A study of optical parameters of amorphous $Se_{90}In_xGe_{10-x}$ thin films before and after heat treatment

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Amorphous thin film of $Se_{90}In_xGe_{10-x}$ (x = 2 and 4) were thermally evaporated onto chemically cleaned glass substrates. Some optical parameters of these films were studied before and after thermal annealing above glass transition temperature of the respective alloys. The optical transmission spectra were measured in thin films of the above glasses in the wavelength range 400-2000 nm using spectrophotometer. The straight forward analysis proposed by Swanepoel has been successfully employed to determine the optical constants. It is observed from the measurements that the values of refractive index (n) and real dielectric constant (ε`) decrease with increase in wavelength while extinction coefficient (k) and imaginary dielectric constant (ε") increase with increase in wavelength. The absorption coefficient (α) measured at strong absorption region also increases with photon energy (hν). Optical band gap (E_g) decreases with In concentration and also after thermal annealing of the films above glass transition temperature. This decrease in band gap could be accounted for by the generation of excess electronic delocalized states on incorporation of Indium as well as on thermal annealing in binary Se-Ge system.

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1. Introduction

Chalcogenide glasses have drawn the attention of scientists due to their technological importance in various solid state devices. These glassy alloys have found applications not only due to their electrical and thermal properties, but also due to their optical properties. Chalcogenide glasses have recently attracted a great deal of interest because of their applications in solid state devices both in scientific and technical field [1]. The current application in chalcogenide materials centers on X-ray imaging and photonics [2]. Many semiconducting glasses, in particular selenium, exhibit [3] a unique property of reversible transformation. This property makes these glasses very useful in optical memory devices. Se alloys have also been studied for their photoconductive properties [4]. Se alloys have also been recognized as promising materials for infrared optical elements [5], infrared optical fibers [6] and for the transfer of information [7]. They have also found application in xerography [8], switching and memory devices [9], photolithography [10] and in the fabrication of inexpensive solar cells [11] and more recently for reversible phase change optical recording [12].

The addition of an impurity has a pronounced effect on the conduction mechanism and the structure of glasses and this effect can be widely different for different impurities. It was believed that impurity has very little effect on the properties of amorphous semiconductors as each impurity atom may satisfy its valence requirements by adjusting its nearest neighbor environment [12]. However, it has been shown that the impurity does affect the electrical properties of these semiconductors [13].

The accurate knowledge of optical constants of amorphous semiconductors is necessary not only for understanding the basic mechanism of these effects, but also for exploiting their interesting technological potentials. Among the existing methods for determining the optical constants, those that are based exclusively on the optical transmission spectra at normal incidence [14,15] have been applied to different crystalline and amorphous materials [16-18].

Chalcogenide glasses have been found to exhibit the change in refractive index under the influence of light, which make it possible to use theses materials to record not only the magnitude but also the phase of illumination. The latter is especially important in holographic optical data storage and in the fabrication of various integrated components and devices such as selective optical filters, mixers, couplers and modulators [19-21].

The Se-Ge system is probably one of the most-studied among the binary systems of chalcogenide glasses. Studies on glasses based on Se-Ge have received much attention because of their interesting electrical and optical properties. The optical properties of amorphous semiconductors have been extensively studied in recent decades because of their wide range of applications and strong dependence on composition.

The present paper reports the measurements of optical constants in amorphous thin films of $Se_{90}In_xGe_{10-x}$ prepared by vacuum evaporation technique. The influence of In and heat treatment on the optical properties of

$Se_{90}In_xGe_{10-x}$ thin films is studied in the present case for x = 2 and 4.

2. Experimental

Glassy alloys of $Se_{90}In_xGe_{10-x}$ are prepared by quenching technique. The glassy nature of the alloy is ascertained by X-ray diffraction. Thin films of these glassy alloys are prepared by vacuum evaporation technique, in which the substrate is kept at room temperature at a base pressure of 10^{-6} Torr using a molybdenum boat. The films are kept inside the deposition chamber for 24 hours to achieve the metastable equilibrium. A Double UV/VIS/NIR Computer Controlled Spectrometer (Hitachi-330) is used for measuring optical transmission of $Se_{90}In_xGe_{10-x}$ thin films as a function of wavelength of the incident light.

3. Results and discussion

3.1 Determination of optical constants

Fig. 1(a) and 1(b) show the variation of transmission (T) with wavelength (λ) in $Se_{90}In_xGe_{10-x}$ thin films before and after the heat treatment respectively. According to Swanepoel's method [15], which is based on Mainfacer [22], the envelope of the interference maxima and minima occured in the spectrum can be utilized for obtaining optical parameters in the present glassy system. This method has, therefore, been used in chalcogenide glasses by various workers [23-25].

In the method proposed by Swanepoel, the optical constants are deduced from the fringe patterns in the transmittance spectrum. In the transmittance region where the absorption coefficient (α = 0), the refractive index n is given by

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

where $N = (2s/ T_m) - (s^2 + 1)/2$

T_m is the envelope function of the transmittance minima and s is the refractive index of the substrate.

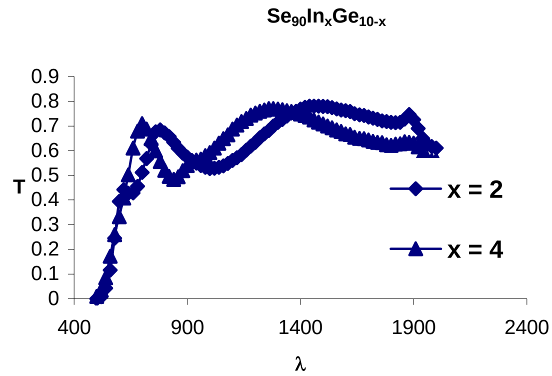
In the region of weak and medium absorption, where (α ≠ 0), the transmittance decreases mainly due to the effect of α and the refractive index n is given by

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

where $N = [2s(T_M - T_m) / T_M T_m] + (s^2 + 1)/2$

and T_M is the envelope function of the transmittance maximum.

In the region of strong absorption, the transmittance decreases drastically due almost exclusively to the influence of α and n can be estimated by extrapolating the values in the other regions. Because the thickness of our film is uniform, interference give rise to the spectrum as shown in Fig. 1(a) & 1(b). The fringes can be used to calculate the refractive index n of the film using eqn. (1) and (2) as indicated previously.



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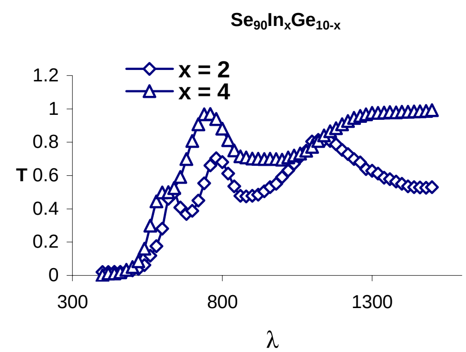

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Fig. 1. a. Variation of transmittance (T) with wavelength (λ) in $Se_{90}In_xGe_{10-x}$ thin films before the heat treatment. b. Variation of transmittance (T) with wavelength (λ) in $Se_{90}In_xGe_{10-x}$ thin films after the heat treatment.

The extinction coefficient k can be calculated from the relation

$$k = \alpha\lambda / (4\pi) = (\lambda / 4\pi d) \ln(1/x) \quad (3)$$

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

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

$$d = \lambda_1\lambda_2 / 2[\lambda_1 n_2 - \lambda_2 n_1] \quad (4)$$

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

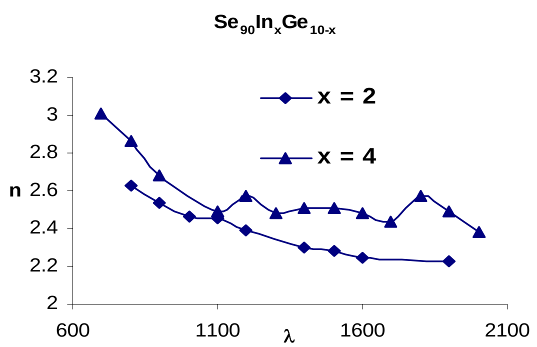
$$x = [E_m - \{E_m^2 - (n^2 - 1)^3 (n^2 - s^4)\}^{1/2}] / [(n - 1)^3 (n - s^2)] \quad (5)$$

where $$E_m = [(8n^2 s/T_m) - (n^2 - 1)(n^2 - s^2)] \quad (6)$$

The spectral distributions of both n and k for $Se_{90}In_xGe_{10-x}$ thin films before and after heat treatment respectively are shown in Figs. 2(a and b) and 3(a and b) and the calculated values are given in Table 1.

Table 1. Optical parameters of $Se_{90}In_xGe_{10-x}$ thin films.

S. No.	Optical Parameters	Before the heat treatment		After the heat treatment	
		x = 2	x = 4	x = 2	x = 4
1.	Refractive Index (n)	2.45	2.49	2.72	2.32
2.	Extinction Coefficient (k)	0.74×10^{-2}	0.44×10^{-2}	1.34×10^{-2}	0.64×10^{-2}
3.	Real Dielectric Constant (ε`)	6.01	6.22	7.40	5.40
4.	Imag. Dielectric Constant (ε”)	3.63×10^{-2}	2.19×10^{-2}	7.29×10^{-2}	2.98×10^{-2}
5.	Optical Band Gap (E_g) in eV.	0.62	0.54	0.58	0.44
6.	Absorption Coefficient (α) in M^{-1} at 1100 nm.	8.40×10^4	4.98×10^4	15.26×10^4	7.27×10^4



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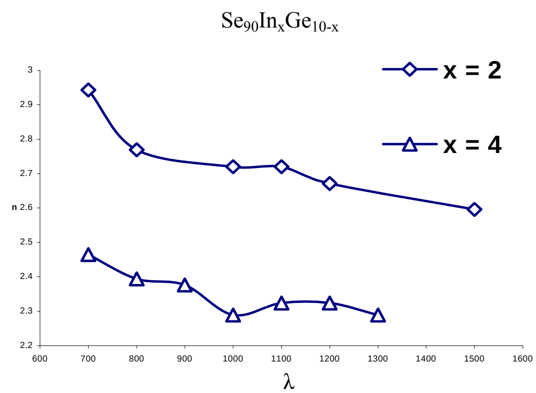

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Fig. 2. a. Variation of refractive index (n) with wavelength (λ) in $Se_{90}In_xGe_{10-x}$ thin films before the heat treatment. b. Variation of refractive index (n) with wavelength (λ) in $Se_{90}In_xGe_{10-x}$ thin films after the heat treatment.

3.2 Determination of dielectric constants

The dielectric constant of $Se_{90}In_xGe_{10-x}$ thin films can be calculated with the help of refractive index n and extinction coefficient k [26]. Real dielectric constant (ε`) can be calculated by the following equation,

$$ε` = n^2 – k^2 \quad (7)$$

while the imaginary dielectric constant (ε”) can be calculated by the following equation,

$$ε” = 2nk \quad (8)$$

The spectral distribution of both real and imaginary dielectric constants for $Se_{90}In_xGe_{10-x}$ thin films before and after the heat treatment respectively are shown in Figs. 4(a and b) and 5(a and b) and the calculated values are also given in Table 1.

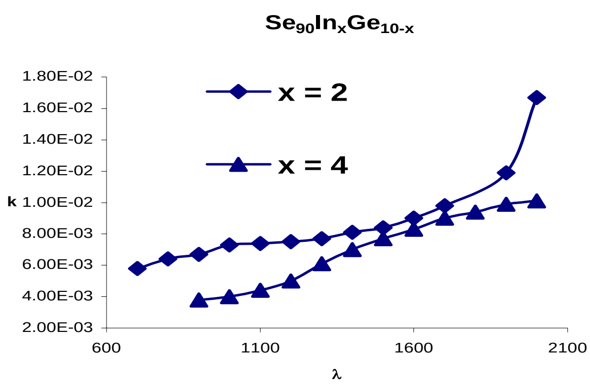
3.3 Absorption coefficient and optical band gap

The absorption coefficient α of $Se_{90}In_xGe_{10-x}$ films can be calculated using the well-known relation

$$α = 4πk / λ \quad (9)$$

in which k is substituted by its value obtained from Fig. 3(a) and 3(b).

The spectral distribution of absorption coefficient α for $Se_{90}In_xGe_{10-x}$ thin films before and after the heat treatment respectively are shown in Fig. 6(a) and 6(b) and the calculated values are also given in Table 1.



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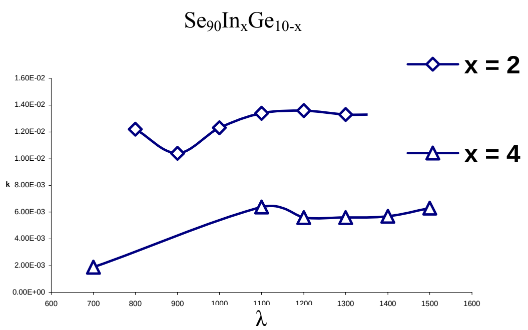

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Fig. 3. a. Variation of extinction coefficient (k) with wavelength (λ) in $Se_{70}Te_{30-x}Ag_x$ thin films before the heat treatment. b. Variation of extinction coefficient (k) with wavelength (λ) in $Se_{90}In_xGe_{10-x}$ thin films after the heat treatment.

The present system of $Se_{90}In_xGe_{10-x}$ obeys the rule of non-direct transition and the relation between the optical band gap, absorption coefficient and energy (hν) of the incident photon is given by [27-29]:

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

The variation of $(\alpha h\nu)^{1/2}$ with photon energy (hν) for $Se_{90}In_xGe_{10-x}$ thin films before and after the heat treatment respectively are shown in Fig. 7(a) and 7(b). The value of indirect optical band gap E_g has been calculated by taking intercept on x-axis. The values of optical band gap E_g are given in Table 1. It is evident from the table that optical band gap E_g decreases with the increase in In concentration in $Se_{90}In_xGe_{10-x}$ system. This could be accounted for by the generation of excess electronic delocalized states on incorporation of Indium in binary Se-Ge system. In Se-Ge-In system, an increase in the density of localized states, on increase in In concentration, has been observed by Singh et.al.[30]. The optical band gap E_g also decreases after the heat treatment above glass transition temperature (at 405 K) as evident from Table 1. As a decrease in band gap has been related to the increase in the density of localized states in the present glassy system, it is expected that the density of localized states may increase after thermal annealing. Similar interpretation has also been given by other workers [31,32] in chalcogenide glasses.

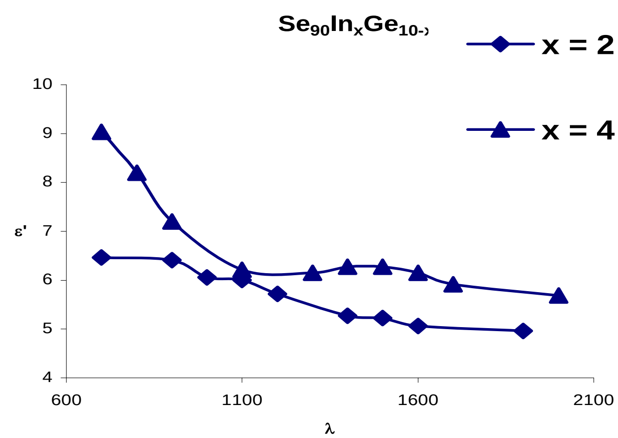

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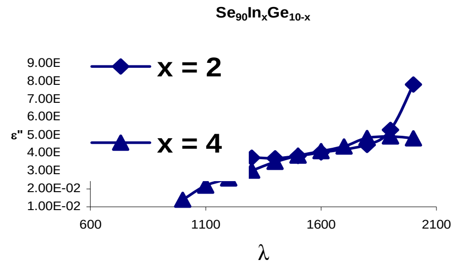
Fig. 4. a. Variation of real dielectric constant (ε`) with wavelength (λ) in $Se_{90}In_xGe_{10-x}$ thin films before the heat treatment. b. Variation of real dielectric constant (ε`) with wavelength (λ) in $Se_{90}In_xGe_{10-x}$ thin films after the heat treatment.



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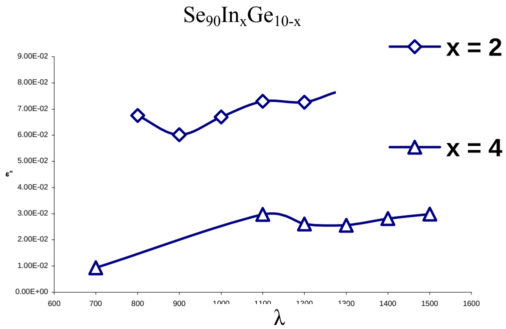

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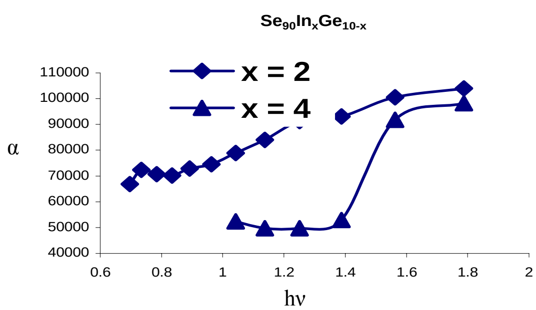
Fig. 5. a. Variation of imaginary dielectric constant (ε") with wavelength (λ) in $Se_{90}In_xGe_{10-x}$ thin films before the heat treatment. b. Variation of imaginary dielectric constant (ε") with wavelength (λ) in $Se_{90}In_xGe_{10-x}$ thin films after the heat treatment.



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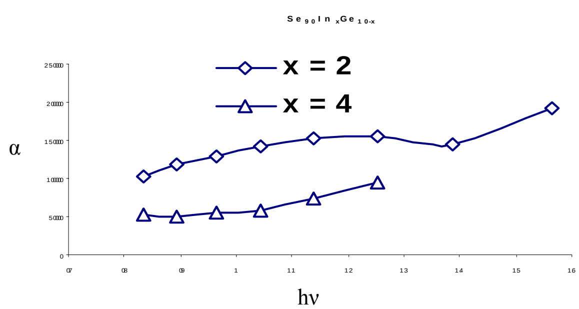

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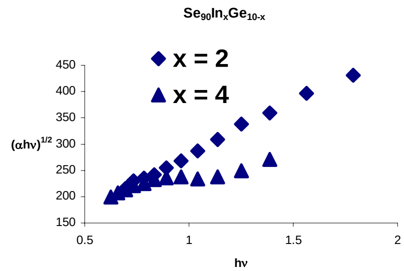
Fig. 6. a. Variation of absorption coefficient (α) with photon energy (hν) in $Se_{90}In_xGe_{10-x}$ thin films before the heat treatment. b. Variation of absorption coefficient (α) with photon energy (hν) in $Se_{90}In_xGe_{10-x}$ thin films after the heat treatment.



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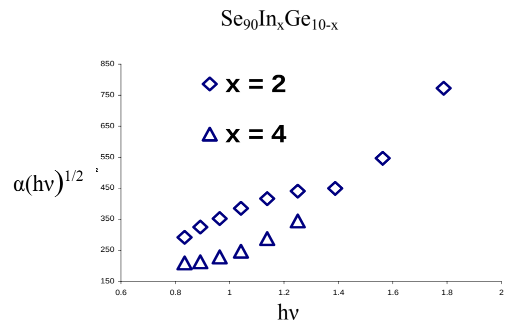

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Fig. 7. a. Variation of $(\alpha h\nu)^{1/2}$ with photon energy (hν) in $Se_{90}In_xGe_{10-x}$ thin films before the heat treatment. b. Variation of $(\alpha h\nu)^{1/2}$ with photon energy (hν) in $Se_{90}In_xGe_{10-x}$ thin films after the heat treatment.

4. Conclusion

The optical transmission spectra of amorphous thin films of $Se_{90}In_xGe_{10-x}$ are obtained in the wavelength range 400-2000 nm by spectrophotometer before and after the heat treatment for x = 2 and 4. It is found that refractive index (n) and real dielectric constant (ε`) decrease with increase in wavelength (λ) while extinction coefficient (k) and imaginary dielectric constant (ε") increase with increase in wavelength. The absorption coefficient (α) measured at strong absorption region also increases with photon energy (hν). Optical band gap E_g decreases with the increase in In concentration in $Se_{90}In_xGe_{10-x}$ system. This could be accounted for by the generation of excess electronic delocalized states on incorporation of Indium in binary Se-Ge system. The optical band gap E_g also decreases after the heat treatment above glass transition temperature. As a decrease in band gap has been related to the increase in the density of localized states in the present glassy system it is expected that density of localized states may increase after thermal annealing.

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