

OPTICAL PROPERTIES OF AMORPHOUS THIN FILMS OF $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$

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The optical constants like refractive index (n), real dielectric constant (ϵ'), extinction coefficient (k), imaginary dielectric constant (ϵ''), absorption coefficient (α) have been studied for $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ films (where $x= 2, 4, 6, 8$) in the wavelength range 400–1200 nm. The transmission spectra, $T(\lambda)$ of the films are obtained by spectrophotometer. Swanepoel method is used to calculate the optical constants and they are plotted as a function of wavelength. It is found that $n, \epsilon', \epsilon'', k, \alpha$ decrease with increase in wavelength. Band gap was found to increase with the increase in Ag concentration.

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1. Introduction

Chalcogenide glasses are obtained by mixing chalcogen elements i.e.S, Se and Te with other elements of periodic table such as Ga, Sb, In, Ag, As and Zn etc. In these glasses short range inter atomic forces are covalent:strong in magnitude and highly directional, where as weak Vander Walls forces contribute significantly to the medium range order .The formation of solid solutions in semiconductors is of interest since it results in a number of other semiconducting materials. There are binary [1–6], ternary [7–12] and multi-component[13–18] alloys of chalcogenide glasses have been extensively studied for many decades .They have widespread commercial and technological applications, such as infrared transmission and detection, memory storage, integrated and non linear optics, biosensors, thermal imaging, xerography, ion- selective potentiometry [19], optical fibers [20-21]. Amorphous materials can be regarded as amorphous semiconductors, if the energy band gap lies between 0.1 and 3eV. The present interest in amorphous semiconductors is due to their scientific and technological importance makes them a particularly active field in solid-state physics. These glasses are transparent in the Visible and Infrared regions [22-24], with the index of refraction ($2 \leq n \leq 3.7$), having optical losses with low value ($\leq 0.3\text{dB/cm}$). The various kinds of photo-induced structural or physico-chemical changes are observed in amorphous chalcogenides [25].

Since the advent of electro photography, amorphous selenium has become a material of commercial importance; it has some disadvantage like short lifetime, low sensitivity and thermal instability. Structural and configurational disorder in the material is made by addition of a third element to the selenium alloys which expands the glass forming area and is beneficial in understanding the structural and optical properties of chalcogenide glasses [26]. In the present work Ag has been chosen as an additive element in amorphous Se – In alloy. Thick/thin films of Se-In-Ag have applications in optical data storage due to larger absorption coefficient and high mobility. Therefore it is reasonable to study the effect of thickness on structural and optical properties of $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ thin films so that it is possible to prepare a semiconductor with specific properties required for certain applications.

The present work deals with the determination of the optical band gap , the absorption coefficient ,the refractive index and the extinction coefficient of $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ thin films.

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2. Experimental

Glass composition $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ ($x = 2, 4, 6, 8$) were prepared from highly pure element Se, In, Ag (99.99% purity). The elements are weighed in accordance with their atomic percentages. (LIBROR, AEG-120) electronic balance was used whose least count was 10^{-4} gm. The material was then sealed in evacuated quartz ampoule with a pressure of 10^{-5} Torr and length of which was (~ 5 cm) and internal diameter was (~ 8 mm). The ampoule containing material was heated to 1000°C and was held at that temperature for 12 hours. This temperature was chosen so that all constituents' elements get melted. The temperature of the furnace was raised slowly at a rate of $3 - 4^\circ\text{C} / \text{minute}$. During heating, the ampoule was constantly shaken for homogeneity. After rocking for about 12 hours, the obtained melt was then rapidly quenched in ice-cooled water. The quenched sample was then taken out by breaking the quartz ampoule. The glassy nature of the sample was analysed by X-ray diffraction. Thin films of a $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ were prepared by vacuum evaporation technique, in which the substrate was kept at room temperature at a pressure of 10^{-6} Torr using a molybdenum boat. The films were kept inside the deposition chamber for 24 hours to achieve the metastable equilibrium. Optical transmission of $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ was measured by a Double UV/VIS/NIR Computer Controlled Spectrometer (Hitachi-330).

3. Results and discussion

The optical behavior of $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ thin films has been analysed using Transmittance data. Optical transmission is a very complex function which depends on wavelength (λ), substrate refractive index (s), refractive index (n) of thin film, thickness (d) and absorption coefficient (α). Swanepoel's method [27-30], which is based on Mainfacer [31], is a simple way to calculate the optical constants of thin films using the envelope of the interference maxima and minima in transmittance spectrum. The Swanepoel's method has been used in chalcogenide glasses by various workers [32-35].

In the present study transmission measurements were made on amorphous thin films of $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ ($x=2, 4, 6, 8$) in the wavelength range 400 nm-1200 nm. The results of these measurements are given in Figs 1 to 4. It is clear from the figure that interference fringes are observed in the measured frequency range and hence Swanepoel's method can be applied for calculating the optical parameters. The transmission curves in the figure show that for lower wavelengths (≤ 400 nm) corresponding to high energies, the transmittance is zero because most of the light is absorbed.

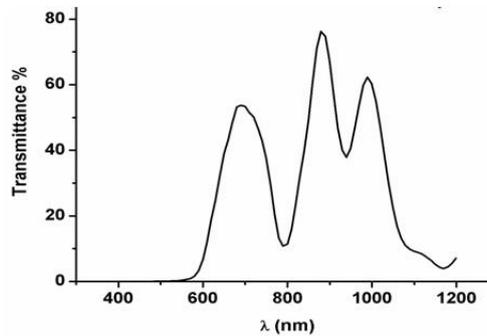


Fig.1. Transmission as a function of wavelength in amorphous thin films of $\text{Se}_{90}\text{In}_8\text{Ag}_2$

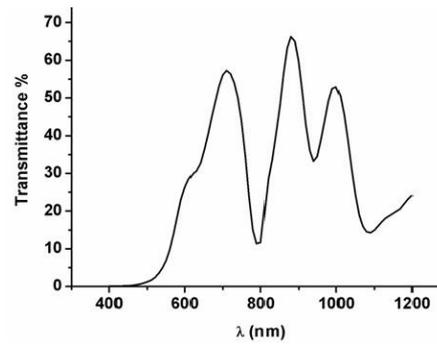


Fig.2. Transmission as a function of wavelength in amorphous thin films of $Se_{90}In_6Ag_4$

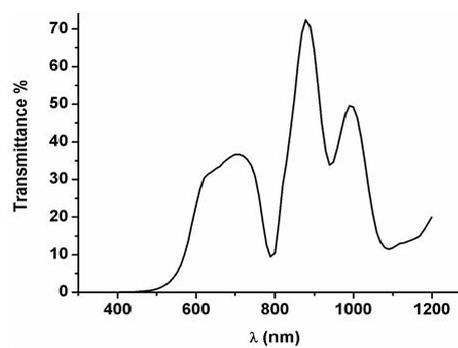


Fig.3. Transmission as a function of wavelength in amorphous thin films of $Se_{90}In_4Ag_6$

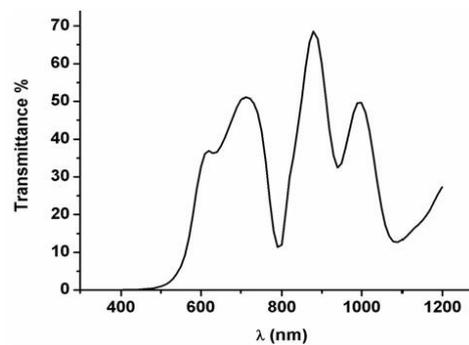


Fig.4. Transmission as a function of wavelength in amorphous thin films of $Se_{90}In_2Ag_8$

3.1. Determination of refractive index

Refractive index is the important optical property of a substance which defines the working performance of a material. This physical quantity is widely influenced from the wavelength of incident light. In multicomponent chalcogenide glasses it is well established that the refractive index extensively depends on the localized density of states and it is influenced by the addition of foreign elements in alloys.

According to Swanepoel method, the optical constants are deduced from the fringe patterns in the transmittance spectrum. The first step is to calculate the maximum and minimum transmittance envelope functions, T_M and T_m respectively. In the transmittance region, the value of

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

Where

$$N = \frac{2s}{T_m} - \frac{(s^2 + 1)}{2}$$

Where Minimum Transmittance envelope functions is T_m and s is the refractive index of the substrate.

In the region of weak and medium absorption, the refractive index n is given by,

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

Where

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

The value of refractive index of the film is calculated using Eq. (1) and (2) and variation of refractive index with wavelength is shown in Fig.5. The refractive index is found to decrease with wavelength which shows normal dispersion behavior of the material.

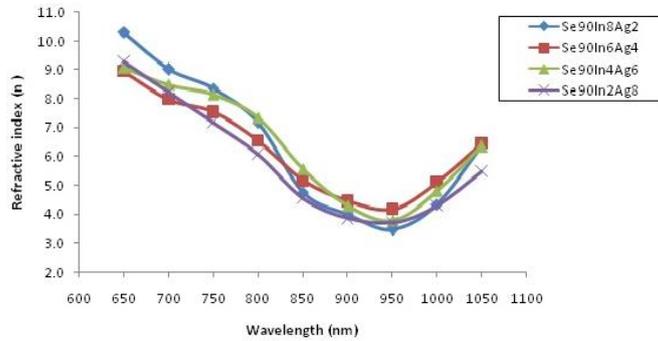


Fig. 5. Variation of refractive index (n) with wavelength (λ)

3.2. Determination of extinction coefficient

The extinction coefficient k is calculated from the relation,

$$k = \frac{\alpha\lambda}{4\pi} = \left(\frac{\lambda}{4\pi d}\right) \ln \left(\frac{1}{x}\right) \quad (3)$$

Where x is the absorbance and d is the film thickness.

If n_1 & n_2 are the refractive indices at two adjacent maxima or minima at λ_1 and λ_2 then the thickness is given by

$$d = \frac{\lambda_1 \lambda_2}{2\lambda_1 n_2 - \lambda_2 n_1} \quad (4)$$

In the region of weak and medium absorption, using the transmission minima T_m , x is given by,

$$x = \frac{[E_m - \{E_m^2 - (n^2 - 1)^3 (n^2 - s^4)^{1/2}\}]}{[(n - 1)^3 (n - s^2)]} \quad (5)$$

Where,

$$E_m = \left[\left(\frac{8sn^2}{T_m}\right) - (n^2 - 1)(n^2 - s^2)\right] \quad (6)$$

The variation of extinction coefficient with the wavelength is shown in Fig.6. As observed from graph the decrease in extinction coefficient with increase in wavelength may be correlated with the increase in the transmittance and decrease in absorption coefficient

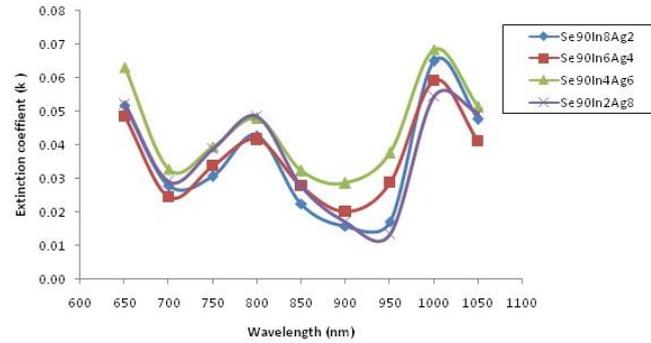


Fig. 6. Variation of extinction coefficient (k) with wavelength (λ)

3.3. Determination of dielectric constants

The dielectric constant of $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ thin films is calculated with the help of refractive index n and extinction coefficient k . Real dielectric constant (ϵ') is calculated by the following equation

$$\epsilon' = n^2 - K^2 \quad (7)$$

While the imaginary dielectric constant (ϵ'') is calculated by the following equation,

$$\epsilon'' = 2nk \quad (8)$$

The spectral distributions of real and imaginary dielectric constant (ϵ' & ϵ'') respectively for $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ films are shown in Figs 7 & 8 respectively while the calculated values are also given in the Table 1.

The real part of dielectric constant is found to decrease with increase in wavelength. The imaginary part of the dielectric constant also decreases with the increase in wavelength. The values of real part of dielectric constant were found to be greater than the imaginary dielectric constant.

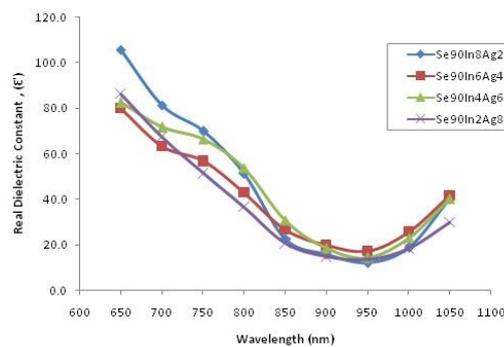


Fig.7. Variation of real dielectric constant (ϵ') with wavelength (λ)

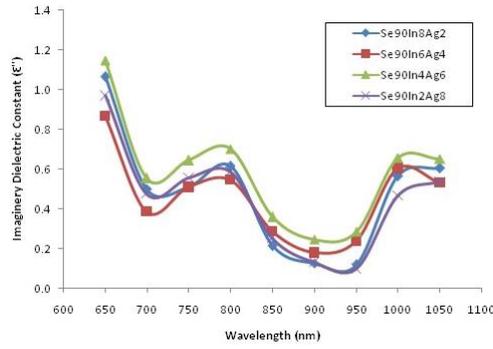


Fig.8. Variation of imaginary dielectric constant (ϵ'') with wavelength (λ)

Table 1. Optical parameters in a $Se_{90}In_{10-x}Ag_x$ films at 700 nm

S. No.	Sample	Refractive index (n)	Extinction Coefficient (k)	Real dielectric constant (ϵ')	Imaginary dielectric constant (ϵ'')
1.	$Se_{90}In_8Ag_2$	9.01	2.77×10^{-2}	81.22	5×10^{-1}
2.	$Se_{90}In_6Ag_4$	7.96	2.43×10^{-2}	63.38	3.8×10^{-1}
3.	$Se_{90}In_4Ag_6$	8.47	3.27×10^{-2}	71.71	5.5×10^{-1}
4.	$Se_{90}In_2Ag_8$	8.20	2.90×10^{-2}	67.30	4.7×10^{-1}

3.4. Absorption coefficient and optical band gap

The absorption coefficient α of $Se_{90}In_{10-x}Ag_x$ films is calculated using the well-known relation,

$$\alpha = \frac{4\pi k}{\lambda} \quad (9)$$

Where k is the extinction coefficient.

The spectral distribution of absorption coefficient α for $Se_{90}In_{10-x}Ag_x$ thin films is shown in Fig 9 and obtained values are given in Table 2. It is observed that the value of α increases linearly with the increase in energy for all the samples of $Se_{90}In_{10-x}Ag_x$.

In chalcogenide glasses, the optical absorption edge spectra generally contain three distinct regions

(i) High absorption region ($\alpha = 10^4 \text{ cm}^{-1}$), which shows the optical transition between valence band and conduction band and determines the optical band gap.

(ii) For α less than about $\sim 10^4 \text{ cm}^{-1}$ there is usually an Urbach tail where α depends exponentially on the photon energy.

(iii) The region ($\alpha \leq 10^2 \text{ cm}^{-1}$) involves low energy absorption and originates from defects and impurities [36].

Chalcogenide glasses exhibit highly reproducible optical edges, which are relatively insensitive to preparation conditions and only the observable absorption [37] with a gap under equilibrium conditions account for the process. In the second process the absorption edge depends exponentially on the photon energy according to the Urbach relation [38]. In crystalline materials, the fundamental edge is directly related to the conduction and valence band, i.e. direct and indirect band gaps, while in the case of amorphous materials a different type of optical absorption edge is

observed. In these materials, α exponentially increases with the photon energy near the energy gap. This type of behavior is observed in many chalcogenides [40].

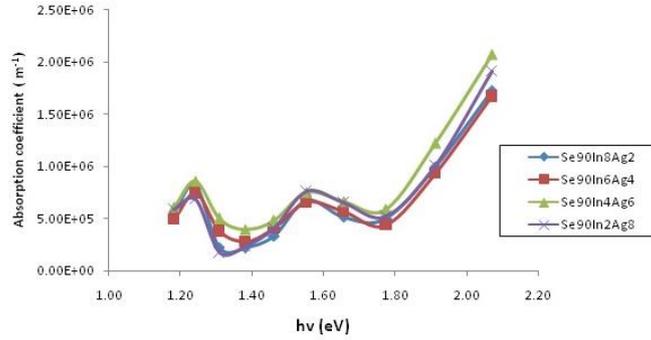


Fig. 9. Variation of absorption coefficient (α) with energy

Table 2. Values of optical band gap and absorption coefficient (α) for $Se_{90}In_{10-x}Ag_x$ thin films

S. No.	Sample	Optical Band Gap (E_g) in eV	Absorption coefficient (α) in m^{-1} at 700 nm
1.	$Se_{90}In_8Ag_2$	1.483	4.98×10^5
2.	$Se_{90}In_6Ag_4$	1.509	4.36×10^5
3.	$Se_{90}In_4Ag_6$	1.595	5.86×10^5
4.	$Se_{90}In_2Ag_8$	1.504	5.21×10^5

The optical band gap is determined from absorption coefficient values as a function of photon energy according to the generally accepted 'non direct transition' model for amorphous semiconductors [38] proposed by Tauc [37]

In the present system of $Se_{90}In_{10-x}Ag_x$, absorption coefficient and energy ($h\nu$) of the incident photon is given by

$$(\alpha h\nu)^{1/2} \propto (h\nu - E_g) \quad (10)$$

The variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for $Se_{90}In_{10-x}Ag_x$ films are shown in Figs. 10-13. The value of indirect optical band gap E_g has been calculated by taking intercept on x-axis and is given in Table 2. It is evident from the table 2 that the value of optical band gap (E_g) increases with increasing Ag concentration. By increasing Ag concentration, the band gap increases which may be due to the increase in grain size, the reduction in the disorder and decrease in density of defect states (which results in the reduction of band tailing).

The increase in the optical band gap can also be discussed on the basis of density of state model proposed by Mott and Davis [39]. Chalcogenide thin films always contain a high concentration of unsaturated bonds or defects. The localized states in the amorphous band gap are present because of these defects.

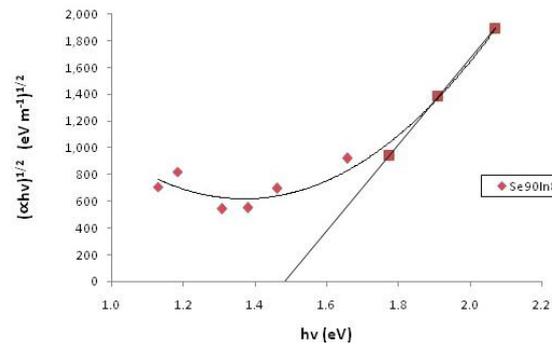


Fig.10. Variation of $(\alpha hv)^{1/2}$ with photon energy ($h\nu$) in thin films of $Se_{90}In_8Ag_2$

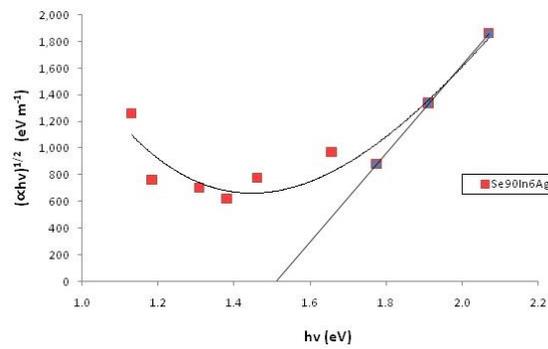


Fig. 11. Variation of $(\alpha hv)^{1/2}$ with photon energy ($h\nu$) in thin films of $Se_{90}In_6Ag_4$

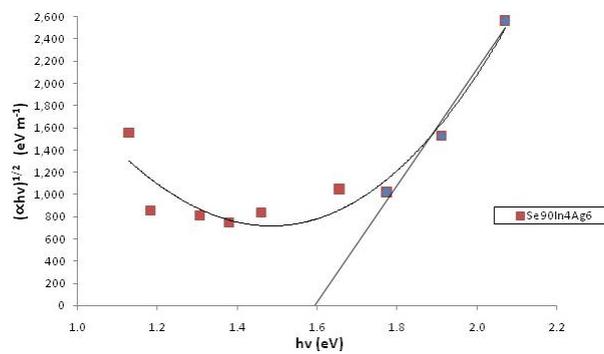


Fig.12. Variation of $(\alpha hv)^{1/2}$ with photon energy ($h\nu$) in thin films of $Se_{90}In_4Ag_6$

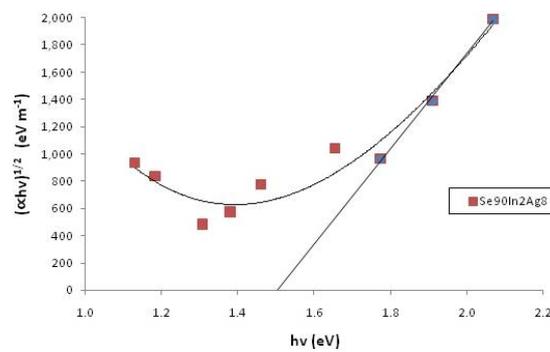


Fig.13. Variation of $(\alpha hv)^{1/2}$ with photon energy ($h\nu$) in thin films of $Se_{90}In_2Ag_8$

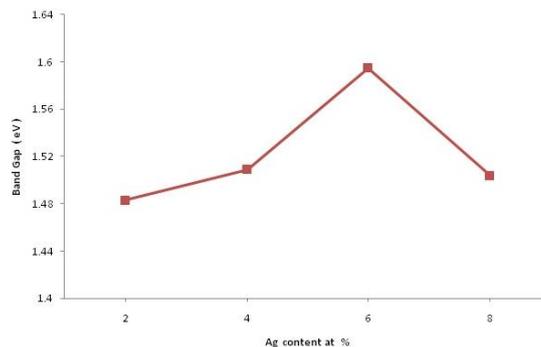


Fig. 14. The compositional dependence of the band gap of $Se_{90}In_{10-x}Ag_x$ films (Where $x=2, 4, 6, 8$)

From Fig. 14 one can see compositional dependence of the band gap of $Se_{90}In_{10-x}Ag_x$ films. The increase in optical band gap with increase in Ag concentration may be due to the decrease in the amount of disorder in the materials and decrease in the density of defect states. A discontinuity in Fig. 14 is observed at 6 atomic percent of Ag. This type of discontinuity has been observed in chalcogenide glasses at a particular average coordination number when structure changes from floppy state to mechanical optimized structure.

4. Conclusions

Thermal evaporation technique was used to prepare thin films of $Se_{90}In_{10-x}Ag_x$. Various parameters related to optical properties were calculated for various samples of $Se_{90}In_{10-x}Ag_x$ based on the generation of the envelopes of the interference maxima and minima in transmission spectrum. It is found that optical band gap increases with increasing Ag concentration. The increase in band gap on incorporation of Ag may be due to increase in disorder in the materials and decrease in the density of defect states.

The optical absorption measurements made on these films indicate that the absorption mechanism is due to indirect transition. Composition dependence of band gap shows a discontinuity at 6 atomic percent of Ag.

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