Chapter 3

Swift heavy ion irradiation induced changes in 
(Ge$_{0.20}$Se$_{0.80}$)$_{0.90}$Ag$_{0.10}$ thin films

3.1 Introduction

Chalcogenide glasses have received much attention in recent years, due to extensive applications in solid states devices. The optical properties of chalcogenide glasses, such as excellent transmittance in the infrared region, continuous shift of optical absorption edge and values of refractive index varies between 2.0 and 3.5, as well as very strong correlation between the former properties and the chemical composition, explain the significant interest in these amorphous materials for the manufacture of filters, antireflection coating and, in general a wide range of optical devices [1-4]. Glassy Chalcogenide materials, based on S, Se and Te, have many unique optical properties, which can be used for a wide variety of applications [1]. These glasses are very promising materials for use in optical elements, such as gratings [2], optical recording media [3] and in fiber optics and guided wave devices in integrated optics, since they certainly exhibit good transparency in the infrared region, especially at the telecommunication wavelengths, 1.3 and 1.55 µm [4]. The energy gap in these materials, as well as tetrahedral semiconductors plays an important role in their electrical and optical properties. These glasses show a variety of photo-stimulated phenomena when exposed to light or other radiations [5, 6]. When these glasses are irradiated with high energy particles or light, bond breaking and bond rearrangement take place, resulting in the change in local structure of these materials. The irradiation of materials with swift heavy ions leads to the creation of a wide variety of defect states in these materials, which changes the physical and chemical properties such as structure, electrical and optical properties of the material. The changes are strongly dependent on the mass of the incident ion, the irradiation energy and fluences. The irradiation may cause ionization or excitation and possible displacement of atoms from their sites in the lattice of the materials. The resultant new electronic configuration coordinates would cause a change in optical properties of the films [7]. In general, these phenomena are associated with the changes in the
optical constants [8] and absorption edge shift [9], allowing the use of these materials in the fabrication of a large number of optical devices.

This chapter deals with the effect of SHI irradiation on the optical, electrical and structural properties of \( \text{Ge}_{0.20}\text{Se}_{0.80}\cdot 0.06\text{Ag}_{0.10} \) thin films. The effect of 100 MeV Ag beam and 85 MeV O beam have been investigated in this chapter. Material in bulk form has been prepared by melt quenching technique, discussed in detail in section 2.2 of chapter 2. The films have been prepared by thermal evaporation technique which is discussed in detail in section 2.3 of chapter 2. These films are then irradiated with two different beams and varying fluence at Inter University Accelerator Centre (IUAC), New Delhi. Optical properties, DC conductivity, photoconductivity, structural, and surface morphology have been studied for pristine and irradiated samples.

3.2 Optical properties

By the term, ‘optical properties of material’ we understand that when a light passes through a given material, it change or affect the characteristics of light passing through it by modifying its propagation vector or intensity. Generally the term ‘optical constant’ is reserved for refractive index \((n)\) and extinction coefficient \((k)\); though many authors use optical coefficients within the same terminology. In general, optical coefficients are related to absorption coefficient. The most important optical constant of a material is its refractive index, which in general depends on the wavelength of the electromagnetic wave, through a relationship called dispersion. In materials where an electromagnetic wave can lose its energy during its propagation, the refractive index becomes complex. The real part is usually the refractive index, \(n\), and the imaginary part is called the extinction coefficient.

There are numbers of experimental techniques available which can be used to determine optical constants of given material [10]. Recently, Collins has provided an extensive in-depth review of ellipsometry for optical measurements [11]. In this technique, change in the polarization of light incident on a sample to sensitively characterize surfaces and thin films. The interaction of incident polarized light with the sample causes a polarization change in the light, which may then be measured by analyzing the light reflected from the sample. One of the most popular and convenient optical measurements involves passing a monochromatic light through a thin sample,
and measuring the transmitted intensity as a function of wavelength, $T(\lambda)$, using a simple spectrophotometer [12].

3.3 The complex refractive index and dielectric constant

The refractive index of an optical or dielectric medium, $n$ can be defined as the ratio of velocity of light $c$ in vacuum to the velocity of light in the medium $v$.

$$n = \frac{c}{v} \tag{3.1}$$

The well known Maxwell’s formula for refractive index of a medium is given by

$$n = \sqrt{\varepsilon_r \mu_r} \tag{3.2}$$

Where $\varepsilon_r$ is the static dielectric constant of medium or relative permittivity, and $\mu_r$ is the relative permeability. Since for nonmagnetic materials $\mu_r = 1$, therefore above relation (3.2) reduce to

$$n = \sqrt{\varepsilon_r} \tag{3.3}$$

Equation (3.3) connects the dielectric properties of a material with the optical properties at any particular frequency of interest. Since $\varepsilon_r$ depends on wavelength of light, so refractive index ($n$) will also depend on wavelength of light which is known as dispersion of light. Electromagnetic wave while propagating through medium loses its energy which is known as attenuation by various mechanisms like generation of phonons, free carrier absorption, scattering etc. In such materials refractive index become a complex function of frequency and called as complex refractive index and denoted by $n^*$ and expressed by relation

$$n^* = n - ik \tag{3.4}$$

The real part is $n$, it is same as the normal refractive index, while the imaginary part is $k$, is called extinction coefficient. Form equation (3.3) we can conclude that if $n$ is a complex, and then $\varepsilon_r$ has to be complex quantity. Therefore, we can express the complex dielectric constant by relation

$$\varepsilon_r^* = \varepsilon_r - i\varepsilon_2 \tag{3.5}$$

Equation (3.3) can be written as

$$n^* = \sqrt{\varepsilon_r^*}$$

Squaring both side

$$(n^*)^2 = \varepsilon_r^*.$$
Using equations (3.4) and (3.5) we get

\[ \varepsilon_1 = n^2 - k^2 \]
\[ \varepsilon_2 = 2nk \]  

The relation between extinction coefficient \( k \) and \( \alpha \) is given by

\[ k = \frac{\alpha \lambda}{4\pi} \]  

(3.6)  

(3.7)

This shows that extinction coefficient \( k \) is proportional to absorption coefficient \( \alpha \).

### 3.4 Absorption edge in amorphous semiconductors

The electronic transitions in crystals between valence and conduction band starts at the absorption edge which corresponds to the minimum energy difference \( E_g \) between the lowest of the conduction and the highest maxima of the valence band. If the minima of the conduction band and maxima of the valence band are at same point in k-space then the electronic transitions are called direct transitions otherwise called as non-direct transition which is phonon assisted.

But in case of amorphous semiconductors, we observe a shift of absorption edge either towards the lower or higher energy.

\[ \text{Fig. 3.1 Schematic representation of absorption edge in amorphous semiconductor} \]
In many amorphous semiconductors, the absorption edge has shape as shown in figure 3.1. Regions B and C are created by transitions within the fully coordinated system, perturbed to some extent by defects, while region A arises from transitions involving the defect states directly. The absorption edge, spanning regions A and B, is therefore particularly complicated and has a defect-induced tail at the lowest energies, an exponential region at intermediate energies, and a power law region at the highest energies. The optical absorption in amorphous semiconductors near the absorption edge is usually characterized by three types of optical transitions corresponding to transitions between tail and tail states, tail and extended states, and extended and extended states. In the small optical absorption coefficient range A (also called the weak absorption tail (WAT)), where \( a < 10^{-1} \text{cm}^{-1} \), the optical absorption is controlled by optical transitions from tail-to-tail states. As stated above, the localized tail states in amorphous semiconductors arise from defects. To some extent, the absolute value of the absorption in region A may be used to estimate the density of defects in the material. In region B, where typically \( 10^{-1} < a < 10^{4} \text{cm}^{-1} \), the optical absorption is related to transitions from the localized tail states above the valence band edge to extended states in the conduction band and / or from extended states in the valence band to localized tail states below the conduction band.

(1) For high absorption coefficient \( (a \geq 10^{4} \text{cm}^{-1}) \); Tauc’s power law \([13]\) states that

\[
cdhv = B(hv - E_{g}^{\text{opt}})^{n}
\]

where B is the slope of Tauc edge called band tailing parameter that depends on the width of localized states in the band gap which are attributed to homopolar bonds in chalcogenide glasses. In the above equation, \( n = 1/2 \) for a direct allowed transition, \( n = 3/2 \) for a direct forbidden transition, \( n = 2 \) for an indirect allowed transition and \( n = 3 \) for an indirect forbidden transition. \( E_{g}^{\text{opt}} \) is the optical band gap.

(2) For intermediate absorption coefficient \( (10^{1} \text{ cm}^{-1} < a < 10^{4} \text{ cm}^{-1}) \); the absorption coefficient follows the Urbach’s exponential relation [14, 15]

\[
a = \alpha_{0} \exp(hv/E_{c})
\]

where \( \nu \) is the frequency of the radiation, \( \alpha_{0} \) is a constant, \( h \) is Planck’s constant and \( E_{c} \) is an energy which is often interpreted as the width of the tail of localized states in the gap region or Urbach energy. The parameter \( E_{c} \) is thought to provide information about the extent of disorder or randomness in amorphous chalcogenide glasses.
Absorption in this region is related to the transition between extended states in one band and localized states in the exponential tail of the other band; hence disorder here refers more towards that of electronic states within the material as compared to irregularity in atomic arrangement. This relation was first proposed by Urbach [14] to describe the absorption edge in alkali halide crystals at high absorption levels. The relation has been found to hold for many amorphous or glassy materials. Tauc [13] believes that it arises from electronic transitions between localized states in the band edge tails and the density of which is assumed to fall off exponentially with energy.

3.5 Measurement of n and α using Swanepoel’s Technique

This method [16] is easiest to apply when thin film does not show much localized absorption band in between interference extremes. This method is based on the upper and lower envelopes of the optical transmission spectra and is very useful for calculating various optical constants.

The film has thickness d and complex refractive index \( n' = n - ik \), where n is refractive index and k is the extinction coefficient which is related to absorption coefficient (α) by following equation

\[
\alpha = \frac{4\pi k}{\lambda} \quad (3.10)
\]
The transparent substrate on which the film is deposited has thickness much larger than the thickness of the film (see figure 3.2). The transparent substrate has index of refraction \( n_s \) and absorption coefficient \( \alpha_s = 0 \). The refractive index of the surrounding medium is \( n_0 = 1 \). Multiple reflections at three interfaces are taken into account while calculating transmission.

![Transmission Spectrum](image)

**Fig. 3.3 Different absorption region in the transmission spectrum**

If the thickness \( d \) is not uniform, then interference effects are destroyed and the transmission curve will be a smooth curve. However, if the film is of uniform thickness then fringes are obtained in the transmission spectrum as shown in Fig. 3.3. From these fringes optical constants are calculated. The transmission spectrum is divided into four regions. In the transparent region, \( \alpha = 0 \) and the transmission is determined by \( n \) and \( s \) through multiple reflections. In the region of weak absorption, \( \alpha \) is small but starts to reduce the transmission. In the region of medium absorption, \( \alpha \) is large and the transmission decreases mainly due to the effect of \( \alpha \). In the region of
strong absorption, the transmission decreases drastically almost exclusively due to the influence of \( a \). First the transmission of the glass substrate alone in the absence of a film is taken.

The interference-free transmission is given by the following expression:

\[
T_s = \frac{(1 - R_s)^2}{1 - R_s^2}
\]  

(3.11)

where

\[
R_s = \left( \frac{s - 1}{s + 1} \right)^2
\]  

(3.12)

\[
T_s = \frac{2s}{s^2 + 1}
\]  

(3.13)

and

\[
s = \frac{1}{T_s} + \left( \frac{1}{T_s} - 1 \right)^{1/2}
\]  

(3.14)

The basic equation for interference fringes is given by

\[
2nd = m\lambda
\]  

(3.15)

where \( m \) is an integer for maxima and half integer for minima. The transmission \( T \) for the case of Fig 3.3 is a complex function and is given by

\[
T = T(\lambda, s, n, d, \alpha)
\]  

(3.16)

If \( s \) is known, then above equation is written in terms of \( n (\lambda) \) and the absorbance \( x(\lambda) \), where \( x \) is defined in the Eq (3.24)

\[
T = T(n, x)
\]  

(3.17)

The rigorous expression for the transmission \( T \) for a system as shown in figure 3.3 is

\[
T = \frac{Ax}{B - Cx \cos \varphi + Dx^2}
\]  

(3.18)

where

\[
A = 16n^2 s
\]  

(3.19)

\[
B = (n + 1)^3(n + s^2)
\]  

(3.20)

\[
C = 2(n^2 - 1)(n^2 - s^2)
\]  

(3.21)

\[
D = (n - 1)^3(n - s^2)
\]  

(3.22)

\[
\varphi = 4\pi nd / \lambda
\]  

(3.23)

\[
x = \exp(-\alpha d)
\]  

(3.24)

The extremes of the interference fringes can be written as...
\[ T_M = \frac{Ax}{B - Cx + Dx^2} \]  \hspace{1cm} (3.25)

\[ T_m = \frac{Ax}{B + Cx + Dx^2} \]  \hspace{1cm} (3.26)

\( T_M \) and \( T_m \) are considered to be continuous functions of \( \lambda \) and thus for \( n(\lambda) \) and \( x(\lambda) \) [17] as shown in figure 3.3.

(i) The Transparent region

In the transparent region, \( a = 0 \) or \( x = 1 \) in Eqs (3.25) and (3.26). Substituting Eqs (3.19-3.24) in equation (3.25) yields

\[ T = \frac{2s}{s^2 + 1} \]  \hspace{1cm} (3.27)

Substituting Eqs (3.19-3.24) in Eq (3.26) for \( x = 1 \) yields

\[ T_m = \frac{4n^2s}{n^2 + n^2(s^2 + 1) + s^2} \]  \hspace{1cm} (3.28)

or

\[ n = \left[ M + (M^2 - s^2)^{1/2} \right]^{1/2} \]  \hspace{1cm} (3.29)

where

\[ M = \frac{2s}{s^2 + 1} \]  \hspace{1cm} (3.30)

\( T_m \) is thus a function of both \( n \) and \( s \), and \( n \) can be calculated from \( T_m \) using Eq (3.29).

(ii) The region of Weak and Medium absorption

In this region, \( a \neq 0 \) and \( x < 1 \):

Subtracting the reciprocal of equation (3.27) from the reciprocal of Eq (3.28) yields an expression which is independent of \( x \)

\[ \frac{1}{T_m} - \frac{1}{T_M} = \frac{2C}{A} \]  \hspace{1cm} (3.31)

Substituting Eq (3.19-3.24) in Eq (3.31) and solving for \( n \) yields

\[ n = \left[ N + (N^2 - s^2)^{1/2} \right]^{1/2} \]  \hspace{1cm} (3.32)

where

\[ N = 2s \frac{T_{me} - T_m}{T_MT_m} + \frac{s^2 + 1}{2} \]  \hspace{1cm} (3.33)
Eq (3.32) can be used to calculate \( n(\lambda) \) from \( T_M \) and \( T_m \). It is identical to formulae derived by Manifacier et al. [17] using the theory of infinite substrate.

Once \( n(\lambda) \) is known, all the constants in Eqs (3.19-3.24) are known and \( x \) can be calculated in various ways. Eqs (3.25) and (3.26) are quadratic equations in \( x \) that can be solved for \( x \) and the results are simplified by using Eqs (3.19-3.24). Solving Eq (3.25) gives

\[
x = \frac{E_M - [E_M^2 - (n^2 - 1)^2 (n^2 - s^4)]^{1/2}}{(n-1)^3(n-s^2)} \tag{3.34}
\]

where

\[
E_M = \frac{8n^2s}{T_M} - (n^2 - 1)(n^2 - s^2) \tag{3.35}
\]

Solving Eq (3.26) gives

\[
x = \frac{E_m - [E_m^2 - (n^2 - 1)^2 (n^2 - s^4)]^{1/2}}{(n-1)^3(n-s^2)} \tag{3.36}
\]

where

\[
E_m = \frac{8n^2s}{T_m} - (n^2 - 1)(n^2 - s^2) \tag{3.37}
\]

Adding the reciprocals of Eqs (3.25) and (3.26) gives

\[
\frac{2T_M T_m}{T_M + T_m} = \frac{Ax}{B + Dx^2} \tag{3.38}
\]

Solving for \( x \), above equation gives

\[
x = \frac{F - [F^2 - (n^2 - 1)^2 (n^2 - s^4)]^{1/2}}{(n-1)^3(n-s^2)} \tag{3.39}
\]

where

\[
F = \frac{8n^2s}{T_i} \tag{3.40}
\]

and

\[
T_i = \frac{2T_M T_m}{T_M + T_m} \tag{3.42}
\]

From Eqs (3.38) and (3.18), it can be seen that \( T_i \) represents a curve passing through the inflection points of the fringes as shown in Figure 3.3.
The interference-free transmission $T_a$, can be calculated from the interference fringes by integrating Eq (3.18) between a maximum and an adjacent minimum

$$T_a = \frac{A}{2} \int_0^\pi \frac{Ax}{B - Cx \cos \varphi + Dx} d\varphi$$

(3.43)

Assuming a narrow integration region where all parameters are constant, the integral yields

$$T_a = \frac{Ax}{[(B - Cx + Dx^2)(B + Cx + Dx^2)]^{1/2}}$$

(3.44)

Substitution of Eqs (3.25) and (3.26) into (3.44) yields

$$T_a = \sqrt{T_m T_w}$$

(3.45)

$T_a$ is thus just the geometric mean of $T_m$ and $T_w$, and Eq (3.45) is a very useful relation. Solving Eq (3.44) for $x$ gives

$$x = \frac{G - [G^2 - (n^2 - 1)^2(n^2 - s^2)]^{1/2}}{(n-1)(n-s^2)}$$

(3.46)

where

$$G = \frac{128n^4 s^3}{T_a^2} + n^2(n^2 - 1)^3(s^2 - 1)^2 + (n^2 - 1)^3(n^2 - s^2)^2$$

(3.47)

Eq (3.46) is equivalent to a well known equation often used in optical and infrared studies. It can also be used to determine $n$ from $T$, in the transparent region where $x=0$. Putting $x = 1$ in Eq (3.46) and solving for $n$ gives

$$n = \frac{H + (H^2 - s^2)^{1/2}}{1.2}$$

(3.48)

where

$$H = \frac{4n^2}{(s^2 + 1)T_m^2} - \frac{s^2 + 1}{2}$$

(3.49)

Then, we can use Eq (3.49) in the linear transmission $T_a$ without interference transmission.

(iii) The region of Strong absorption

In the region of strong absorption, the interference fringes disappear. It is not possible to calculate $n$ and $x$ independently in this region from transmission spectrum alone. Values of $n$ can be estimated by extrapolating the values calculated in the other parts of the spectrum. The values of $x$ can then be calculated using any of the four formulae presented in the previous section with their appropriate curves. For very large $a$, the
four curves $T_M$, $T_o$, $T_i$, $T_m$ converge to a single curve $T_o$ i.e. $T_o = T_m$. If interference effects are ignored, equation (3.18) can be written for $x \ll 1$ as

$$T_o \equiv \frac{ax}{b}$$  \hspace{1cm} (3.50)

or

$$x \equiv \frac{(n + 1)^2(n + \frac{\lambda_0}{s})}{16n^2s} T_o$$  \hspace{1cm} (3.51)

(iv) Determination of thickness of thin films

The refractive index of the substrate can be determined by measuring the transmission spectrum of the clean substrate alone and using Eq (3.14) to calculate the value of $s$. For the calculation of $n$ in the region of weak and medium absorption, the values of $T_M$ and $T_m$ at different $\lambda$ must be obtained. If $n_1$ and $n_2$ are the refractive indices at two adjacent maxima (or minima) at $\lambda_1$ and $\lambda_2$, it follows from Eq (3.15) that the thickness of thin film ($d$) is given by:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}$$  \hspace{1cm} (3.52)

Owing to the optical absorption, Eqs (3.15) and (3.52) are not valid at the interference maxima and minima, but are valid at the tangent points. A set of $d$’s is obtained by solving Eq (3.52) for each pair of consecutive tangent points. The mean ($d$) so calculated is used together with the first refractive indices, to determine the order numbers from Eq (3.15): $m$ being an integer for an upper tangent point and a half-integer for a lower tangent point. More accurate values of $d$’s are obtained by taking the corresponding integral and half-integral $m$’s. Using these $m$’s and the mean values of $d$’s, a set of $n$’s are again calculated. The absorption coefficient can be determined from the Eq (3.24), where $x$ is the absorbance given by Eq (3.34).

3.6 Ag ions irradiation effects on (Ge$_{0.20}$Se$_{0.80}$)$_{0.90}$Ag$_{0.10}$ thin films

3.6.1 Optical measurements

The optical constants of (Ge$_{0.20}$Se$_{0.80}$)$_{0.90}$Ag$_{0.10}$ thin films have been calculated using Swanepoel’s technique discussed in last section 3.5. Using different ions species of different energies and fluence leads to deposition of different electronic energies to materials through which they pass. Glassy alloy of Ag$_{0.10}$(Ge$_{0.20}$Se$_{0.80}$)$_{0.90}$ has been prepared by melt quenching technique. The materials (5N pure) are weighed.
in accordance with their atomic weight percentage. The weighed materials are sealed in evacuated (~10^{-5} mbar) quartz ampoules and heated up to 1000 °C in a rocking furnace at a heating rate of 3-4 °C/min. Ampoules have been frequently rocked at the highest temperature for 10 hours. The quenching is done in ice cold water immediately after taking out the ampoules from the furnace. Thin films of the alloy are prepared by thermal evaporation technique on well-degassed Corning 7059 glass substrates at room temperature and base pressure of ~ 2×10^{-5} mbar using a molybdenum boat. Amorphous nature of the films is confirmed by the absence of any sharp peak in the X-ray diffractograms of the films. The refractive index in the region, where the absorption coefficient α ≈ 0 is calculated by using equations (3.32) and (3.33). Figure 3.4 shows the normal incidence optical transmission spectra of pristine $\text{Ag}_{0.10}(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}$ and Ag ion irradiated thin films at different fluences.

![Transmission spectrum of $\text{Ag}_{0.10}(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}$ thin film at different fluence of Ag ions](image)

The envelopes of the transmission spectrum, $T_{\text{max}}$ and $T_{\text{min}}$, have been observed from these transmission curves. Using equation (3.32), the values of $n$ are calculated at wavelengths corresponding to the tangent points. If $n_1$ and $n_2$ are the refractive indices...
at two adjacent tangent points at \( \lambda_1 \) and \( \lambda_2 \), then according to the basic equation (3.15) for interference fringes:

\[
2nt = m\lambda
\]

where \( m \) is an order number.

The thickness \( t \) is given by equation (3.52)

\[
t = \frac{\lambda_1 \lambda_2}{4(n_2 - n_1)}
\]

Using equation (3.15), new more precise values of the refractive index and the film thickness were determined by a procedure which was explained in detail in [16]. The film thickness is found to be around 450 nm. The determined values of refractive index at different wavelengths have been plotted in Fig. 3.5 for different fluences. Fig. 3.6 shows the variation of refractive index \( n \) (at \( \lambda = 550 \text{ nm} \)) with fluence. It is clear from the figure that the values of \( n \) first increases (i.e. \( 1 \times 10^{11} \text{ ions/cm}^2 \)) and then decreases as fluence increases.

![Graph](image_url)

**Fig. 3.5 Plot of Refractive index (n) vs hv at different fluence Ag ions**

The data on the dispersion of the refractive index, \( n(\lambda) \) have been calculated using the single-effective-oscillator model proposed by Wemple and DiDomenico [18, 19].
They found that all the data can be described to an excellent approximation by the following relation:

$$n^2(h\nu) = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2}$$  \hspace{1cm} (3.53)

where $h\nu$ is the photon energy, $E_o$ is the oscillator energy and $E_d$ is the dispersion energy. Plotting $(n^2 - 1)^{-1}$ vs. $(h\nu)^2$ allows us to determine the oscillator parameters, by fitting a linear function to the smaller energy data.

Fig 3.7 shows the plot of $(n^2 - 1)^{-1}$ vs. $(h\nu)^2$, which is a straight line. $E_d$ and $E_o$ can be directly determined from the slope, $(E_dE_o)^{-1}$ and the intercept, $E_o/E_d$, on vertical axis. The values of $E_o$ and $E_d$ for this alloy thin film is similar to that of the other Se rich alloys reported in the literature [20, 21].

These values are given in the Table 3.1. It is clear from the table that after the Ag ion irradiations, the values of $n$ and $E_d$ first increases from $(2.47\pm 0.004)$ to $(3.42\pm 0.004)$ and $(14.89\pm 0.01)$ to $(16.04\pm 0.01)$ eV respectively and then decreases from $(3.42 \pm 0.004)$ to $(2.46\pm 0.004)$ and $(16.14\pm 0.01)$ to $(13.36\pm 0.01)$ eV respectively. The value of $E_o$ decreases from $(4.02\pm 0.01)$ to $(3.50\pm 0.01)$ eV after the ion irradiations at all Ag ion fluences (see Table 3.1).
Table 3.1 The refractive index (n), the extinction coefficient (k), real part of dielectric constant (ε1), imaginary part of dielectric constant (ε2), the oscillator energy (E₀), the oscillator strength (E₁) and optical gap (E₂OPT) respectively.

<table>
<thead>
<tr>
<th>Fluence (ions/cm²)</th>
<th>n</th>
<th>k</th>
<th>ε₁</th>
<th>ε₂</th>
<th>E₀</th>
<th>E₁</th>
<th>E₂OPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>2.47</td>
<td>0.12</td>
<td>6.08</td>
<td>0.59</td>
<td>4.02</td>
<td>14.89</td>
<td>1.84</td>
</tr>
<tr>
<td>1×10¹¹</td>
<td>3.42</td>
<td>0.07</td>
<td>11.69</td>
<td>0.52</td>
<td>3.97</td>
<td>16.04</td>
<td>1.80</td>
</tr>
<tr>
<td>3×10¹¹</td>
<td>2.74</td>
<td>0.09</td>
<td>7.49</td>
<td>0.52</td>
<td>3.71</td>
<td>16.14</td>
<td>1.76</td>
</tr>
<tr>
<td>1×10¹²</td>
<td>2.65</td>
<td>0.10</td>
<td>7.01</td>
<td>0.54</td>
<td>3.66</td>
<td>14.93</td>
<td>1.74</td>
</tr>
<tr>
<td>3×10¹²</td>
<td>2.52</td>
<td>0.12</td>
<td>6.33</td>
<td>0.59</td>
<td>3.61</td>
<td>16.49</td>
<td>1.72</td>
</tr>
<tr>
<td>1×10¹³</td>
<td>2.46</td>
<td>0.10</td>
<td>6.03</td>
<td>0.60</td>
<td>3.50</td>
<td>13.36</td>
<td>1.68</td>
</tr>
</tbody>
</table>

Fig. 3.7 Plot between (n²-1⁻¹) and (hv)² at different fluence Ag ions.
The real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric constant [22] for Ag$_{0.10}$(Ge$_{0.20}$Sc$_{0.80}$)$_{0.90}$ films have been calculated using the relation (3.6)

$$\varepsilon_1 = n^2 - k^2 \quad \& \quad \varepsilon_2 = 2nk \quad (3.6)$$

The values of complex dielectric constant (real and imaginary parts) ($\varepsilon_1$ and $\varepsilon_2$) have been plotted in Fig. 3.8(a) and 3.8(b). The real part $\varepsilon_1$ of the dielectric constant first increases at lower ion fluence and then decreases at higher ion fluences, while the imaginary part $\varepsilon_2$ first decreases and then increases with photon energy in all ion fluences.

![Fig. 3.8 (a) $\varepsilon_1$ vs. hv, (b) $\varepsilon_2$ vs. hv at different fluence of Ag ions](image)

The absorption coefficient ($\alpha$) [23] is calculated from the relation (3.24)

$$x = \exp(-\alpha L)$$

where $x$ is absorbance as described elsewhere [16]. The experimentally determined values of $\alpha$'s are plotted in Fig. 3.9. In order to complete the computation of the
optical constants \((n, k)\), the dimensionless extinction coefficient \(k\), is obtained from the already known \(\alpha\) values, using the basic equation, i.e. \(k = \alpha \lambda / 4\pi\) and are plotted in Fig. 3.10. These values have been shown in the Table 3.1. It is clear from the figure and table that the value of extinction coefficient \((k)\) first decreases at lower ion fluence and then increases at higher fluences.

The absorption coefficient of amorphous semiconductors [23] in the strong-absorption region \((\alpha \geq 10^4 \text{ cm}^{-1})\), assuming parabolic valence- and conduction band edges, is given by eq. (3.8)

\[
\alpha(hv) = B(hv - E_{opt}^2) / (hv)
\]

where \(E_{opt}^2\) is the energy distance between the valence and conduction band mobility edges. The parameter \(B\) given by the slope of the plots is an interesting parameter, since it can be taken as a measure of the disorder. Finally, the optical gap \((E_{opt})\) is calculated from the intersection of the plot \((ahv)^{1/2}\) vs. \(hv\) with the abscissa axis as shown in Fig. 3.11. The value of \(E_{opt}\) continuously decreases from \((1.84 \pm 0.01)\) to \((1.68 \pm 0.01)\) eV as the fluence of Ag increases from \(1 \times 10^{11}\) to \(1 \times 10^{13}\) ions/cm\(^2\) (see Table 3.1).

![Fig. 3.9 Variation of absorption coefficient (a) with hv at different fluence of Ag ions](image-url)
Fig. 3.10 Plot of extinction coefficient ($k$) with $h\nu$ at different fluence of Ag ions.

Fig. 3.11 Plot between $(a\nu)^{1/2}$ and $h\nu$ at different fluence of Ag ions.
The decrease of $E_{\text{g}^{\text{opt}}}$ from $(1.84 \pm 0.01)$ to $(1.68 \pm 0.01)$ eV is explained by the fact that the binding energy of Ag-Se bond (202.5 kJ mol$^{-1}$) is smaller than that of the Ge-Se bond (484.1 kJ mol$^{-1}$). Therefore, there is a smaller energy splitting take place between the states of the valence and conduction band. In chalcogenide glasses, the lone pair orbital forms the valence band and the conduction band is formed by the antibonding orbital [24]. The Ag irradiations excite the electrons from the lone pair and bonding states to higher energy states. Vacancies created in these states are immediately filled by the outer electrons with Auger process that in turn induce more holes in the lone pair and bonding orbital leading to a vacancy cascade process as suggested by Kamboj et al. [24]. In this process, bond breaking or ionization of atoms is easier to occur which leads to a change in the local structure of the amorphous network, which results in the increase in band tailing and hence reduce the band gap.

3.6.2 Atomic Force Microscopy

Fig 3.12 shows the 3D images of pristine and Ag beam irradiated thin films with different fluence from $1 \times 10^{11}$ to $1 \times 10^{13}$ ions/cm$^2$. 

(a) Pristine
(b) $1 \times 10^{11}$ ions/cm$^2$
(c) $3 \times 10^{11}$ ions/cm$^2$
(d) $1 \times 10^{12}$ ions/cm$^2$
Fig. 3.12 The 3D images of (a) pristine sample, (b) irradiated at $1 \times 10^{11}$, (c) $3 \times 10^{11}$, (d) $1 \times 10^{12}$, (e) $3 \times 10^{12}$, (f) $1 \times 10^{13}$ ions cm$^{-2}$ respectively

In case of pristine sample root mean square roughness (rms) is 2.3 nm. After irradiation at lower fluence, $1 \times 10^{11}$ ions/cm$^2$ roughness increases to 2.5 nm. For next higher fluences $3 \times 10^{11}$, $1 \times 10^{12}$, $3 \times 10^{12}$ and $1 \times 10^{13}$, the surface roughness is 1.9 nm, 2.7 nm, 2.0 nm and 13.1 nm respectively.

3.6.3 Raman spectroscopy

Fig.3.13 (a) & (b) show the Raman spectra of pristine and after Ag ion irradiation at $1 \times 10^{11}$ ions/cm$^2$. It is observed that in pristine sample three bands appearing are: a band at 193 cm$^{-1}$ (peak I) accompanied by a side band near 209 cm$^{-1}$ (peak II) and a band near 253 cm$^{-1}$ (peak III). Band I is assigned to the stretching mode of GeSe$_{4/2}$ corner-sharing tetrahedral (193 cm$^{-1}$), whereas band II arises from the vibrations of Se atoms in the four member rings composed of two edge sharing tetrahedral (209 cm$^{-1}$). Finally band III originates from Se-Se bonds in Se$_n$ chains. While in case of the sample irradiated at fluence $1 \times 10^{11}$ ions/cm$^2$, there is slight change in positions of band II (211 cm$^{-1}$) and band III (254 cm$^{-1}$) in comparison to pristine sample. We have observed the shift in peak positions toward lower wave number (cm$^{-1}$), in comparison to the Raman spectra observed by Dwivedi et al. [27]. Sugai [30] has observed the band positions at 195 cm$^{-1}$ [Ge(Se)$_{4/2}$ corner-sharing tetrahedral], 213.1 cm$^{-1}$ [vibrations of Se atoms in the four member rings composed of two edge-sharing tetrahedral] and band near 259.1 cm$^{-1}$ [Se-Se bonds in Se chains]. It is clear from Fig.3.13 (a) & (b) that after ion irradiation; the band position does not
change to much extent. The relative area shown in table 3.2 is just the percentage of area of individual peak divided by sum of areas of all peaks. On comparing the relative areas of the spectra, we find that upon irradiation, the relative area of the peak II remain unchanged (see Table 3.2). Therefore the irradiation does not affect the number of ES GeSe$_4$ bonds. Further, the ratio of relative area of band I to band II increase, whereas the ratio of the band III to band II decrease. Furthermore, the sum of the relative area of band I and band III, normalized to band II, is 0.96 and remains unchanged upon irradiation. This invariance indicates that the irradiation convert Se-Se bridges linked with corner-sharing GeSe$_4$ units (peak I) to the Se-Se chains (peak III). It is important to note that after irradiation the there is decrease in the relative area of the peak III corresponding to the Se$_n$ chain. This may be due to formation of Ag$_2$Se phase which is Raman silent leading to depletion in the Se$_n$ chain [28]. Observed increase in the refractive index (see Fig. 3.6) at $1\times10^{11}$ ions/cm$^2$ may be due to formation of this silver rich Ag$_2$Se phase leading to increase in local structural ordering of the material. A decrease in the value of refractive index at higher Ag ion fluences ($\geq3\times10^{11}$ ions/cm$^2$), may be due to the increase in the disorder which occurs due to heavy ion irradiations.

![Fig. 3.13 Raman spectra (a) pristine film (b) irradiated at $1\times10^{11}$ ions/cm$^2$](image_url)
Amorphous Ge$_{20}$Se$_{80}$ alloy has the structure of Se-Se bridges linked with GeSe$_{4/2}$ edge-sharing units [25]. In Ge-Se-Ag system, interstitial voids are chemically ordered around the cation-centered structural units [Ge(Se)$_{4}$ tetrahedral]. Extrinsic atoms (Ag) are assumed to occupy these interstitial voids, thereby, reducing the disorder in the system [26]. Dwivedi et al. [27] have made the Raman measurements on 1 MeV Kr$^{++}$ ion irradiated a-Ge$_{21.5}$Se$_{78.5}$ thin films. They observed the band positions at 201 cm$^{-1}$ [Ge(Se)$_{4/2}$ corner-sharing tetrahedral], 215 cm$^{-1}$ [vibrations of Se atoms in the four member rings composed of two edge-sharing tetrahedral] and a band near 263 cm$^{-1}$ [Se-Se bonds in Se chains]. Upon Kr$^{++}$ irradiation, the intensity of the vibrational mode at 263 cm$^{-1}$ related to Se-Se bonds in chains increases. Also, upon comparing the relative areas of the spectra, they found that upon irradiation, the relative area of band at 201 cm$^{-1}$ is unchanged which indicates that the irradiation does not affect the number of corner shared (CS) Ge(Se)$_{4/2}$. They have also shown that irradiation converts Se-Se bridges linked with [27] edge sharing Ge(Se)$_{4/2}$ units to Se-Se linear chains. The full width half maxima (FWHM) of the band at 201 cm$^{-1}$ decreases after irradiation. The observed decreases in the width of this peak upon irradiation may mean a decrease in disorder. This decrease also indicates that irradiation increases ordering in the local structures [27].

Table 3.2 Peak position, width and corresponding relative area of pristine and irradiated sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak position</th>
<th>Peak II (cm$^{-1}$)</th>
<th>Peak III (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CS GeSe$_{4/2}$</td>
<td>ES GeSe$_{4/2}$</td>
<td>Se-Se chains</td>
</tr>
<tr>
<td>Pristine</td>
<td>193.3±0.16</td>
<td>209.6±0.80</td>
<td>253.4±0.28</td>
</tr>
<tr>
<td>Width</td>
<td>17.1±0.50</td>
<td>10.5±2.96</td>
<td>43.1±1.09</td>
</tr>
<tr>
<td>Relative area</td>
<td>34</td>
<td>3</td>
<td>62</td>
</tr>
<tr>
<td>Irradiated</td>
<td>193.7±0.19</td>
<td>211.3±0.64</td>
<td>254.4±0.42</td>
</tr>
<tr>
<td>(1×10$^{11}$ ions/cm$^{2}$)</td>
<td>19.5±0.61</td>
<td>8.2±2.38</td>
<td>48.9±1.71</td>
</tr>
<tr>
<td>Relative area</td>
<td>39</td>
<td>3</td>
<td>57</td>
</tr>
</tbody>
</table>
Using the same arguments, we can explain the observed increase in the refractive index \(n\) and the oscillator strength \(E_\text{g}\) at lower Ag ion fluence. Upon irradiation of Ag\(_{0.10}\)(Ge\(_{0.26}\)Se\(_{0.74}\))\(_{0.90}\) thin films with Ag ions with fluence \(1\times10^{11}\) ions/cm\(^2\), Se-Se bridges linked with edge-sharing GeSe\(_{4}\) units, are converted into Se-Se linear chains.

Ag may form the heteropolar bonds with these Se-Se chains. Upon irradiation, this material may phase separated into an Ag\(_2\)Se rich glass and decreasing the disorder in the material as suggested by Mitkova \textit{et al.} [28]. In Se rich compositions, Ag acts as a network modifier and phase separates into an Ag\(_2\)Se rich glass. They have made the Raman measurements on Se rich (Ge\(_x\)Se\(_{1-x}\))\(_{1-y}\)Ag\(_y\) glassy system. Their Raman results suggest that Ag, present at triangular interstitial sites with coordination number (CN) = 3 in \(\alpha\)-Ag\(_2\)Se, may be a good representation of the glass structure. Such a network will possess \(n_c = 3.33\) and from equation \(n_c = (5/2) r_m - 3\), yield \(r_m = 2.53\). Here the symbols \(n_c\) and \(r_m\) are known as mean constraints per atom and mechanical effective connectivity of the network. This value of \(r_m\) reside close to the critical connectivity (\(r_c\)) = 2.40 to optimize the glass forming tendency within the constrain counting theory [29].

### 3.6.4 Electrical properties

In chalcogenide glasses, due to the absence of long range order as well as the defect states, their exist the localized states in the mobility gap. A systematic study of electrical properties is a way of understating the defects states in the chalcogenide glasses [31, 32]. The DC conductivity of the most of the chalcogenide glasses near the room temperature obeys the relation \(\sigma = \sigma_0 \exp(-\Delta E/kT)\) with constant activation energy \(\Delta E\) over the whole temperature range of the measurements. The pre exponential factor \(\sigma_0\) is often situated in the range \(10^5\) to \(10^7\) \(\Omega^{-1}\)cm\(^{-1}\) but it can be as low as \(10^{-5}\) \(\Omega^{-1}\)cm\(^{-1}\) and as high as \(10^6\) \(\Omega^{-1}\)cm\(^{-1}\). The electrical conductivity of the amorphous materials depends either upon the motion of the charge carries in the extended state beyond the mobility edge or in the localized state near the band edge. The activation energy is usually referred to half of the energy gap. The activation energy is usually situated in the range of 0.5 – 1.0 eV although values are as low as 0.2 eV and as high as 1.5 eV have been observed.
3.6.4.1 DC conductivity

Three principle contributions to conductivity as described by Davis et al [33] are as follows:

(a) Band conduction of electrons excited above $E_c$ or holes below $E_v$.

In this case conductivity can be written for electrons as

$$\sigma = \sigma_0 \exp(-\frac{(E_c - E_F)}{kT})$$

(3.53)

The separation of $E_F$ from mobility edge will change with temperature $T$, but assuming the temperature dependence to be a linear one

$$E_F - E_c = \Delta E - \gamma T$$

(3.54)

eq (3.53) becomes

$$\sigma = C \exp\left(-\frac{\Delta E}{kT}\right)$$

(3.55)

where $C$ is

$$C = e \gamma (E_c) kT \mu \exp\left(\frac{\gamma}{k}\right)$$

or in general

$$\sigma = \sigma_0 \exp(-\frac{\Delta E}{kT})$$

(3.56)

where $\sigma_0$ is pre-exponent factor.

(b) Thermally assisted tunneling in the localized states

In this case, the contribution to conductivity comes from the thermally assisted tunneling in the localized states near the mobility edges, near $E_A$ and $E_B$ (Fig 1.6). Tunneling process involves the emission or absorption of phonon which intern make an additional hopping energy $\Delta W_1$ in addition to activation energy $\Delta E$ needed to raise the electron to the appropriate localized state at $E$. Then the equation (3.55) becomes

$$\sigma = \sigma_1 \exp[-(E_c - E_F + \Delta W_1 / kT)]$$

(3.57)

(c) Tunneling conduction near $E_F$ is of form

$$\sigma = \sigma_2 \exp[-(\Delta W_2 / kT)]$$

(3.58)

where, $\Delta W_2$ has the same physical meaning as $\Delta W_1$. Since the density of state near $E_F$ is smaller than near $E_A$ and $E_B$, one expect $\sigma_1 < \sigma_2$. As the temperature is lowered the number of phonons available for absorption decreases so that tunneling is restricted to seek centers which are not nearest but to the centers which lies in the range $kT$. Mott derived the relation so called for variable range hopping process.

$$\sigma = const \exp[-(T_n / T)^{1/4}]$$

(3.59)
where \( T_0 \) is derived by Ambegoaker et al. [34]

\[
T_0 = 16\alpha^3 / \text{kg}(E_F)
\] (3.60)

### 3.6.4.2 Steady State Photoconductivity

Photoconductivity depends on both the mobility of carrier \( \mu \) and their recombination time \( \tau \) and hence product of these two i.e. \( \mu \tau \) becomes a very important factor. The photoconduction depends very strongly on the temperature and excitation intensity. When a quantum of radiation is absorbed, charged carrier are generated which either trapped or recombine at the states near Fermi level giving photocurrent proportional to generation rate or if recombination take place from the lowest state and is not temperature activated, then the photocurrent is proportional to square root of generation rate.

If \( \Delta n \) is the excess density of carriers due to relaxation, then the photocurrent is given by [35]

\[
I_{ph} = e\mu D E \Delta n
\] (3.61)

where \( E \) is the applied field and \( \mu D \) is drift mobility for these carriers. The life time of one of these carriers in the states between which the quasi-equilibrium is maintained is denoted by \( \tau \) and \( \Delta n \) is given by

\[
\Delta n = G \tau
\] (3.62)

where \( G \) is the number of carrier pairs generated per unit time per unit volume and

\[
\tau = \frac{1}{b(\Delta n + n_0)}
\] (3.63)

where \( b = pa^3 \), \( a \) is the spatial extent of the state and \( p \) is the chance per unit time that an electron in a band edge localized state, overlapping the recombination center, recombine.

Hence

\[
\Delta n = \frac{1}{(\Delta n + n_0)}
\] (3.64)

and after the radiation is cut off, \( \Delta n \) decays as

\[
\frac{d[\ln(\Delta n)]}{dt} = -\frac{\Delta n}{\tau} = -b\Delta n(\Delta n + n_0)
\] (3.65)
According to Simmons and Taylor [36], the variation of photocurrent with temperature can be divided into three regimes. In regime I, the photocurrent is less than the dark current and increases with decreasing temperature. This increase may be due to the fact that at high temperatures, concentration of thermal carriers exceeds photo current carriers. The rate of recombination in this regime is determined by the dark carrier concentration as $I_{ph} < I_{dark}$ (hence $\Delta n < n_0$) and this regime can be written as

$$\Delta n = \frac{G}{bn_0}$$

or

$$I_{ph} = \frac{e\mu P E}{bn} G$$

In regime II, the photocurrent is greater than the dark current and it decreases with decreasing temperature. The recombination in this regime is by electrons and holes, both of which are generated by radiation. Here $(1/r)$ is proportional to the number of photo excited carriers. As $\Delta n \gg n_0$, therefore

$$\Delta n = \sqrt{\frac{G}{b}}$$

and

$$\frac{d(\Delta n)}{dt} = -\frac{1}{\Delta n} = bt + const$$

which is a characteristic of bi-molecular decay. In regime III, value of photocurrent is proportional to $G$ and photocurrent falls rapidly, approaching a temperature independent value.

### 3.6.4.3 Transient photoconductivity

Transient photoconductivity employs the method of measuring the rise and decay of $I_{ph}$ with respect to time after illuminating the sample with light radiations. On starting the illumination, the traps start to fill up and density of the photon generated carrier’s increases. The increase in the number of filled traps and mobile carriers continue until generation rate approaches recombination rate and equilibrium is reached in carrier production and a steady state is observed in the conductivity. Here, since the traps are not activated by holes, they have no effect while radiation
continues. The steady state will be maintained as long as the illumination continues. Once the illumination is turned off, the decay in photoconductivity will follow. Transient photoconductivity is a very useful method to determine the energy distribution of various species of gap states which influences the carrier motilities and life times in materials, assuming the response to be controlled by multi-trapping processes [37]. This method provides very valuable information about the material quality for various photoconductive applications.

Presence of traps (or gap states) plays a significant role in the recombination mechanism. When the material is exposed to light, a certain proportion of generated free carriers are captured by these traps. These filled traps will be emptied after the exciting light is switched off, at a rate depending upon their cross-section and ionization energy. If it is assumed that the traps, which are contributing to photoconductivity, are of same kind and are located very close to the Fermi level, then the decay time constant ($\tau_d$) will have a single value and the equation of decay can be written as [38]

$$\frac{dp}{dt} = \frac{d(p_0 + \Delta p)}{dt} = \frac{d\Delta p}{dt} = \frac{\Delta p}{\tau}$$ \hspace{1cm} (3.70)

or

$$\Delta p = \Delta p_0 \exp(-t/\tau_d)$$ \hspace{1cm} (3.71)

where $\Delta p_0$ is the density of carriers at $t = 0$. However, if different kinds of traps with different energetic depths in the band gap are present, then the decay time constant will be a multi-valued function. The situation can still be represented by the relation similar to Eq. (3.71), where single valued $\tau_d$ is replaced by a multi-valued $\tau_d$. As $\tau_d$ is a multi-valued function, its value changes with time during decay and thus, will result in a non-exponential decay curve. By calculating the slope at any time $t$, one can calculate the value of $\tau_d$ at time $t$ using the relation [39]

$$\tau_d = \left[\frac{1}{\Delta p_0} \frac{d\Delta p}{dt}\right]^{-1}$$ \hspace{1cm} (3.72)

Eq. (3.72) is just a mathematical manipulation of Eq. (3.70). Fuhs and Stuke [39] have defined this decay time constant as differential life time. To analyze the decay rate at
various intensities and temperatures, the concept of differential life time ($\tau_d$) has been used. According to them

$$\tau_d = \left[ \frac{1}{I_{ph}} \left( \frac{dI_{ph}}{dt} \right) \right]^{-1}$$

(3.73)

The values of $\tau_d$ at different times can be calculated using Eq. (3.73) from the slopes (at different times) of $I_{ph}$ vs. time plots.

3.6.5 Electrical measurements

3.6.5.1 DC conductivity

Thin films of the alloy are prepared by vacuum evaporation technique on well-degassed Corning 7059 glass substrates at room temperature and base pressure of $\sim 2 \times 10^{-5}$ mbar using a molybdenum boat. After deposition the thin films are left in deposition chamber in dark for 24 hours so that thin films can attain thermal equilibrium [40]. Aluminum electrodes are used with planer geometry of the film (1cm×1cm; electrode gap $\sim 2$ mm) for electrical measurements of pristine and irradiated samples. The electrical measurements of the pristine and irradiated films are performed by mounting them in a specially designed metallic sample holder. A vacuum of about $10^{-3}$ mbar is maintained throughout these measurements. The temperature dependent dark conductivity ($\sigma_d$) measurements for Ag$_{0.10}$(Ge$_{0.20}$Se$_{0.80}$)$_{0.90}$ thin films before and after irradiation with different fluence are shown in Fig 3.14.

The plots of $\ln \sigma_d$ versus $1000/T$ are found to straight lines indicating that conduction is through an temperature activated process having single activation energy in the temperature range of 303-373 K. In the most of chalcogenide glasses, $\sigma_d$ can, therefore be expressed by the Arrhenius relation [41], using equation (3.56)

$$\sigma = \sigma_0 \exp(-\Delta E_d / kT)$$

where $\sigma_0$ is material related pre-exponential factor, $\Delta E_d$ is the activation energy for dc conduction, $k$ is Boltzmann’s constant and $T$ is the temperature. The value of dark activation energy ($\Delta E_d$) are estimated from the slope of $\ln \sigma_d$ versus 1000/T. For determination of $\sigma_0$ the values of $\Delta E_d$ and $\sigma_d$ are inserted in equation (3.56) and calculated subsequently at room temperature. The values of $\Delta E_d$ and $\sigma_d$ are listed in table 3.3 along with pre-exponent factor ($\sigma_0$).
It is observed that dc activation energy ($\Delta E_d$) for pristine sample is 0.39 eV which decreases to 0.28 eV when irradiated up to $3 \times 10^{12}$ ions/cm$^2$, but with further increases in fluence to maximum value $1 \times 10^{13}$, activation energy show increase in its value to 0.34 eV. It is clear from the table 3.3 that $\sigma_d$ in case of pristine sample is $7.02 \times 10^7$ $\Omega^{-1}$ cm$^{-1}$. When thin films are irradiated with Ag ions fluence $1 \times 10^{11}$ ions/cm$^2$, the value of $\sigma_d$ decreases to $3.32 \times 10^7$ $\Omega^{-1}$ cm$^{-1}$. With further increase of fluence from $1 \times 10^{11}$ to $1 \times 10^{12}$ ions/cm$^2$, the value of $\sigma_d$ increase from $3.32 \times 10^7$ to $1.68 \times 10^6$ $\Omega^{-1}$ cm$^{-1}$. When fluence is further increased from $1 \times 10^{12}$ to $1 \times 10^{13}$ ions/cm$^2$, the value of $\sigma_d$ continue to decrease up to $4.38 \times 10^7$ $\Omega^{-1}$ cm$^{-1}$.

The decrease in dc activation energy can be explained on the basis that in chalcogenide materials the lone pair orbital forms the valence band, whereas the conduction band is formed by the antibonding orbital [42]. Kamboj et al. [24] have studied the effect of $^{12}$C$^{6+}$ ions irradiation on the electrical properties of GeSe and Se$_{90}$Sb$_{10}$In$_x$ ($x=0, 5, 10, 15$), which shows that dc activation energy decreases from
0.68 to 0.43 eV. They have explained their results by using the fact that high energy heavy ion excite the electrons from the lone pair and bonding states to higher energy states. Vacancies created in these states are immediately filled by the outer electrons with Auger process that in turn induce more holes in the lone pair and bonding orbital leading to a vacancy cascade process. In this process, bond breaking or ionization of atoms is easier to occur which leads to a change in the local structure order of the amorphous network resulting in decrease in the dc activation energy due to enhanced tailing of the valence band [24].

Table 3.3 The dc conductivity ($\sigma_d$), the pre-exponential factor ($\sigma_0$), the activation energy for dc conduction ($\Delta E_d$), photoconductivity ($\sigma_{ph}$), the activation energy of photoconduction ($\Delta E_{ph}$), photosensitivity ($\sigma_{ph}/\sigma_d$), differential life time ($\tau_d$) of Ag$_{0.10}$Ge$_{0.20}$Se$_{0.80}$ thin films irradiated with different fluence of Ag ions

<table>
<thead>
<tr>
<th>Fluence (ions/cm$^2$)</th>
<th>$\sigma_d$ (Ω$^{-1}$ cm$^1$)</th>
<th>$\sigma_0$</th>
<th>$\Delta E_d$ (eV)</th>
<th>$\sigma_{ph}$ (Ω$^{-1}$ cm$^1$)</th>
<th>$\Delta E_{ph}$ (eV)</th>
<th>$\sigma_{ph}/\sigma_d$</th>
<th>$\tau_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>7.02x10$^{-7}$</td>
<td>2.41</td>
<td>0.39</td>
<td>1.22x10$^{-7}$</td>
<td>0.16</td>
<td>0.17</td>
<td>107</td>
</tr>
<tr>
<td>$1x10^{11}$</td>
<td>3.32x10$^{-7}$</td>
<td>0.22</td>
<td>0.35</td>
<td>1.53x10$^{-7}$</td>
<td>0.22</td>
<td>0.46</td>
<td>59</td>
</tr>
<tr>
<td>$3x10^{11}$</td>
<td>1.24x10$^{-6}$</td>
<td>0.07</td>
<td>0.28</td>
<td>4.22x10$^{-7}$</td>
<td>0.17</td>
<td>0.34</td>
<td>133</td>
</tr>
<tr>
<td>$1x10^{12}$</td>
<td>1.68x10$^{-6}$</td>
<td>0.38</td>
<td>0.32</td>
<td>5.16x10$^{-7}$</td>
<td>0.14</td>
<td>0.31</td>
<td>121</td>
</tr>
<tr>
<td>$3x10^{12}$</td>
<td>1.31x10$^{-6}$</td>
<td>0.07</td>
<td>0.28</td>
<td>3.86x10$^{-7}$</td>
<td>0.13</td>
<td>0.29</td>
<td>71</td>
</tr>
<tr>
<td>$1x10^{13}$</td>
<td>4.38x10$^{-7}$</td>
<td>0.27</td>
<td>0.34</td>
<td>0.44x10$^{-7}$</td>
<td>0.30</td>
<td>0.10</td>
<td>82</td>
</tr>
</tbody>
</table>

By using the same argument, observed decrease in the dc activation energy from 0.39 to 0.28 eV in our case can be explained. However, increase in dc activation to 0.34 at highest fluence $1x10^{13}$ ions/cm$^2$. may be due to fact that there are two competitive process take place during irradiation. During irradiation one process is damage formation which increases the dangling bonds by irradiation and other defect annihilation reduces them. Sreekumar et al have explained the optical band gap enhancement in γ-In$_2$Se$_3$ from 2 to 2.8 eV by using fact that 90 MeV silicon beam irradiation cause annihilation of localized energy bands near the band edges [43]. So,
irradiation with Ag ions at higher fluence $1 \times 10^{13}$ ions/cm$^2$ may lead to annihilation of localized energy state as a result the band tailing decrease cause increase in the activation energy.

### 3.6.5.2 Steady State Photoconductivity

The variation of steady state photoconductivity ($\sigma_{ph}$) of $\text{Ag}_{0.10}(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}$ thin films with temperature at a particular intensity (1035 lux) is shown in Fig 3.15 at different fluence of Ag ions. The value of activation energy ($\Delta E_{ph}$) for photoconductivity is 0.16 eV for pristine sample, which shows an increase in value from 0.16 to 0.22 eV when irradiated with Ag ions with fluence $1 \times 10^{11}$ ions/cm$^2$. When ion beam fluence is further increased from $1 \times 10^{11}$ to $3 \times 10^{12}$ ions/cm$^2$, the value of $\Delta E_{ph}$ decreases from 0.22 eV to 0.13 eV. The value of $\Delta E_{ph}$ increases to 0.30 eV at highest fluence $1 \times 10^{13}$ ions/cm$^2$.

![Fig 3.15 Temperature dependence of photoconductivity of $\text{Ag}_{0.10}(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}$ thin films at different fluences of Ag ions.](image)

The value of photoconductivity ($\sigma_{ph}$) continuously increases from $1.22 \times 10^{-7}$ $\Omega^{-1}$ cm$^{-1}$ (pristine sample) to $5.16 \times 10^{-7}$ $\Omega^{-1}$ cm$^{-1}$ at fluence of $1 \times 10^{12}$ ions/cm$^2$. Upon further
increase of fluence from $1 \times 10^{12}$ ions/cm$^2$ to $1 \times 10^{13}$ ions/cm$^2$, the value of $\sigma_{ph}$ decreases from $5.16 \times 10^{-7} \ \Omega^{-1} \ cm^{-1}$ to $0.44 \times 10^{-7} \ \Omega^{-1} \ cm^{-1}$. The values of $\sigma_{ph}$ are given in table 3.3.

Photosensitivity is an important parameter for characterization of a photoconductor from optoelectronic point of view. It is the ratio of photoconductivity ($\sigma_{ph}$) to dark conductivity ($\sigma_{d}$). The value of photosensitivity for $\text{Ag}_{0.10} \text{Ge}_{0.20} \text{S}_{0.70} \text{Se}_{0.30}$ thin films at ambient temperature (303K) and at an intensity of (1035 lux) are calculated for different irradiation fluence and shown in table 3.3. Plot of photosensitivity versus fluence is shown in Fig.3.16. The value of photosensitivity first increases from 0.17 (pristine sample) to 0.46 when irradiated upto $1 \times 10^{11}$ ions/cm$^2$. Further increases of fluence from $1 \times 10^{11}$ ions/cm$^2$ to $1 \times 10^{13}$ ions/cm$^2$ cause continue decrease in the value of photosensitivity from 0.46 to 0.10.

![Fig. 3.16 Variation of photosensitivity vs. ion beam fluence.](image-url)
3.6.5.3 Transient photoconductivity measurements

For the measurement of transient photoconductivity of pristine and irradiated samples, thin film samples have been illuminated with white light. The rise and decay of photocurrent ($I_{ph}$) has been noted using a digital picoammeter. All the measurements are done at 300K and at an intensity of illumination 1035 lux with accuracy in $I_{ph}$ measurements 1pA. The rise and decay of photocurrent for pristine and irradiated samples are shown in Fig.3.17.

![Figure 3.17](image)

Fig.3.17 (a)-(f) Photocurrent rise and decay for $Ag_{0.10}/Ge_{0.20}Se_{0.80})_{0.90}$ thin films at different fluence of Ag ions.

It is clear from the results that the photocurrent rises in a monotonic manner upto the steady state in Fig.3.17 (a)-(c). But in case of higher fluence $1\times10^{13}$ ion/cm$^2$ (Fig. 3.17-(f)) the decay of $I_{ph}$ is slow as soon as light is turned off. Fig. 3.17(a)-(e) shows that initial decay of $I_{ph}$ show a sudden drop in value of $I_{ph}$ as soon as light is turned off and thereafter the decay process becomes slow. During decay, $I_{ph}$ does not reach zero.
for a long time after the incident light is switched off. Rapid decay of $I_{ph}$ is often attributed to a localized-localized recombination mechanism according to which the trapped carriers recombine directly with carrier of opposite sign [44, 45].

To understand the trapping effects, the persistent photocurrent is subtracted from measured photocurrent and then corrected current (in pA) is plotted for pristine and irradiated samples and shown in Fig. 3.18. In the case of single trap level these curves must be straight lines. However, in the present case, these curves do not maintain the same slope and the slope goes on decreasing continuously as the time of decay increases.

![Figure 3.18](image-url)

**Fig. 3.18 Time dependence of photocurrent decay for Ag$_{0.10}$Ge$_{0.20}$Se$_{0.80}$ thin films at different fluence of Ag ions.**

This indicates that the traps exist at all the energies in the band gap which have different time constants and hence give non-exponential decay of photoconductivity.
To analyze the decay rates in the case of non-exponential decay, the differential lifetime ($\tau_d$) has been calculated using the equation (3.73) given by Fuhs and Stuke [39]. In the case of exponential decay, the differential lifetime will be equal to the carrier lifetime. However, in the case of non-exponential decay, $\tau_d$ will increase with time and only the value at $t=0$ will correspond to the carrier lifetime. From the slope of $I_{ph}$ versus time curves, we have calculated the values of $\tau_d$ using equation (3.73) at various times of the decay curves.

Fig.3.19 shows the variation of $\tau_d$ (for sample irradiated at $1\times10^{11}$ ions/cm$^2$) with time at room temperature 300K and intensity 1035 lux. This confirms the non-exponential decay in the present case. Similar behavior has been observed for the case of pristine and those samples irradiated at all higher fluences.

It is observed that the value of $\tau_d$ decreases from 107 to 59 when pristine film is irradiated with fluence $1\times10^{11}$ ions/cm$^2$. The decrease in the carrier lifetime $\tau_d$ at this fluence is due to the fact that irradiation with have ions leads to defect annihilations which may result in faster decay of photocurrent and hence smaller carrier lifetime ($\tau_d$) [43]. Further increase in fluence from $1\times10^{11}$ to $3\times10^{11}$, the $\tau_d$ increase to 133, after that with increase in fluence to $3\times10^{12}$ the $\tau_d$ value decreases to 71. At highest

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fluence of $1 \times 10^{13}$ ions/cm$^2$ the value of $\tau_d$ is found to be 82. The observed increase in the carrier life time ($\tau_d$) in case when fluence is increased from $1 \times 10^{11}$ to $3 \times 10^{11}$, possibly due to the fact that irradiation induces more defects [24, 42].

The nature of photoconductivity varies from material to material. The decay of $I_{ph}$ follows many different patterns. In some cases, the decay of $I_{ph}$ has been reported to be non-exponential [46] whereas power law decay has been observed for many other semiconductors [39]. In materials, having traps in the mobility gap, the recombination time of carriers is same as carrier life time when free carrier density is more than trapped carrier density [47]. If the free carrier density is much less than the trapped carriers, then the recombination process is dominated by the rate of trap emptying and is much larger than carrier life time, resulting in a slow decay. The increase in photosensitivity ($\sigma_{ph}/\sigma_d$) from 0.17 (pristine sample) to 0.46 and decrease in $\tau_d$ from 107 (pristine) to 56, after irradiation at fluence $1 \times 10^{11}$ ions/cm$^2$ suggests that density of defect state decreases after irradiation. Also, faster decay of photocurrent indicates the decrease in density of defect states (Fig 3.18-b). The sharp decrease in photosensitivity $\sigma_{ph}/\sigma_d$ and photoconductivity $\sigma_{ph}$ when irradiation fluence is $1 \times 10^{13}$ (see Fig 3.18-f) ions/cm$^2$ indicate the increase in defect state which in turn resulting increase in life time $\tau_d$.

3.6.6 Conclusions

We have studied in section 3.6 the effect of 100 MeV Ag ions irradiation effect on the optical properties (in section 3.6.1), and found that heavy ions irradiation leads to change in the optical constants which are presented in the table 3.1. We have observed an increase in refractive index at lower fluence followed by reversal in trend at higher fluence of Ag beam. The optical band gap $E_g^{\text{opt}}$ shows decrease in the value from (1.84±0.01) to (1.68±0.01) after all irradiation fluences. So, we can use heavy ion irradiation where tailoring of band gap is required. Other optical parameters are listed in table 3.1 show significant dependence on the ion beam fluence. In the AFM analysis, we observed change in the surface roughness. Also the results from the Raman spectroscopy the depletion in the intensity of Se-Se chains, may be due to formation of Ag$_2$Se face which is Raman silent leads to increase in refractive index. The data on electrical properties the dc conductivity ($\sigma_d$), dark activation energy ($\Delta E_d$), photoconductivity ($\sigma_{ph}$), photo activation energy ($\Delta E_{ph}$), photosensitivity and
differential life time shows dependence on fluence. The decrease in activation energy \((\Delta E_d)\) after Ag ions irradiation has been explained on the basis of fact that high energy heavy ion excite the electrons from the lone pair and bonding states to higher energy states. Vacancies created in these states are immediately filled by the outer electrons with Auger process that in turn induce more holes in the lone pair and bonding orbital leading to a vacancy cascade process. Therefore irradiation leads to enhancement in band tailing of the valence band [24] which decreases the dc activation energy. During irradiation with heavy ions, there are two competitive process take place. One process is damage formation [24] which increases the dangling bonds and other is defect annihilation reduces them [43]. So increase in the dc activation energy is possibly due to annihilation of defects.

3.7 Oxygen ions irradiation effects on \((\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}\text{Ag}_{0.10}\) thin films

3.7.1 Optical properties

In this section, we have studied the effect of 85 MeV oxygen ions irradiation on the optical properties of \((\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}\text{Ag}_{0.10}\) thin films. Films of about area 1 cm\(^2\) have been mounted on sliding ladder and irradiated with O (85 MeV) ions beam using 15 UD pelletron facility at Inter University Accelerator Centre, New Delhi. Ion beam fluence has been varied from \(1 \times 10^{12}\) to \(1 \times 10^{14}\) ions/cm\(^2\). In order to expose the whole target area, the beam is magnetically scanned in the x-y plane for uniform irradiation. SRIM calculations have shown that the nuclear energy loss is 0.08 eV/Å, which is negligible in comparison to electronic energy loss 0.12 keV/Å (table 2.2) for these films using above O ion irradiation. Transmission spectra of the substrate with and without \(\text{Ag}_{0.10}(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}\) thin film have been measured by computer controlled spectrophotometer [Solar TII, MS 2004], in the transmission range 400–1000 nm. The spectrophotometer was set with a suitable slit width of ±1 nm, in the above spectral range. All optical measurements have been performed at room temperature (300 K).

Fig.3.20 shows the normal incidence optical transmission spectra of \(\text{Ag}_{0.10}(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}\) thin film before and after O ion irradiations at different fluences. The envelopes of the transmission spectrum, \(T_{\text{max}}\) and \(T_{\text{min}}\) have been observed from these transmission curves. Using the transmission spectra, value of refractive index \((n)\) is calculated at different wavelength by Swanepoel’s methods as discussed in section 3.5.

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The determined values of refractive index at different photon energies have been plotted in Fig. 3.21 at different fluences. Fig. 3.22 shows the variation of refractive index (n) with fluence. It is clear from the figure that the values of n first increases (at $1 \times 10^{12}$ ions/cm$^2$) and then decreases as fluence increases.

The data on the dispersion of the refractive index, n($\lambda$) have been calculated using the single-effective-oscillator model proposed by Wemple and DiDomenico [18, 19]. They found that all the data can be described to an excellent approximation by the following eq (3.53):

$$n^2(h\nu) = 1 + \frac{E_d E_0}{E_0^2 - (h\nu)^2}$$

where $h\nu$ is the photon energy, $E_0$ is the oscillator energy and $E_d$ is the so-called dispersion energy. Plotting $(n^2 - 1)^{-1}$ vs. $(h\nu)^2$ allows us to determine the oscillator parameters, by fitting a linear function to the smaller energy data. Fig.3.23 shows the plot of $(n^2-1)^{-1}$ vs. $(h\nu)^2$, which is a straight line. $E_d$ and $E_0$ can be directly determined
from the slope, \((E_0E_d)^{-1}\) and the intercept, \(E_0/E_d\), on vertical axis. The values of \(E_0\) and \(E_d\) for this alloy thin film is similar to that of the other Se rich alloys reported in the literature [20, 21]. These values are given in the table 3.4.

**Fig. 3.21** Plot of Refractive index \((n)\) vs \(h\nu\) at different fluence of oxygen ions

**Fig. 3.22** Variation of refractive index \((n)\) with fluence
It is clear from the table that after ion O irradiation, the values of \( n \) and \( E_d \) first increases from \( (2.47 \pm 0.004) \) to \( (2.89 \pm 0.004) \) and \( (14.89 \pm 0.01) \) to \( (20.44 \pm 0.01) \) eV respectively and then decreases from \( (2.89 \pm 0.004) \) to \( (2.58 \pm 0.004) \) and \( (20.44 \pm 0.01) \) to \( (18.48 \pm 0.01) \) eV respectively. The value of \( E_0 \) increases from \( (4.02 \pm 0.01) \) to \( (4.29 \pm 0.01) \) eV after irradiation with \( 1 \times 10^{14} \) ions/cm\(^2\) (see Table 3.4).

![Plot between \((n^2-1)^{-1}\) and \((hv)^2\) at different fluence of oxygen beam](image)

Fig. 3.23 Plot between \((n^2-1)^{-1}\) and \((hv)^2\) at different fluence of oxygen beam

The real \((\varepsilon_1)\) and imaginary \((\varepsilon_2)\) parts of the dielectric constant for \( \text{Ag}_{0.10}(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90} \) films has been calculated using equation (3.6). The values of complex dielectric index (real and imaginary parts) \((\varepsilon_1\) and \(\varepsilon_2)\) have been plotted in Fig.3.24 (a) & (b). The real part \(\varepsilon_1\) of the dielectric constant, first increases at lower ion fluence and then decreases at higher fluence, while the imaginary part \(\varepsilon_2\) first decreases at lower fluence followed by increase at higher fluence.

The absorption coefficient \((\alpha)\) is calculated from the equation (3.24). The experimentally determined values of \(\alpha\), are plotted in Fig.3.25. In order to complete the computation of the optical constants \((n, k)\), the dimensionless extinction
coefficient \( k \), is obtained from the already known \( \alpha \) values, using the basic equation, i.e. \( k = \alpha \lambda / 4 \pi \). The values of extinction coefficient \( (k) \) have also been calculated using this equation and are plotted in Fig. 3.26. These values have been shown in the Table 3.4. It is clear from the figure and the table that the value of extinction coefficient \( (k) \) first decreases at lower ion fluence and then followed by increase at higher fluences.

The absorption coefficient of amorphous semiconductors in the strong-absorption region \( (\alpha \geq 10^4 \text{ cm}^{-1}) \), assuming parabolic valence- and conduction band edges, is given by equation (3.8)

\[
\alpha(hv) = B(hv - E_{\text{opt}})^2 / (hv)
\]

where \( E_{\text{opt}} \) is the energy distance between the valence and conduction band mobility edges. The parameter \( B \) given by the slope of the plots is an interesting parameter, since it can be taken as a measure of the disorder.

\[\frac{\varepsilon_2}{\varepsilon_1} \text{ vs. } hv \]

**Fig. 3.24** (a) \( \varepsilon_2 \) vs. \( hv \), (b) \( \varepsilon_1 \) vs. \( hv \) at different fluence

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Fig. 3.25 Variation of absorption coefficient (a) with hv at different fluence of oxygen ions

![Graph showing variation of absorption coefficient (a) with hv at different fluence of oxygen ions]

Fig. 3.26 Plot of extinction coefficient (k) with hv at different fluence of oxygen ions

![Graph showing plot of extinction coefficient (k) with hv at different fluence of oxygen ions]
Finally, the optical gap ($E_{g}^{opt}$) is calculated from the intersection of the plot ($a(hv)^{1/2}$ vs. $hν$ with the abscissa axis as shown in Fig.3.27. The value of $E_{g}^{opt}$ for pristine sample is $(1.84 \pm 0.01)$ eV. The value of $E_{g}^{opt}$ to continuously decrease to $(1.76 \pm 0.01)$ eV when film is exposed to fluence $1 \times 10^{14}$ ions/cm$^2$ (see Table 3.4).

**Fig. 3.27 Plot between $(a(hv)^{1/2}$ and $hν$ at different fluence of oxygen beam**

Using the dispersion relation, the dielectric constant of a material can be calculated. According to the model of MOSS [48], which states that the free carriers contribution to dispersion are relatively small, the data corresponding to the wavelength range lying below the absorption edge of the material are useful. So, the high frequency properties of the Ag$_{0.10}$(Ge$_{0.20}$Se$_{0.80}$)$_{0.90}$ thin film can be treated as a single oscillator at wavelength $\lambda_o$. According to Zemel et al. [49], the refractive index $n_o$ of an empty lattice at infinite wavelength ($\lambda_\infty$, average interband oscillator wavelength) is given by

$$\frac{(n_o^2 - 1)}{(n^2 - 1)} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2$$

Fig. 3.28 shows the plot between $(n^2 - 1)^{-1}$ vs. $\lambda^2$. The values of $\lambda_o$ and $n_o$ have been calculated using these plots. The values of $n_o^2 = \varepsilon_o$ and $\lambda_o$ are inserted in the table 3.4.
Fig. 3.28 Plot between \((n^2 - 1)^{-1}\) vs. \(\lambda^2\) at different fluence of oxygen ions

From the table 3.4, it is clear that the value of \(\varepsilon_o\) first increases from 4.4 to 6.2 when irradiated with fluence \(1\times10^{12}\) ions/cm\(^2\) and followed by decrease from 6.2 to 5.3 after irradiation with higher fluences. The value of \(\lambda_0\), first increases from 316 to 321 and followed by decrease in value from 321 to 289 after irradiation with higher fluence.

Equation (3.74) can be written as [50]

\[
(n^2 - 1) = \left( \frac{S_0 \lambda_0^2}{1 - \left( \frac{\lambda^2}{\lambda_0^2} \right)} \right)
\]

where \(S_0\) is the average oscillator strength and is given by

\[
S_o = \frac{(n_o^2 - 1)}{\lambda_o^2}
\]

The value \(S_o\) first increases from 3.14E+13 to 5.34E+13 when irradiated with fluence \(1\times10^{12}\) ions/cm\(^2\), followed by decrease in its value from 5.34E+13 to 5.14E+13 after irradiation with all fluences. The dissipation factor \(\tan \delta\) can be calculated according to the relation [51].
Fig. 3.29 shows the plot of dissipation factor tanδ as a function of frequency. It is clear from the figure that the dissipation factor increases with increasing photon energy.

\[
\tan \delta = \frac{\varepsilon_2}{\varepsilon_1}
\]  

(3.77)

The absorption coefficient \(\alpha\) can be used to calculate the optical conductivity \(\sigma_{\text{opt}}\) as follows [52]

\[
\sigma_{\text{opt}} = \frac{\alpha n c}{4\pi}
\]

(3.78)

where \(\alpha\) \(\rightarrow\) absorption coefficient, \(n\) \(\rightarrow\) refractive index and \(c\) \(\rightarrow\) velocity of light.

The optical response of a material is most conveniently studied in terms of optical conductivity \(\sigma_{\text{opt}}\). Fig. 3.30 shows the plot of \(\sigma_{\text{opt}}\) as a function of photon energy \((hv)\) for pristine and irradiated \(\text{Ag}_{0.10}(\text{Ge}_{0.20}\text{Sc}_{0.80})_{0.90}\) thin film. The optical conductivity directly depends on the absorption coefficient and the refractive index of material and is found to follow the same trend as that of absorption coefficient with increasing energy. It is clear from the figure that the optical conductivity increases as the photon energy increases.
energy increases which is due to the high absorbance of $\text{Ag}_{0.10}(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}$ thin film and may be also due to the electron excited by photon energy [52].

![Graph](image_url)

**Fig. 3.30** Plot between $\sigma_{\text{opt}}$ vs photon energy ($h\nu$) at different fluence of oxygen ions

**Table 3.4** The refractive index ($n$), absorption coefficient ($\alpha$), extinction coefficient ($k$), optical gap ($E_g^{\text{opt}}$), oscillator energy ($E_0$), oscillator strength ($E_0$), real dielectric const ($\varepsilon_1$), imaginary dielectric const ($\varepsilon_2$), high frequency dielectric constant ($\varepsilon_\infty$), average oscillator strength ($S_0$) and average interband oscillator wavelength ($\lambda_0$) of $\text{Ag}_{0.10}(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90}$ film at different oxygen ions fluences.

<table>
<thead>
<tr>
<th>Fluence</th>
<th>$n$</th>
<th>$\alpha$</th>
<th>$k$</th>
<th>$E_g^{\text{opt}}$</th>
<th>$E_0$</th>
<th>$E_\infty$</th>
<th>$\varepsilon_1$</th>
<th>$\varepsilon_2$</th>
<th>$\varepsilon_\infty$</th>
<th>$\sigma_{\text{opt}}$</th>
<th>$S_0$</th>
<th>$\lambda_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>2.47</td>
<td>16497</td>
<td>0.120</td>
<td>1.84</td>
<td>4.02</td>
<td>14.89</td>
<td>6.08</td>
<td>0.59</td>
<td>4.4</td>
<td>1.61</td>
<td>3.14</td>
<td>316</td>
</tr>
<tr>
<td>1 x $10^{12}$</td>
<td>2.89</td>
<td>15442</td>
<td>0.074</td>
<td>1.82</td>
<td>3.92</td>
<td>20.44</td>
<td>8.37</td>
<td>0.43</td>
<td>6.2</td>
<td>2.66</td>
<td>5.34</td>
<td>321</td>
</tr>
<tr>
<td>3 x $10^{12}$</td>
<td>2.85</td>
<td>17280</td>
<td>0.083</td>
<td>1.80</td>
<td>3.72</td>
<td>18.10</td>
<td>8.12</td>
<td>0.47</td>
<td>5.9</td>
<td>2.78</td>
<td>4.21</td>
<td>334</td>
</tr>
<tr>
<td>1 x $10^{13}$</td>
<td>2.68</td>
<td>20125</td>
<td>0.096</td>
<td>1.88</td>
<td>4.02</td>
<td>18.14</td>
<td>7.16</td>
<td>0.51</td>
<td>5.5</td>
<td>2.69</td>
<td>4.75</td>
<td>308</td>
</tr>
<tr>
<td>3 x $10^{13}$</td>
<td>2.61</td>
<td>23881</td>
<td>0.114</td>
<td>1.77</td>
<td>4.17</td>
<td>18.27</td>
<td>6.82</td>
<td>0.60</td>
<td>5.4</td>
<td>2.68</td>
<td>4.98</td>
<td>297</td>
</tr>
<tr>
<td>1 x $10^{14}$</td>
<td>2.58</td>
<td>23009</td>
<td>0.110</td>
<td>1.76</td>
<td>4.29</td>
<td>18.48</td>
<td>6.62</td>
<td>0.57</td>
<td>5.3</td>
<td>2.93</td>
<td>5.14</td>
<td>289</td>
</tr>
</tbody>
</table>
The decrease of $E_{g\text{opt}}$ from $(1.84 \pm 0.01)$ to $(1.76 \pm 0.01)$ eV is explained by the fact that the binding energy of Ag-Se bond (202.5 kJ mol$^{-1}$) is smaller than that of the Ge-Se bond (484 kJ mol$^{-1}$). Therefore, there is a smaller energy splitting between the states of the valence and conduction band takes place. In chalcogenide glasses, the lone pair orbital forms the valence band and the conduction band is formed by the antibonding orbital [42]. The oxygen ion irradiations excite the electrons from the lone pair and bonding states to higher energy states. Vacancies created in these states are immediately filled by the outer electrons with Auger process that in turn induce more holes in the lone pair and bonding orbital leading to a vacancy cascade process as suggested by Kamboj et al. [43]. In this process, bond breaking or ionization of atoms is easier to occur which leads to a change in the local structure of the amorphous network leading to decrease in band gap of material.

### 3.7.2 Atomic force microscopy

Fig 3.31 shows the three dimensional images of pristine and oxygen beam irradiated $Ag_{0.10}(Ge_{0.20}Se_{0.80})_{0.90}$ thin films with different fluence from $1 \times 10^{12}$ to $1 \times 10^{14}$ ions/cm$^2$. It is observed that pristine film exhibits smoother surface with rms roughness 1.74 nm and the average grain size 89 nm, whereas the surface roughness increased to 6.19 nm when irradiated with fluence $1 \times 10^{12}$ ions cm$^{-2}$. With further increase in the fluence up to $3 \times 10^{12}$ ions cm$^{-2}$ roughness decreases to 1.95 nm. The surface roughness is 2.15 and 1.73 for fluence of $1 \times 10^{13}$ and $3 \times 10^{13}$ ions/cm$^2$ respectively. When fluence is increase to its maximum $1 \times 10^{14}$ ions cm$^{-2}$ value, the surface roughness has value 2.97 (see table 3.5).

#### Table 3.5 Root mean square roughness (rms) of ion irradiated thin films

<table>
<thead>
<tr>
<th>Fluence (ions/cm$^2$)</th>
<th>RMS Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>1.74</td>
</tr>
<tr>
<td>$1 \times 10^{12}$</td>
<td>6.19</td>
</tr>
<tr>
<td>$3 \times 10^{12}$</td>
<td>1.95</td>
</tr>
<tr>
<td>$1 \times 10^{13}$</td>
<td>2.15</td>
</tr>
<tr>
<td>$3 \times 10^{13}$</td>
<td>1.73</td>
</tr>
<tr>
<td>$1 \times 10^{14}$</td>
<td>2.97</td>
</tr>
</tbody>
</table>
3.7.3 Raman spectroscopy

Fig. 3.32 shows the Raman spectra of pristine and oxygen ion irradiated Ag_{0.10}(Ge_{0.20}Sc_{0.80})_{0.90} thin films. It is observed that in pristine and irradiated samples four peaks appearing are: 193.8 cm^{-1} (peak I), 209.9 cm^{-1} (peak II), 237.4 cm^{-1} (peak III) and 257.4 cm^{-1} (peak IV) as shown in Fig. 3.32.
Peak I is assigned to the stretching mode of $\text{GeSe}_{4/2}$ corner-sharing tetrahedral ($193.8 \text{ cm}^{-1}$), whereas peak II arises from the vibrations of Se atoms in the four member rings composed of two edge sharing tetrahedral $209.9 \text{ cm}^{-1}$. The peak at $237.4 \text{ cm}^{-1}$, we identify with already reported band arising from stretching vibrations of Se atoms in helical chain like and ring like arrangements [53]. The peak at $257.4 \text{ cm}^{-1}$ is similar to that reported as arising from Se-Se chains [54]. We have observed shift in peak positions of peak towards lower wave number in comparison with Raman spectra observed by Dwivedi et al [27]. Also, Sugai [30] has observed the peak positions at $195 \text{ cm}^{-1}$ ($\text{GeSe}_{4/2}$ corner-sharing tetrahedral), $213.1 \text{ cm}^{-1}$ (vibrations of Se atoms in the four member rings composed of two edge-sharing tetrahedral) and band near
259.1 cm\(^{-1}\) (Se-Se bonds in Se chains). Table 3.6 shows the relative area, peak position and full width at half maxima (FWHM).

### Table 3.6 Peak position, width and corresponding relative area of pristine and irradiated \(Ag_{0.10}(Ge_{0.20}Se_{0.80})_{0.90}\) thin films at different oxygen ions fluences.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak I (cm(^{-1}))</th>
<th>Peak II (cm(^{-1}))</th>
<th>Peak III (cm(^{-1}))</th>
<th>Peak IV (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CS(^2)GeSe(_{4+2})</td>
<td>ES(^3)GeSe(_{4+2})</td>
<td>Se-Se helical chains</td>
<td>Se-Se chains</td>
</tr>
<tr>
<td>Pristine</td>
<td>Peak position</td>
<td>193.8</td>
<td>209.9</td>
<td>237.4</td>
</tr>
<tr>
<td></td>
<td>Width</td>
<td>15.86±0.34</td>
<td>15.59±2.09</td>
<td>17.8±2.24</td>
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<tr>
<td></td>
<td>Rel. Area</td>
<td>40</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Irradiated (1\times10^{12})</td>
<td>Peak position</td>
<td>193.8</td>
<td>209.9</td>
<td>237.4</td>
</tr>
<tr>
<td></td>
<td>Width</td>
<td>16.6±0.38</td>
<td>14.05±1.18</td>
<td>6.6±0.43</td>
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<tr>
<td></td>
<td>Rel. Area</td>
<td>47</td>
<td>11</td>
<td>6</td>
</tr>
<tr>
<td>Irradiated (1\times10^{13})</td>
<td>Peak position</td>
<td>193.8</td>
<td>209.9</td>
<td>237.4</td>
</tr>
<tr>
<td></td>
<td>Width</td>
<td>16.2±0.38</td>
<td>16.2±1.40</td>
<td>7.4±0.61</td>
</tr>
<tr>
<td></td>
<td>Rel. Area</td>
<td>42</td>
<td>11</td>
<td>6</td>
</tr>
<tr>
<td>Irradiated (1\times10^{14})</td>
<td>Peak position</td>
<td>193.8</td>
<td>209.9</td>
<td>237.4</td>
</tr>
<tr>
<td></td>
<td>Width</td>
<td>15.08±0.45</td>
<td>14.4±0.90</td>
<td>5.96±0.35</td>
</tr>
<tr>
<td></td>
<td>Rel. Area</td>
<td>36</td>
<td>16</td>
<td>8</td>
</tr>
</tbody>
</table>

It is clear from table that the relative area of peak I corresponding to corner-sharing GeSe\(_{4+2}\) increase upon ions irradiation with fluence \(1\times10^{12}\) ions/cm\(^2\) from 40 to 47, while that of edge-sharing GeSe\(_{4+2}\) increases from 7 to 11. The, sum of relative area of peak I and peak II, corresponding to corner-sharing GeSe\(_{4+2}\) and edge-sharing GeSe\(_{4+2}\) increase 47 to 58. Also, irradiation with fluence \(1\times10^{12}\) ions/cm\(^2\) decreases the relative area of peak (III) at wave number 237.4 cm\(^{-1}\) arising from stretching.
vibrations of Se atoms in helical chain like and ring like arrangements and the relative area of peak IV corresponding to Se-Se chains, from 10 to 6 and 43 (pristine sample) to 36 respectively. Therefore, irradiation causes the formation of more corner-sharing (CS) GeSe$_{4/2}$ and the edge-sharing (ES) GeSe$_{4/2}$ structural units in the network at the expense of both helical like and linear chain structure corresponding to peak III and IV, respectively. When ions fluence increases to $1 \times 10^{13}$ ions/cm$^2$, the relative area of corner-sharing GeSe$_{4/2}$ further decreases from 47 to 42, while area of edge-sharing GeSe$_{4/2}$ remains same. On the other hand, at same ions fluence, the relative area of peak III (helical like chains) remains same, while the relative area of peak IV (Se-Se chains) increases from 36 to 41. The sum of relative of peak III and peak IV increase from 42 (at $1 \times 10^{12}$ ions/cm$^2$) to 47. Further increase in fluence from $1 \times 10^{13}$ ions/cm$^2$ to $1 \times 10^{14}$ ions/cm$^2$, we observed that relative area of peak I (corner-sharing GeSe$_{4/2}$) decreases from 42 to 36 and peak II (edge-sharing GeSe$_{4/2}$) increase from 11 to 36, while the relative area of peak III increases from 6 to 8 and peak IV decreases slightly from 41 to 40. It is important to note that after irradiation at $1 \times 10^{12}$ ions/cm$^2$, there is decrease in the relative area of the peak IV corresponding to the Se-Se chains 43 (pristine sample) to 36. This may be due to formation of Ag$_2$Se phase which is Raman silent leading to depletion in the Se-Se chains [28]. Observed increase in the refractive index at $1 \times 10^{12}$ ions/cm$^2$ may be due to formation of this silver rich Ag$_2$Se phase leading to increase in local structural ordering of the material. This indicates increase in local ordering of material, result an increase in refractive index. The decrease in the value of refractive index at higher oxygen ion fluences ($>1 \times 10^{12}$ ions/cm$^2$), may be due to the increase in the disorder which occurs due to heavy ion irradiations.

3.7.4 Electrical Properties

3.7.4.1 DC Conductivity measurements

The dark conductivity measurements ($\sigma_d$) of Ag$_{0.10}$(Ge$_{0.20}$Se$_{0.80}$)$_{0.90}$ thin films irradiated with oxygen ions have been carried out over the temperature range of 303-373K. A vacuum of $10^{-3}$ mbar is maintained in the sample holder during various electrical measurements. The temperature dependence of dark conductivity $\sigma_d$ for thin films of Ag$_{0.10}$(Ge$_{0.20}$Se$_{0.80}$)$_{0.90}$ for pristine and irradiated samples is measured and plotted in Fig. 3.33. It is observed that the plots of ln$\sigma_d$ vs 1000/T are straight lines over the measured temperature range. This implies that conduction in
Ag_{0.16}(Ge_{0.20}Se_{0.80})_{0.90} thin films is an activated process having single activation energy. The value of $\Delta E_d$ decreases from 0.39 eV to 0.21 eV when irradiated at fluence $1 \times 10^{12}$ ions/cm$^2$, followed by increase in the value from 0.21 eV to 0.31 eV as the fluence is increased to $3 \times 10^{13}$ ions/cm$^2$. Then the value of $\Delta E_d$ again decreases from 0.31 eV to 0.25 eV as the fluence is increased to $1 \times 10^{14}$ ions/cm$^2$.

![Fig. 3.33 Temperature dependence of dark conductivity of Ag_{0.16}(Ge_{0.20}Se_{0.80})_{0.90} thin films at different fluence of oxygen beam](image)

The value of $\sigma_d$ continuously increases from $7.02 \times 10^{-7}$ $\Omega^{-1}$ cm$^{-1}$ to $1.46 \times 10^{-6}$ $\Omega^{-1}$ cm$^{-1}$ as the pristine sample is irradiated with fluence of $3 \times 10^{12}$ ions/cm$^2$, followed by decrease in its value to $1.16 \times 10^{-6}$ $\Omega^{-1}$ cm$^{-1}$, when ion beam fluence increased to $1 \times 10^{13}$ ions/cm$^2$. The value of $\sigma_d$ again increase to $1.35 \times 10^{-6}$ $\Omega^{-1}$ cm$^{-1}$ as fluence is increased to $3 \times 10^{13}$ and then value of $\sigma_d$ decreases to $8.28 \times 10^{-7}$ $\Omega^{-1}$ cm$^{-1}$ at the highest fluence. The values of $\sigma_d$, $\sigma_0$ and $\Delta E_d$ are given in table 3.7.

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The decrease in dc activation energy from 0.39 to 0.21 eV when pristine film is irradiated with oxygen ions having fluence $1 \times 10^{12}$ ions/cm$^2$, can be explained on the basis that irradiation cause enhancement of band tails in the valence band as also observed in other chalcogenide thin films [24, 42]. Singh et al. have observed similar decrease in the dc activation energy ($\Delta E$) in Ni ions irradiated As$_2$Se$_3$ [55]. However, increase in dc activation to 0.31 at fluence $3 \times 10^{13}$ ions/cm$^2$, may be due to the fact that there are two competitive process take place during irradiation. During irradiation, one process is damage formation which increases the dangling bonds by irradiation and other defect annihilation reduces them. So, irradiation with oxygen ions at higher fluence $3 \times 10^{13}$ ions/cm$^2$ may leads to annihilation of localized energy state as a result the band tailing decrease cause increase in the activation energy [43].

### Table 3.7 Dark conductivity ($\sigma_d$), the pre-exponential factor ($\sigma_0$), the activation energy for dc conduction ($\Delta E_d$), photoconductivity ($\sigma_{ph}$), the activation energy of photoconduction ($\Delta E_{ph}$), photosensitivity ($\sigma_{ph}/\sigma_d$), differential life time ($\tau_d$) of Ag$_{0.10}$Ge$_{0.20}$Se$_{0.80}$ thin films irradiated with different oxygen ions fluence

<table>
<thead>
<tr>
<th>Fluence (ions/cm$^2$)</th>
<th>$\sigma_d$ ($\Omega^{-1}$cm$^{-1}$)</th>
<th>$\sigma_0$</th>
<th>$\Delta E_d$ (eV)</th>
<th>$\sigma_{ph}$ ($\Omega^{-1}$cm$^{-1}$)</th>
<th>$\Delta E_{ph}$ (eV)</th>
<th>$\sigma_{ph}/\sigma_d$</th>
<th>$\tau_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>7.02×10$^{-7}$</td>
<td>2.410</td>
<td>0.39</td>
<td>1.22×10$^{-7}$</td>
<td>0.16</td>
<td>0.17</td>
<td>107</td>
</tr>
<tr>
<td>$1 \times 10^{12}$</td>
<td>1.16×10$^{-6}$</td>
<td>0.015</td>
<td>0.21</td>
<td>2.18×10$^{-7}$</td>
<td>0.11</td>
<td>0.18</td>
<td>77</td>
</tr>
<tr>
<td>$3 \times 10^{12}$</td>
<td>1.46×10$^{-6}$</td>
<td>0.002</td>
<td>0.22</td>
<td>3.2×10$^{-6}$</td>
<td>0.08</td>
<td>0.22</td>
<td>24</td>
</tr>
<tr>
<td>$1 \times 10^{13}$</td>
<td>1.16×10$^{-6}$</td>
<td>0.005</td>
<td>0.23</td>
<td>7.12×10$^{-7}$</td>
<td>0.07</td>
<td>0.61</td>
<td>62</td>
</tr>
<tr>
<td>$3 \times 10^{13}$</td>
<td>1.35×10$^{-6}$</td>
<td>0.411</td>
<td>0.31</td>
<td>1.2×10$^{-7}$</td>
<td>0.06</td>
<td>0.08</td>
<td>91</td>
</tr>
<tr>
<td>$1 \times 10^{14}$</td>
<td>8.28×10$^{-7}$</td>
<td>0.646</td>
<td>0.25</td>
<td>4.28×10$^{-8}$</td>
<td>0.12</td>
<td>0.05</td>
<td>72</td>
</tr>
</tbody>
</table>

### 3.7.4.2 Steady state photoconductivity

The temperature dependence of steady state photoconductivity ($\sigma_{ph}$) for Ag$_{0.10}$Ge$_{0.20}$Se$_{0.80}$ thin films before and after irradiation with oxygen ions is shown in Fig. 3.34. The measurements are carried in the temperature range 303-373K. The value of photoconductivity ($\sigma_{ph}$) increases from $1.22\times10^{-7}$ $\Omega^{-1}$cm$^{-1}$ for pristine sample to $0.32\times10^{-6}$ $\Omega^{-1}$cm$^{-1}$ when fluence is increased to $3 \times 10^{12}$ ions/cm$^2$. The value of $\sigma_{ph}$ decreases continuously from $0.32\times10^{-6}$ $\Omega^{-1}$cm$^{-1}$ to $4.28\times10^{-8}$ $\Omega^{-1}$cm$^{-1}$ when...
fluence is increased to its highest value $1 \times 10^{14}$ ions/cm$^2$. Fig. 3.35 shows the variation of photosensitivity with the variation in the ion beam fluence.

Fig. 3.34 Temperature dependence of photoconductivity of Ag$_{0.10}$(Ge$_{0.20}$Se$_{0.80})_{0.90}$ thin films at different fluence of oxygen beam

Fig. 3.35 Variation of photosensitivity vs. ion beam fluence

From the figure it is clear that photosensitivity increases from 0.17 to 0.61 as the pristine sample is irradiated with fluence of $1 \times 10^{13}$ ions/cm$^2$. Then the value of $\sigma_{ph}/\sigma_d$
\( \sigma_d \) continuously decreases from 0.61 to 0.05 when fluence increased from \( 1 \times 10^{13} \) to \( 1 \times 10^{14} \) ions/cm\(^2\). The values of \( \sigma_{\text{ph}} \), photosensitivity (\( \sigma_{\text{ph}} / \sigma_d \)) are given in table 3.7.

### 3.7.4.3 Transient photoconductivity

Fig. 3.36 shows the rise and decay of photocurrent (\( I_{\text{ph}} \)) at room temperature (303 K) for the thin film of \( \text{Ag}_{0.10}(\text{Ge}_{0.20}\text{Se}_{0.80})_{0.90} \) before and after irradiation with different oxygen beam fluence.

The value of \( I_{\text{ph}} \) rises to maximum value as soon as light is turned on (\( t=0 \)). The time for which light is on (90 seconds) the value of \( I_{\text{ph}} \) shows slight decrease from maximum value at \( t=0 \). When light is turned off (after 90 seconds) the value of \( I_{\text{ph}} \) drops sharply from maximum value. The rapid decay of \( I_{\text{ph}} \) is often attributes to
‘localized-localized’ recombination mechanism according to which the trapped carrier recombine directly with the carriers of opposite sign [44, 45].

A persistent photocurrent is also observed in the decay of photocurrent in these samples. This type of photoconductive decay has also been reported in other chalcogenide glassy semiconductors [56-58]. To understand the trapping effects, the persistent photocurrent is subtracted from measured photocurrent and then corrected photocurrent (in pA) is plotted for pristine and irradiated samples and shown in Fig. 3.37. In the case of single trap level, these curves must be straight lines. However, in the present case, these curves do not maintain the same slope and the slope goes on decreasing continuously as the time of decay increases. This indicates that the traps exist at all the energies in the band gap which have different time constants and hence give non-exponential decay of photoconductivity.

Fig. 3.37 Time dependence of photocurrent decay for Ag$_{0.10}$Ge$_{0.20}$Se$_{0.80}$Ag$_{0.50}$ thin films at different fluence of oxygen ions.
To analyze the decay rates in the case of non-exponential decay, the differential lifetime ($\tau_d$) has been calculated using the equation (3.73) given by Fuhs and Stuuc [39]. In the case of exponential decay, the differential lifetime will be equal to the carrier lifetime. However, in the case of non-exponential decay, $\tau_d$ will increase with time and only the value at $t=0$ will correspond to the carrier lifetime. From the slope of $I_{ph}$ versus time curves, we have calculated the values of $\tau_d$ using equation (3.73) at various times of the decay curves. It is observed that the value of $\tau_d$ decreases continuously from 107 sec to 24 sec when pristine film is irradiated with fluence $3 \times 10^{12}$ ions/cm$^2$. Further increase in fluence from $3 \times 10^{12}$ ions/cm$^2$ to $3 \times 10^{13}$ ions/cm$^2$, the value of $\tau_d$ increases to 91 sec, after that with increase in fluence to $1 \times 10^{14}$ ions/cm$^2$, the $\tau_d$ value decreases to 72 sec. The increase in photosensitivity ($\sigma_{ph}/\sigma_d$) from 0.17 for pristine sample to 0.18 after irradiation with oxygen ions at fluence $1 \times 10^{12}$ ions/cm$^2$, indicate that the density of defect state decreases. Also, decrease in the value of $\tau_d$ from 107 sec to 77 sec, at this fluence indicates faster decay of photocurrent due to low defect density. Therefore, irradiation with heavy ions leads to annihilation of defects state [43] which may results in the faster decay of photocurrent and small carrier life time. Also irradiation at higher fluence may cause production of more defects [24, 42] leads to increase in carrier life time.

3.7.4.4 Conclusions

In sections 3.7 we have studied the effect of 85 MeV oxygen beam irradiation on optical, electrical and structural properties of $\text{Ag}_{0.10}\text{Ge}_{0.20}\text{Se}_{0.80}$ thin films. The optical constants like refractive index, optical band gap shows dependence on the ion beam fluence. The band gap of material shows decrease in its value from ($1.84 \pm 0.01$) eV from ($1.76 \pm 0.01$) eV after oxygen beam irradiation. The oxygen ion irradiations excite the electrons from the lone pair and bonding states to higher energy states. Vacancies created in these states are immediately filled by the outer electrons with Auger process that in turn induce more holes in the lone pair and bonding orbital leading to a vacancy cascade process as suggested by Kamboj et al. [24]. In this process, bond breaking or ionization of atoms is easier to occur which leads to a change in the local structure of the amorphous network leading to decrease in band gap of material. The refractive index $n$ first increases from ($2.47 \pm 0.004$) to ($2.89 \pm 0.004$) when fluence is $1 \times 10^{12}$ ions/cm$^2$, followed by decrease in its value from
(2.89±0.004) to (2.58±0.004) after all irradiation fluence. Observed increase in the refractive index at 1×10^{12} ions/cm^2 may be due to formation of this silver rich Ag_2Se phase leading to increase in local structural ordering of the material. This indicates increase in local ordering of material, result an increase in refractive index. The decrease in the value of refractive index at higher oxygen ion fluences (>1×10^{12} ions/cm^2), may be due to the increase in the disorder which occurs due to heavy ion irradiations. The other optical constants also show variation with ion beam irradiation fluence. All the optical constants also listed in table 3.4.

The Raman spectra of pristine and oxygen ion irradiated Ag_{0.1}(Ge_{0.2}Se_{0.8})_{0.90} thin films. It is observed that in pristine and irradiated samples four peaks appearing are: 193.8 cm^{-1} (peak I), 209.9 cm^{-1} (peak II), 237.4 cm^{-1}(peak III) and 257.4 cm^{-1} (peak IV) as shown in Fig. 3.32. Irradiation with fluence 1×10^{12} ions/cm^2 causes the formation of more corner-sharing (CS) GeSe_{4/2} and the edge-sharing (ES) GeSe_{4/2} structural units in the network at the expense of both helical like and linear chain structure corresponding to peak III and IV, respectively.

The electrical properties of Ag_{0.1}(Ge_{0.2}Se_{0.8})_{0.90} thin films before and after irradiation have been studied. The dc dark conductivity (\sigma_d), the pre-exponential factor (\sigma_0), the activation energy for dc conduction (\Delta E_d), photoconductivity (\sigma_{ph}), the activation energy of photoconduction (\Delta E_{ph}), photosensitivity (\sigma_{ph}/\sigma_d), differential life time (\tau_d) of Ag_{0.1}(Ge_{0.2}Se_{0.8})_{0.90} thin films irradiated with different oxygen ions fluence have been inserted in table 3.7. The variation of dc activation has been explained on the basis of has been explained on the basis of the fact that irradiation cause change in the density of defect states [24, 43, 55].
References


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