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Optical property modification by Sb addition into $As_{40}Se_{60}$ alloys

R. NAIK AND B. DAS

Department of Physics, Utkal University, Bhubaneswar

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Abstract: : The present report shows the optical property modification due to the addition of Sb matrix into $As_{40}Se_{60}$ compound. There is no structural change between $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_{02}$ alloy which is confirmed from the X-ray diffraction study. The transmission is found to be decreased with addition of Sb where as the optical absorption increases. The optical band gap is found to be decreased with Sb incorporation into $As_{40}Se_{60}$ thin film. The degree of disorderness1 increases which is reflected from the Tauc parameter and Urbach energy. The width of the localized state increases thus decreasing the optical band gap.

Key words: Amorphous semiconductor; Chalcogenides; Optical property; Band gap; Thin film.

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1. Introduction

Chalcogenide amorphous semiconductor is one of the most prospective material which is studied extensively during several decades. This material is generally found in the form of glass. Chalcogenide glasses always contain one or more chalcogen element (sulphur, selenium or tellurium) in combination with elements from IV^{th}, V^{th} or VI^{th} group of the periodic system of elements [1]. These glasses form covalent bonds and have less ionic conductivity (~9%) and their properties are significantly different from oxide glasses. They have attracted considerable attention due to their infrared transparency, low phonon energy, and high non-linear optical properties. They have been explored as promising candidates for optical memories, gratings, switching devices [2].

Because of their low phonon energy and high refractive indices, these glasses are used for high efficiency fiber amplifier [3]. They are used for optoelectronics (photoresists, optical storage, optical waveguides, optical fiber, optical gratings, and optical circuits) as infrared elements and devices for acousto-optic devices, holography, xerography and information storage media [4,5]. In addition, chalcogenide glasses with enhanced ionic conductivity have been developed and found to exhibit properties suitable for electro-chemical applications.

The As_xSe_{1-x} system is the most studied among the binary systems of semi conducting chalcogenide glasses [6] and there are a number of works on the effect of addition of different elements on the physical properties of the stoichiometric $As_{40}Se_{60}$ glass [7, 8]. The addition of Sb to As-Se system expands the glass forming area and also creates compositional and configurational disorder in the system [9]. The maximum Sb content that forms glass in this ternary system is 20 at.% [10]. The ternary Sb–As–Se glasses are formed by adding Sb atoms in the As–Se system. The corresponding substitution does not alter drastically the basic structure of glass, since both As and Sb are isovalent elements [11].

The present paper reports the optical properties change in $As_{40}Se_{60}$ due to the addition of 2% Sb ($As_{40}Se_{58}Sb_{02}$). Optical constants such as the refractive index, absorption coefficient (α) and thickness of the films are determined using Swanepoel method [12] form the transmission spectra measured in the spectral range 600–1200 nm. The optical band gap, Tauc parameter and Urbach energy is determined from the optical absorption edge.

2. Experimental details

Bulk glass of $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_{02}$ was prepared by conventional melt quenching technique. Materials of As, Se and Sb (99.995% pure) were weighed according to their atomic percentage using stoichiometric calculation and sealed in a quartz ampoule in a vacuum of 10^{-5} Torr. The sealed ampoule was kept inside a rotating furnace at 1000 ^{0}C for 36 h to make the melt homogeneous. The bulk glass was obtained by quenching the ampoule in ice cooled water.

Thin films were prepared by thermal evaporation method at a base pressure of 1 x10^{-5} Torr from the prepared bulk glass onto the glass substrates (microscope slides). During the deposition process (at normal incidence), the substrates were suitably rotated in order to obtain the films of uniform thickness. The thicknesses of the films were around 1000 nm. The amorphous state of the film was checked by X-ray Diffractometer (XRD). The optical absorption spectra were taken by

using the Fourier Transform Infrared (FTIR) spectrometer in the visible wavelength range of 400–1200 nm.

3. Results and Discussions

3.1. X-Ray diffraction analysis:

The X-ray diffraction patterns, taken at room temperature are shown in Fig.1. The absence of sharp structural peaks of the thin films confirms the amorphous nature of $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ thin films. The width of broad hump was from 20^0-35^0.

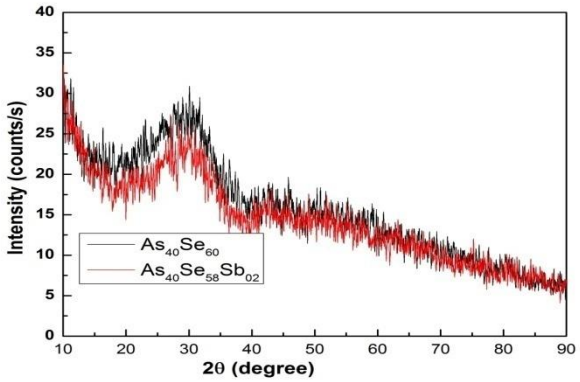

Fig-1. XRD pattern of for $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ thin films

3.2. FTIR Data analysis

(a) Transmission

Optical constant of $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ thin films can be evaluated using transmission spectra. Fig-2 shows the transmission plots of $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ thin films. Oscillatory nature of transmission is the result of interference pattern, which show the uniformity of the prepared films. It is clear that transmission of $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ thin films increases with wavelength. The transmittance of $As_{40}Se_{60}$ thin film is higher than that of $As_{40}Se_{58}Sb_2$ thin film. Transmittance of $As_{40}Se_{60}$ thin film varies with interference pattern from 75% to 85% in the wavelength range 600nm to 1200nm which shows high values of transmission in the film. But the transmittance of $As_{40}Se_{58}Sb_2$ thin film varies with interference pattern from 65% to 80% as shown in fig-2.So, the addition of Sb into $As_{40}Se_{60}$ decreases the transmission.

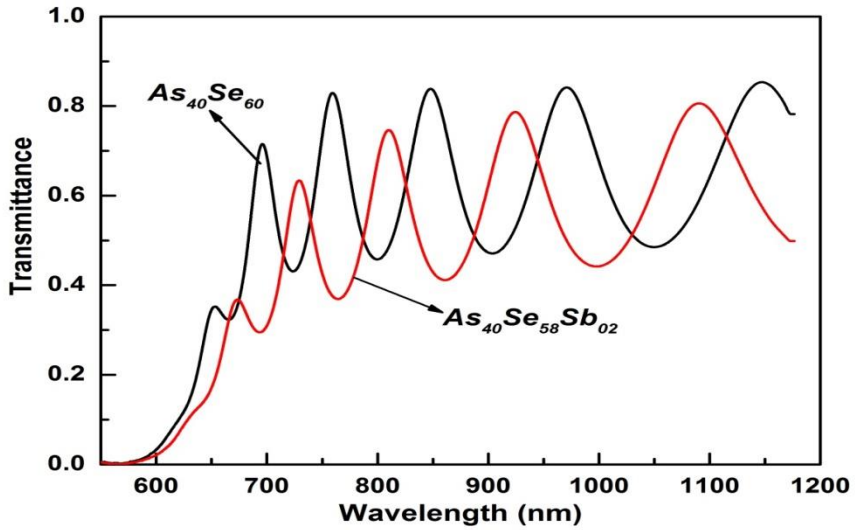

Fig-2. Transmission spectra of $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ thin films

(b) Determination of refractive index

The refractive index of the thin film can be determined by measuring the transmission spectrum from Swanepoel method. The refractive index (n) is obtained using the following expression:

$$N= [M+ (M^2-S^2)^{1/2}]^{1/2} \quad (1)$$

where $M= [2S(T_M-T_m/T_MT_m)] + (S^2+1)/2]$. (2)

T_M and T_m are maximum and minimum transmission values at a particular wavelength, S is the refractive index of the substrate (glass substrate-1.51). Refractive index is obtained by extrapolating envelops corresponding to T_M to T_m. The fringes are used to calculate the refractive index (n) of the thin films using above equations. The values of T_M, T_m and λ for $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ films from fig-2 are given in the table 1and 2 respectively.

The refractive index is found to decrease with the increase in wavelength and increases with Sb addition as shown in fig-3. Refractive index is increased for $As_{40}Se_{58}Sb_2$ due to local structural modification which brings the Sb atoms

close to the As & Se atoms. There will be change in the bond length & bond angle of various bonds due to this modification.

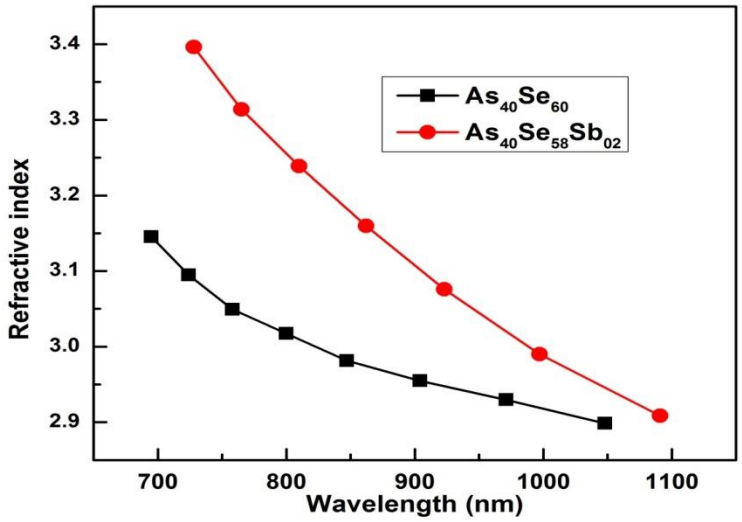

Fig-3. Refractive index vs wavelength plots for $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ thin films

(c) Determination of thickness

If n_1 and n_2 are the refractive indices of two adjacent maxima or minima having wavelength λ_1 and λ_2 then the values of thickness was determined by Swanepoel method:

$$d=\lambda_1\lambda_2/2(\lambda_1 n_2-\lambda_2 n_1) \qquad (3)$$

The values of d calculated from this equation for $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ are shown in table 1 and 2 respectively. The average values of d_1 is 1004 nm. These values of d_1 can now used with n_1 to determine the orders of numbers for the extremes from the equation.

$$2nd=m\lambda \qquad (4)$$

A big increase in accuracy now results in taking the exact integer of half integer values of n for each λ and calculated the thickness d_2 from the above equation using the values of n_1 again.

The average values of d_2 are given in the table. Using the accurate values of m and d_2, n was again calculated for each λ using the above equation.

Table -1. Determination of thickness of$As_{40}Se_{60}$ thin film

λ	T_M	T_m	n_1	d_1	M	d_2	n_2
695	0.7110	0.3802	3.2331		9	967.3378	3.1454
724	0.7664	0.4320	3.0217		8.5	1018.3009	3.0946
758	0.8249	0.4427	3.0590	811.2637	8	991.1735	3.0494
800	0.8360	0.4574	3.0011	1184.1500	7.5	999.6334	3.0172
847	0.8433	0.4648	2.9757	957.1266	7	996.2361	2.9815
904	0.8484	0.4735	2.9416	1005.2419	6.5	998.7761	2.9548
971	0.8521	0.4772	2.9297	1008.0149	6	994.2997	2.9297
1048	0.8620	0.4834	2.9153	1058.8565	5.5	988.5775	2.8985

Mean d_1=1004.1089nm, Mean d_2=994.2918 nm, Mean n_2=3.0088

Table-2. Determination of thickness of $As_{40}Se_{58}Sb_2$ thin film

Λ	T_M	Tm	n_1	d_1	M	d_2	n_2
728	0.6323	0.3279	3.4579		7	736.8634	3.3963
765	0.6829	0.3689	3.2547		6.5	763.8952	3.3140
810	0.7435	0.3895	3.2318	657.9067	6	751.9029	3.2390
862	0.7615	0.4109	3.1329	806.3800	5.5	756.6471	3.1597
923	0.7877	0.4272	3.0839	770.7646	5	748.2408	3.0757
997	0.8022	0.4417	3.0293	936.1873	4.5	740.5176	2.9901
1091	0.8218	0.4745	2.8961	728.1910	4	753.4270	2.9085

Mean d_1=779.8859nm, Mean d_2=750.2134 nm, Mean n_2=2.7604

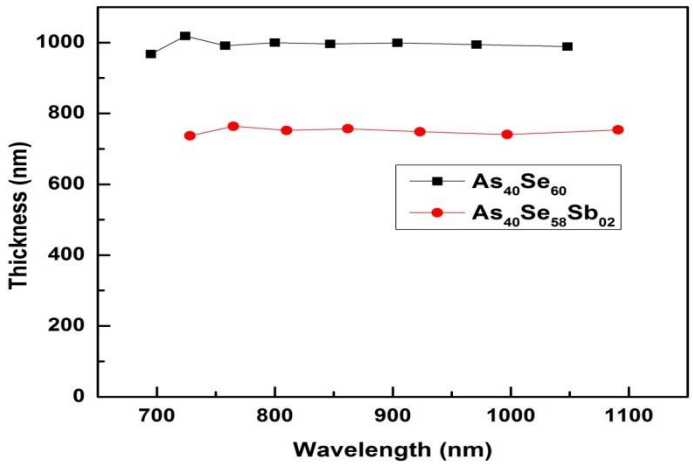

Fig-4. Thickness vs wavelength plots for $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ thin films

It is clear from the Fig-4, that the thickness remains constant throughout the film for both the cases which indicates the homogeneity in the film.

(d) Absorption coefficient (α)

The measurement of the absorption coefficient α as a function of frequency v of the incident beam provides information to determine the band gap E_g of a material. The absorption coefficient (α) can be calculated using the equation

$$\alpha = (1/d)\ln(1/T) \qquad (5)$$

where d is thickness of thin film and T is transmission. The absorption coefficients (α) versus wavelength (λ) for both the films (as-prepared) are shown in the fig-5.Whenever any electromagnetic wave propagates through the medium, its loss by absorption and scattering process is represented by the absorption coefficient. The reduction of α with wavelength shows that the material is getting transparent at higher wavelength, which makes it a useful optical material in higher wavelength range. In crystalline material the fundamental edge is directly related to transition from the conduction band to valence band and associated with direct and indirect the band gaps, where as in case of amorphous materials, the transitions are termed as non-direct owing to the absence of electronic band structure in the k-space. In the absorption process, a photon of known energy excites an electron from a lower to higher energy states, corresponding to an absorption edge.

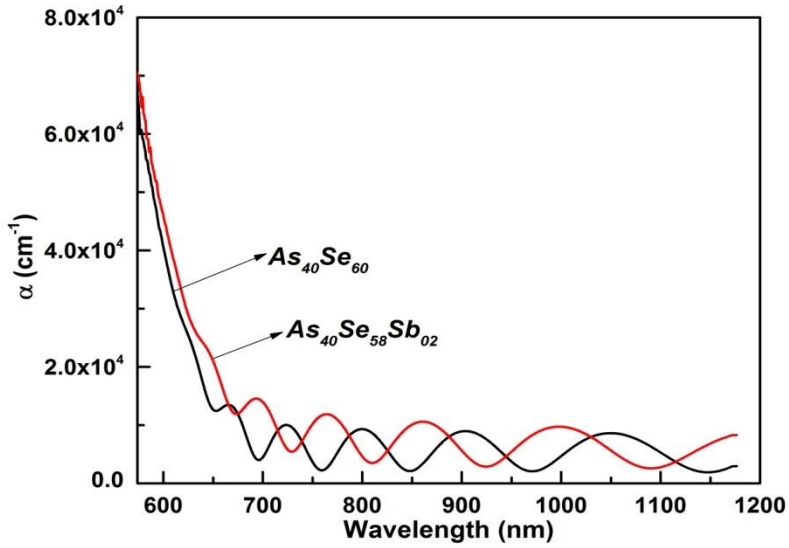

Fig-5. Absorption coefficient of $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ Thin film

(e) Optical band gap

The fundamental absorption edge in most amorphous semiconductors follows an exponential law. The optical absorption spectrum is the most productive tool for developing the energy band diagram. The absorption coefficient of amorphous semiconductors in the high absorption region ($\alpha = 10^4$ cm^{-1}) follows an exponential law according to Tauc [13]

$$(\alpha h\nu)^{1/m} = B^{1/m}(h\nu - E_g) \qquad (6)$$

where ν is the frequency of the incident beam, B is a constant, E_g is optical band gap and m is an exponent, which can be assumed to have values of 1/2, 3/2, 2 and 3 depending on the nature of electronic transition responsible for the absorption: m =1/2 for allowed direct transition, m = 3/2 for forbidden direct transition, m = 2 for allowed indirect transition and m =3 for forbidden indirect transition [14]. The best fit of the experimental results of $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ thin films using Eq. (6), with m = 2 i.e., the variation curve of $(\alpha h\nu)^{1/2}$ with hν is shown in fig.6. This indicates that the absorption in thin films of $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ is due to non-direct transition. Plotting the dependence of $(\alpha h\nu)^{1/2}$ on photon energy (hν) will give a straight line and the y intercept gives the value of the optical band gap as shown in Fig-6.

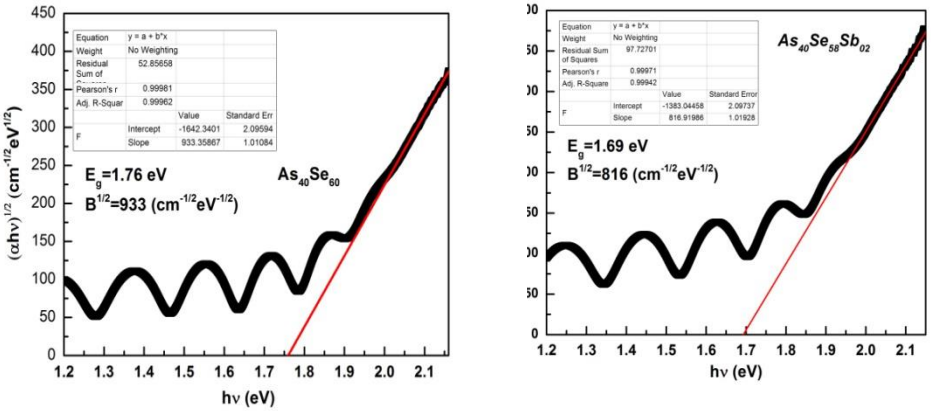

Fig-6. $(\alpha h\nu)^{1/2}$ vs $(h\nu)$ for $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ thin films

The slope of the fitting gives the value of $B^{1/2}$. The constant B includes information on the convolution of the valence band and conduction band states and on the matrix element of optical transitions, which reflects not only the k selection rule but also the disorder induced spatial correlation of optical transitions between the valence band and conduction band [15]. Moreover, B is highly dependent on the character of the bonding [16]. The reflection loss was not as that much as compared to the high absorption in the band gap region. The optical band gap of the films $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ are found to be1.76 eV and 1.69 eV respectively. The band gap is decreased by 0.07 with addition of 2 % Sb in $As_{40}Se_{60}$. The values of $B^{1/2}$ for $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ films are found to be 933 and 816 $cm^{-1/2}eV^{-1/2}$ respectively. This decrease in tauc parameter indicates the increase in disorderness due to which the band tail extends into the gap region which results in the decrease of optical band gap.

(f) Urbach energy

Chalcogenide glasses have been found to exhibit highly reproducible optical edges, which are relatively intensive for preparation conditions and only the observable absorption with a gap under equilibrium conditions account for the first process. In amorphous materials, a different type of optical absorption edge is observed and absorption coefficient increases exponentially with photon energy near the energy gap. This type of behavior has also been observed in other chalcogenides. The optical absorption edge is known as the urbach edge and is given by [17],

$$\alpha(h\nu) = \alpha_0 \exp(h\nu/E_e) \qquad (7)$$

where α_0 is constant and corresponds to the Urbach energy (the width of the band tail of the localized states in the band gap). In this region, transition between (defect) states in the gap and the band take place. Plotting the dependence of log(α) on photon energy will give a straight line, which gives the width of the tails of the localized states into the gap at band edges. It is known as the Urbach energy which is a useful parameter to evaluate the degree of disorderness. The value of Urbach energy (E_e) for the $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ are found to be 182 meV and 160 meV respectively. The decrease in Urbach energy supports the decrease in optical band gap.

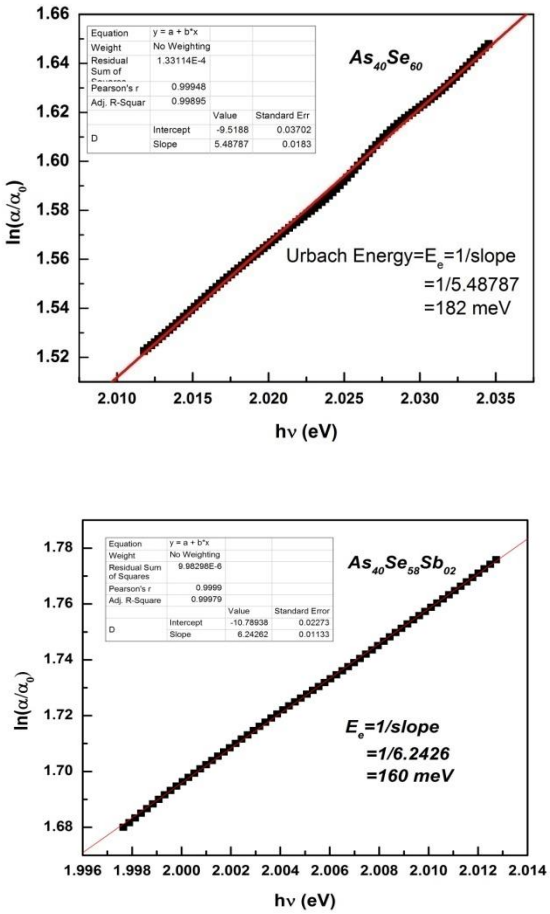

Fig-7. log(α/α_0) for $As_{40}Se_{60}$ and $As_{40}Se_{58}Sb_2$ thin films

4. Conclusion

The addition of Sb into $As_{40}Se_{60}$ alloy does not change the structural property, but changes the optical property to a great extent. The transmission % decreases with Sb addition whereas the absorption coefficient increases. The optical band gap decreases with Sb addition as a result of increased band tailing. The Tauc parameter and urbach energy which are related to the degree of disorderness, shows the changes with Sb content. The width of localized states increases with the addition of Sb content thus decreasing the optical band gap.

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