preparation of the thin films of Sb_2Se_3 has been explored by number of methods including vacuum evaporation [3], solution growth [4], direct fusion of antimony and selenium [5], and spray pyrolisis [2]. Among the outstanding features of Sb_xSe_{1-x} alloys, the continuous variation of energy band gap and lattice constant, as well as electrical properties, with the composition is of particular significance [6, 7]. Few studies on the electrical and optical properties of Sb_2Se_3 [8, 9] have been conducted. The optical characteristics of Sb_2Se_3 films change significantly under thermal treatment or laser irradiation [10]. It is reported that the absorption and reflectivity differences between amorphous and crystalline states in Sb-rich Sb_xSe_{100-x} films (x > 40%) increase while the transmission difference decreases on shorter wave lengths [7, 11].

2. Experimental details

The different compositions of the glassy Sb_xSe_{1-x} (x = 0.4,0.5 and 0.6) alloys are prepared in bulk form by quenching technique. For a particular composition, elemental constituents of five nines purity in desired stochiometric ratios are sealed in an evacuated quartz ampoule (10^{-5} Torr). The sealed ampoules are heated at ~1000°C in an electric furnace with a rocking arrangement for about 24 h under continuous rocking and thereafter quenched into ice-cooled water. Bulk specimens as obtained are further used for the preparation of the planar thin film samples by vacuum evaporation technique for the optical absorption measurements. These films have been deposited on Corning 7059 glass substrates at a base pressure ~10^{-5} Torr. The amorphous nature of bulk as well as thin films has been checked by XRD technique. The film thickness is ranging from 0.4 to 0.5μm. Optical absorption of the thin films is measured using a computerized spectrophotometer SOLAR – TII (MS-2004). The films are mounted in a specially designed metallic sample holder under vacuum.

3. Results and discussions

3.1. Temperature dependence of the energy gap

The transmittances (T) of Sb_xSe_{1-x} (x=0.4, 0.5, 0.6) are recorded at different temperatures from (100 to 400K) in the wavelength range 400-1100nm. Fig. 1 shows the transmission spectra of a-Sb_2Se_3 thin films. The similar types of spectra have been observed for other compositions also (results not shown here). Using these spectral data, the absorption coefficient (α), is calculated using the relation [12],

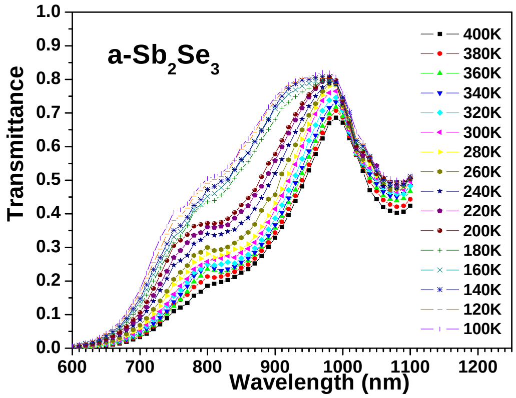

Fig. 1: Plot of transmittance as a function of wavelength at different temperatures.

$$\alpha = 1/d \ln (T) \tag{1}$$

where α is absorption coefficient and d is the film thickness. From the calculated absorption coefficient (α) data, it is clear that α of amorphous SbSe thin films increases with increasing photon energy. The strong absorption edge shifts to lower photon energies as temperature increases. In order to determine the optical gap energy (E_g) from the optical absorption spectra, measured around the absorption edge, we have used Tauc equation [13-14]:

$$(\alpha h\nu)^{1/n} = B\,(h\nu - E_g) \tag{2}$$

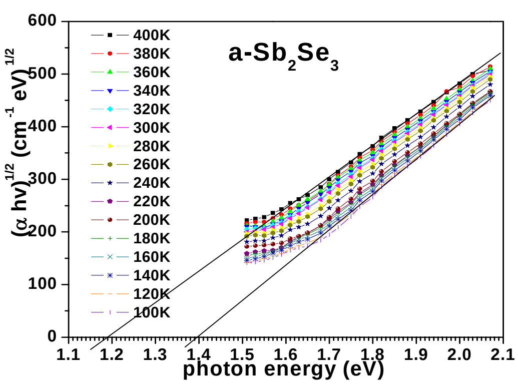

Fig. 2: Plots of $(\alpha h\nu)^{1/2}$ vs. hν at different temperatures for a-Sb_2Se_3 thin films.

where B is a parameter depending on the transition probability and n is a number characterizing of the transition process. In accordance to Eq. (2), the non-direct transition energy gap (E_g) for Sb_xSe_{1-x} (x=0.4, 0.5, 0.6) at all temperatures has been obtained from the plot of $(\alpha h\nu)^{1/2}$ vs. hν as shown in figs [2, 3, 4]. The X-axis interception in these figures allows the determination of the energy gap of amorphous Sb_xSe_{1-x} (x=0.4, 0.5, 0.6) thin films at all temperatures between 100-400K. It is clear from these figures that the value of E_g decreases from 1.40 eV to 1.18 eV for Sb_2Se_3, 1.14 eV to 0.95 eV for SbSe and 0.97 eV to 0.86 eV for Sb_3Se_2 as the temperature increases from 100K to 400K.

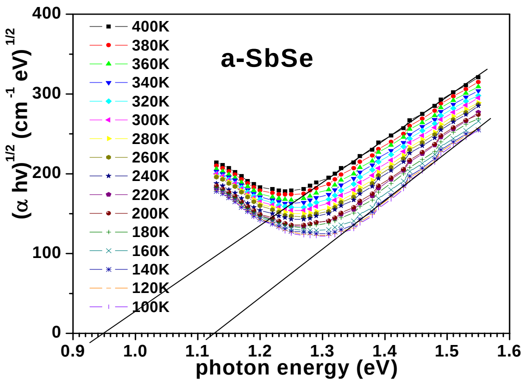

Fig. 3: Plots of $(\alpha h\nu)^{1/2}$ vs. hν at different temperatures for a- SbSe thin films

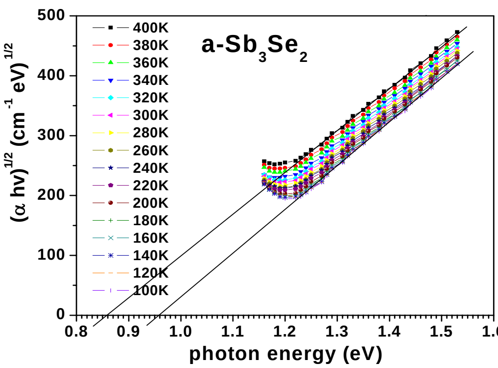

Fig. 4: Plots of $(\alpha h\nu)^{1/2}$ vs. hν at different temperatures for a- Sb_3Se_2 thin films

The thermal variation of the energy gap (E_g) is given as following [15, 16]:

$$\left(\frac{\partial E_g}{\partial T}\right)_P = \left(\frac{\partial E_g}{\partial T}\right)_{thermal\ \to \exp} + \left(\frac{\partial E_g}{\partial T}\right)_{(el-ph)coupling} \tag{3}$$

where the first term depends on lattice expansion and the second term depends on electron –phonon interaction.

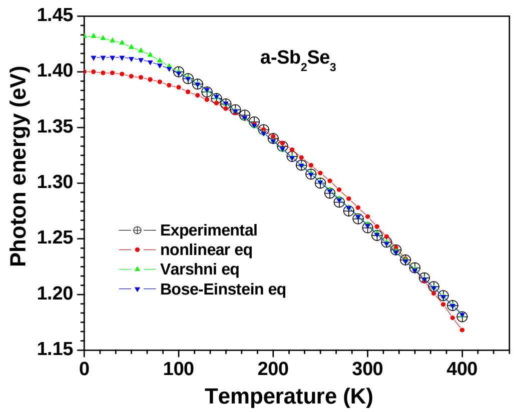

Fig. 5: Experimental and fitted values of energy gap with temperature for Sb_2Se_3 thin films.

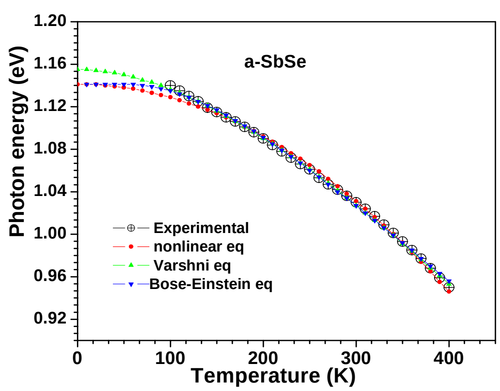

Fig. 6: Experimental and fitted values of energy gap with temperature for SbSe thin films.

Passler [17] found the complicated algebraic expressions such as the one which leads the temperature reach to zero (T→ 0), then E_g (T) can be expressed as,

$$E_g(T) = E_g(0) - \alpha T^P \tag{4}$$

where E_g (T) is the band gap at specific temperature, E_g (0) is the value of band gap at absolute zero temperature, parameter $\alpha = dE_g/dT$ is the rate of change of the band gap with temperature and p is an adjustable parameter, fits to E_g (T) for a large number of materials. Moreover, the E_g – T variation is linear fit when adjustable parameter p=1 and nonlinear fit when parameter p=2 [18]. The analysis of the temperature dependence of E_g is usually done by a three-parameter fit to Varshni's empirical equation [19]:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \tag{5}$$

where α and β are constants and Eg (0) is the energy gap at zero temperature. The energy gap of a semiconductor varies with temperature due to three distinct effects attributable to phonons. We found that our results have got the best fitting with the Varshni equation. The values of $E_g(0)$, α and β for Sb_xSe_{1-x} (x=0.4, 0.5, 0.6), at different temperatures (100-400K), have been plotted in figures (5, 6, 7) and inserted in table 1. A semiempirical relation, accounting for these in an averaged way, is the Bose-Einstein type of expression [20]:

$$E_g(T) = E_g(0) - \frac{2\alpha_B}{\exp\left(\frac{\theta_B}{T}\right) - 1} \tag{6}$$

where α_B represents the strength of the electron–phonon interaction and θ_B corresponds to the mean phonon energy in units of temperature. Recently, other expressions with an allowance for phonon dispersion (upto a standard deviation) have also been suggested [21]. But, we have not used them here since the extra fitting parameter becomes important only at very low temperatures.

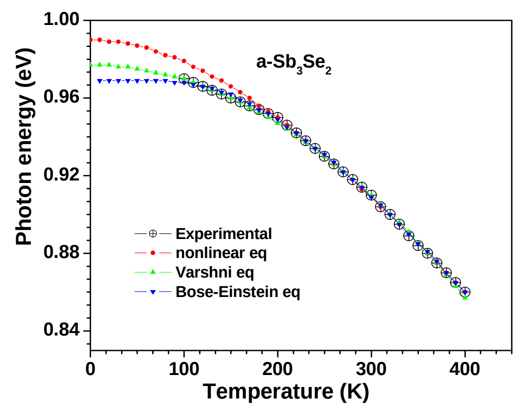

Fig. 7: Experimental and fitted values of energy gap with temperature for Sb_3Se_2 thin films.

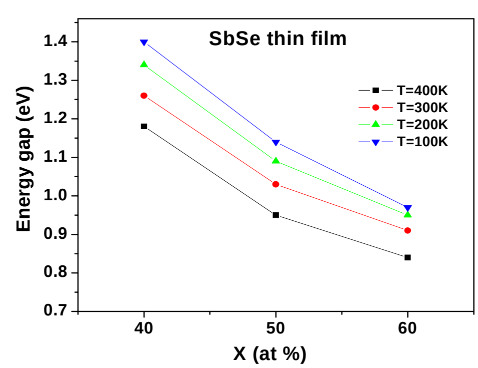

Fig. 8: Optical energy gap as a function of x in Sb_xSe_{1-x} thin films in the range 100-400K.

The value of Eg at different temperatures along with the least-square fits to Eqs. (4) and (5) are obtained and inserted in Table 1. The absolute zero value of energy gap (E_g) and the rate of change of the Eg with temperature according to varshni equation for amorphous Sb_2Se_3 are found to be: 1.43 eV and 9.30 x10^{-4} eV/K, for a-SbSe 1.16 eV and 1.17x10^{-3} eV/K and for a-Sb_3Se_2 0.99 eV and 8.40x10^{-4} eV/K. We have found that the energy gap decreases with increase in Sb percentage and an increase in energy gap with decrease of temperature in these thin films.

Table 1. Variation of energy gap with temperature for different equation for SbSe thin films.

Thin films	Linear Eq $E_g(T)=E_g(0)+\alpha T$	Non Linear Eq $E_g(T)=E_g(0)+\alpha T^2$	Varshni $E_g(T)=E_g(0)-(\alpha T^2/(\beta+T))$	Bose-Einstein $E_g(T)=E_g(0)-[2\alpha/(\exp(\theta_B/T)-1)]$
Sb_2Se_3	$E_g(0)$=1.46 eV α= -5.66x10^{-4} eV/K	$E_g(0)$= 1.40 eV α= -1.45x10^{-6} eV/K	$E_g(0)$= 1.43 eV α = 9.3x10^{-4} eV/K β = 194 K	$E_g(0)$= 1.41 eV α = 0.125 eV θ_B = 293 K
SbSe	$E_g(0)$=1.19 eV α= -4.86x10^{-4} eV/K	$E_g(0)$= 1.14 eV α= -1.22x10^{-6} eV/K	$E_g(0)$= 1.16 eV α=1.17x10^{-3} eV/K β = 525 K	$E_g(0)$= 1.14 eV α = 0.16 eV θ_B = 398 K
Sb_3Se_2	$E_g(0)$= 0.99 eV α = -2x10^{-4} eV/K	Eg(0)= 0.977 eV α= -7.48x10^{-7} eV/K	$E_g(0)$= 0.99 eV α = 8.4x10^{-4} eV/K β = 631 K	$E_g(0)$= 0.96 eV α = 0.18 eV θ_B = 586 K

The main reason of the decrease in optical energy gap with increase in temperature is because of two common effects: first is due to the thermal expansion of the lattice coupled with the change of the electron energies with volume. As temperature increases, the band gap energy decreases because the crystal lattice expands and the interatomic bonds are weakened. Weaker bonds means less energy is needed to break a bond and an electron can easily go to conduction band. The second contribution is the direct renormalization of band energies by electron-phonon interaction. With increase in temperature, the electron –phonon interaction increase and this yield to reduce transport of electrons from valence band to conduction band by scattering, therefore, the transmission will decrease.

4. Conclusions

Thin films of a-Sb_xSe_{1-x} (x = 0.4, 0.5, 0.6) are prepared by physical vapour deposition technique. The amorphous nature of these thin films has been checked by XRD technique. The temperature dependence of the optical energy gaps in temperature range of 100-400K, are fitted with four equations beginning with linear, non linear, Varshni and Bose Einstein equations. The results have got appeared the best fitting with the Varshni equation. The absolute zero value of energy gap (E_g) and the rate of change of the Eg with temperature, according to varshni equation for amorphous Sb_2Se_3 thin films are found to be: 1.43eV and 9.30x10^{-4} eV/K, for a-SbSe 1.16eV and 1.17x10^{-3} eV/K and for a-Sb_3Se_2 0.99eV and 8.40x10^{-4} eV/K. We have found that the energy gap decreases with increase in Sb percentage and an increase in energy gap with decrease of temperature.

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