CHAPTER IV

Structural and Optical Properties of Ge-Se-Te System


In this chapter we have discussed the preparation and characterization of the Ge-Se-Te system and their bonding arrangement from far-infrared transmission study. Optical properties viz. refractive index, absorption coefficient, optical energy gap have been reported using ultraviolet-visible-near infrared spectroscopy. A detailed account on the effect of deposition parameter has also been discussed on the optical properties for Ge-Se-Te thin films.

4.1 Ge-Se-Te System

The Ge-Se-Te system is of special interest in view of the fact that it forms glasses over a wide domain of compositions. The glass forming region in the ternary Ge-Se-Te system extends to complete replacement of Se by Te, with the rest being Ge. Ge-Se-Te system is an important system as the addition of Te to Ge-Se system creates a configurational and compositional disorder with respect to binary system. Therefore, it is a suitable system for the investigation of its structural and optical properties. The glassy alloys of the system $Ge_{10}Se_{50-x}Te_x$ ($0 < x < 50$) were prepared by conventional melt quenching technique (chapter 3). The high purity (99.999%) elemental constituents were weighed and mixed in seal evacuated (at $\sim 10^{-4}$ Pa) quartz ampoules. The ampoules were kept inside a furnace where the temperature was increased up to 1000 $^\circ$C at a heating rate of 2-3 $^\circ$C/min. The ampoules were frequently rocked for 24 hours at the highest temperature to make the melt homogeneous. The melt in the quartz ampoule was then quenched into ice-cold water.

Thin films of the glassy alloys of $Ge_{10}Se_{50-x}Te_x$ ($x = 0, 10, 20, 30, 40, 50$) were prepared on glass substrates by vacuum evaporation technique at a base pressure $\sim 10^{-4}$ Pa. The bulk samples as well as their thin films were characterized by X-ray diffraction (XRD) technique. Figure 4.1.1 shows the XRD patterns for bulk samples while figure 4.1.2 shows XRD patterns for their thin films. The lack of any sharp peak indicates the amorphous nature of bulk glasses as well as their thin films.
Figure 4.1.1 XRD patterns for Ge$_{10}$Se$_{90-x}$Te$_x$ bulk glasses.

Figure 4.1.2 XRD patterns for Ge$_{10}$Se$_{90-x}$Te$_x$ thin films.
4.2 Far-infrared transmission

4.2.1 Introduction

An understanding of the structure of an amorphous material is essential to understand its physical properties. Determining the structure of glasses is difficult for two main reasons. First, unlike for the crystal, there is no direct probe such as X-ray diffraction that can determine the structure of a glass uniquely. This is due to the absence of long range order in the glasses. Second, the glass may be in one of many possible metastable states. These metastable states consist of different atomic configurations which may differ only slightly from one another and result in physical properties very similar to one another. The particular state in which a glass resides is dependent on its history of preparation. That is, the glass forming ability is influenced by the quenching rate, the amount of the sample prepared and the temperature from which the melt of sample is quenched. Infrared (IR) absorption of solids can provide useful information about the lattice vibrational density and structure of solids. In order that the mode of vibration can absorb, a mechanism for coupling the vibration motion to electromagnetic radiation must exist. The basic mechanism is that the motion produces an oscillatory dipole moment which can be driven by oscillating electric field of radiation. Raman scattering in solids is associated with the change of polarizability corresponding to the vibrational modes. The vibrations that contribute to IR absorption can be quantitatively separated into different types of modes characterized by three frequency regimes: low frequency acoustic modes, intermediate frequency bond bending modes and high frequency bond stretching modes. The bond stretching mode generally yield the most direct structural information since their frequencies are determined primarily by nearest neighbour interactions and thus relative IR activity by local molecular symmetry.

Infrared and Raman measurements have been made as a useful means of obtaining information about the structure of chalcogenide glasses [1-9]. In this case this is essentially important to investigate vibrational spectra in the fundamental band region. Several authors [10-13] have measured the IR and Raman spectra of pure glassy Se in order to understand the structure. Structural investigations have also been made for binary chalcogenide glasses as S-Se, Se-Te, As-Se and Ge-Se alloys by
measuring the IR and Raman spectra [10-17]. These studies reveal that the pure glassy Se consists of Se₈ puckered rings and Seₙ spiral chains [10,11,13,14] and in S-Se and Se-Te glasses S₈₋₅Seₙ and Se₈₋₅Teₓ mixed rings were formed [14,16]. On the other hand it was considered in As-Se and Ge-Se glasses that AsSe₃ pyramidal molecules [14,16] and GeSe₄ tetrahedral molecules [14,15,17] were formed as a local configuration.

The Ge-Se system provides a wide range of concentrations for which it is possible to obtain bulk amorphous compounds. The Ge-Se system has been widely probed using IR and Raman spectroscopy [1,2,15,18-24]. Alloys of glassy GeₓSe₁₋ₓ system with Ge concentration range 0 < x < 0.5 are supposedly composed of Se chain, Ge₅(Se₇/₂)₄ tetrahedral, Geₓ(Seₓ/₂)₂ ethane like and Ge(Sex/₂)₂ structural units in proportions varying to comply with the actual x-values. Substitution of tellurium (Te) into Ge-Se system makes the system of interest. The system Ge₁₀Se₉₀₋ₓTeₓ (0 < x < 50) has been studied here with emphasis on the effect of Te. The system is of quite interest as this was shown that addition of Te into Ge-Se increases the transparency range of the glasses [25-27]. Thus addition of Te to Ge-Se provides an ideal system for optical study in far-IR region. To have a better understanding of the optical properties one should have the knowledge of its structural constituents. This makes the authors to have a detailed structural study of the Ge₁₀Se₉₀₋ₓTeₓ (0 < x < 50) system in the far-IR region.

4.2.2 Experimental details

Far-infrared transmission measurements were obtained in the spectral range 50-650 cm⁻¹ at room temperature using Thermo Nicolet Nexus 670 FT-IR Spectrometer. The resolution during the measurements was set at 2 cm⁻¹. Measurements were made using the polyethylene pellet method. To take account of the polyethylene absorption, the spectrum of polyethylene was used as reference spectrum. The sample spectrum was divided by the reference spectrum to nullify the polyethylene absorptions.
4.2.3 Results and discussion

The IR spectra of $\text{Ge}_{10-x}\text{Se}_{20}x\text{Te}_x$ where $x = 0, 10, 20$ and $x = 30, 40, 50$ glassy alloys are shown in figures 4.2.1 and 4.2.2 respectively. The IR spectra of Ge-based chalcogenide glasses have been largely interpreted in terms of isolated molecular units. Two different models have been proposed for the structure of Ge-Se glasses.

In the first model [15] called chain crossing model (CCM) the four fold tetrahedrally coordinated Ge-atoms act as chain crossing points in Se chain structure. In second model [28] known as random covalent network model (RCNM), the tetrahedrally coordinated Ge-atoms bond to other Ge-atoms as readily as to the two fold Se-atoms. In the chemical bond approach, to explain the structure of chalcogenide glasses Bicerno and Ovshinsky [29] proposed that atoms of one type combine more favourably with atoms of different type and the bonds are formed in the sequence of decreasing bond energy until all available valencies of the atoms are filled. Keeping this view in mind the energies of various possible bonds in $\text{Ge}_{10-x}\text{Se}_{20}x\text{Te}_x$ system have been calculated on the basis of relation [30]

$$D(A-B) = \left[ D(A-A) + D(B-B) \right]/2 + 23(\chi_A - \chi_B)^2$$

(1)

where $\chi_A$ and $\chi_B$ are the electronegativities of the atoms $A$ and $B$ and $D(A-A)$ and $D(B-B)$ are the bond energies of $A-A$ and $B-B$ bonds respectively. The relative probabilities of formation of different bonds have also been calculated using the probability function $\exp(D/K_B T)$ at room temperature as well as 1000 °C at which the samples were prepared. The results are shown in table 4.2.1.

When Ge is introduced into Se, it is four fold tetrahedral coordinated [31]. $\text{GeSe}_4$ tetrahedral molecules have four fundamental modes ($\nu_1, \nu_2, \nu_3, \nu_4$) [32]. Although only the $\nu_3$ and $\nu_4$ modes are infrared active in $\text{GeSe}_4$ molecules, it is expected that all the fundamental modes appear in infrared absorption spectra because of breakdown of selection rules in glassy materials. Considering first the $\text{Ge}_{10}\text{Se}_{90}$ bulk glass the main absorption bands appears at ~ 84 cm$^{-1}$, 102 cm$^{-1}$, 150 cm$^{-1}$, 175 cm$^{-1}$, 220 cm$^{-1}$ and 280 cm$^{-1}$ along with three shoulders at ~ 127 cm$^{-1}$, 137 cm$^{-1}$ and 193 cm$^{-1}$. The existence of these absorption bands is in good agreement with the earlier reported results by Ball and Chamberlain [18]. The band at 84 cm$^{-1}$ has been
assigned to $Se_8$ [$E_2$ mode] [18] while the sharp absorption band at 102 cm$^{-1}$ has been assigned to $A_2$ mode of trigonal $Se$ which is strongly infrared active. Ohsaka [14] has also reported infrared active fundamental band in spectra of $Se$ containing $Te$ at 102 cm$^{-1}$ and assigned it to $A_2$ mode of trigonal $Se$. The shoulders at 127 cm$^{-1}$ and 137 cm$^{-1}$ have been assigned to $Se$ polymeric chains. Absorption peaks at 150 cm$^{-1}$ and 175 cm$^{-1}$ have been observed and assigned to $GeSe_2$ mode [18] which is active in Raman mode. Ball et al [18] has reported $GeSe_4$ ($v_1$) mode at 197 cm$^{-1}$ for $Ge_{1.5}Se_{0.5}$ glassy alloy so a shoulder at 193 cm$^{-1}$ may be assigned to $v_1$ mode of $GeSe_4$ tetrahedra. A comparatively weak band at 220 cm$^{-1}$ has been assigned to $GeSe_2$ mode. Fukunaga et al [33] also found a weak band at 220 cm$^{-1}$ for $GeSe_2$ and attributed it to the vibrations of Ge-Ge bonds. Ksendzov et al [34] have reported that glasses have increasing ability to relax and optimize bent $Se-Se-Se$ bonds because the large chemically ordered clusters become floppy [35]. So they assigned band at 280 cm$^{-1}$ to vibrations of nearly isolated $F_2$ mode of $Ge(Se_{1/2})_4$ tetrahedra which are connected with $Se$ chains outside the clusters [33] because of lack of symmetry and relaxation of selection rules. In our spectra a band at 280 cm$^{-1}$ may thus be assigned to an isolated $F_2$ mode of $Ge(Se_{1/2})_4$ tetrahedra.

When $Te$ is substituted for $Se$ in $Ge_{1.0}Se_{90-x}Te_x$, the absorption band at 84 cm$^{-1}$ starts to split into bands at ~ 79 cm$^{-1}$ and 89 cm$^{-1}$. The absorption band at 79 cm$^{-1}$ has been assigned to $v_2$ ($E$) mode of $GeTe_2$ structural unit [36] and absorption peak at 89 cm$^{-1}$ has been assigned to $E_1$ mode due to $Se_8$ rings. A strong vibrational band at 102 cm$^{-1}$ remains at its same position for $x = 10$ while for other higher $Te$ concentrations i.e. $x = 20, 30, 40, 50$ this absorption band is observed to shift towards higher wavelength and is found at 100 cm$^{-1}$. The absorption band at 150 cm$^{-1}$ for $x = 0$ [$GeSe_2$ mode] is found missing for $x = 10$ at.% of $Te$ but appears sharply for $x \geq 20$ at.% of $Te$ content. Andrikopoulos et al [37] have assigned this vibrational mode to symmetric stretching vibration of $Te-Te$ bond. In present case i.e. for $Ge-Se-Te$ system this strong vibrational mode at 150 cm$^{-1}$ is assigned to symmetric stretching of $Te-Te$ bonds. The presence of $Te-Te$ bonds at higher frequency is due to the fact that stretching modes occurs at higher frequencies. A weak absorption band at 163 cm$^{-1}$ is observed in all the compositions containing $Te$ content. This weak band has been attributed to $v_1$ ($A_1$) vibrational mode for $GeTe_2$. Phillips [36] has also reported $v_1$ ($A_1$)
Figure 4.2.1 Far-IR transmission spectra of $Ge_{10}Se_{50-x}Te_{x}$ ($x = 0, 10, 20$) glassy alloys. The ordinate scale for different $x$-values is shifted for clarity.

Figure 4.2.2 Far-IR transmission spectra of $Ge_{10}Se_{50-x}Te_{x}$ ($x = 30, 40, 50$) glassy alloys. The ordinate scale for different $x$-values is shifted for clarity.
Table 4.2.1 Bond energy and the relative probabilities of various bonds in $Ge_{10}Se_{90-x}Te_x$ ($x = 0, 10, 20, 30, 40, 50$) glassy alloys. The probability of the Ge-Se bond has been taken as unity.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond energy (kcal/mol)</th>
<th>Relative probability at the following Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>27 °C</td>
</tr>
<tr>
<td>Ge-Se</td>
<td>49.1</td>
<td>1</td>
</tr>
<tr>
<td>Se-Se</td>
<td>44.0</td>
<td>$1.93 \times 10^{-3}$</td>
</tr>
<tr>
<td>Se-Te</td>
<td>40.6</td>
<td>$6.50 \times 10^{-7}$</td>
</tr>
<tr>
<td>Ge-Ge</td>
<td>37.6</td>
<td>$4.36 \times 10^{-9}$</td>
</tr>
<tr>
<td>Ge-Te</td>
<td>37.4</td>
<td>$3.05 \times 10^{-9}$</td>
</tr>
<tr>
<td>Te-Te</td>
<td>33.0</td>
<td>$1.91 \times 10^{-12}$</td>
</tr>
</tbody>
</table>
vibrational mode for GeTe$_2$ at 161 cm$^{-1}$ in Ge-Te glassy alloys. The absorption bands of 175 cm$^{-1}$ [GeSe$_2$ Raman Mode], 220 cm$^{-1}$ [GeSe$_2$] and 280 cm$^{-1}$ [$F_2$ mode of Ge($Se_{1/2}Te$)] which appears for $x = 0$ have not been observed when Te is substituted for Se in Ge$_{10}$Se$_{90-x}$Te$_x$ glassy alloy while 127 cm$^{-1}$, 137 cm$^{-1}$ [Se polymeric chain] and 193 cm$^{-1}$ [$v_1$ mode of GeSe$_4$] remains at their positions though their intensity changes for some of the compositions.

On the addition of Te to Ge-Se system a well resolved doublet at 113 cm$^{-1}$ and 117 cm$^{-1}$ has been observed and two distinguishable absorption peaks are observed at 211 cm$^{-1}$ and 217 cm$^{-1}$ in all the compositions ($x = 10, 20, 30, 40, 50$). The intensity of these peaks increase with the increase of Te content. The doublet at 113 cm$^{-1}$ and 117 cm$^{-1}$ has been associated with $v_1$ ($A_1$) vibrational frequency of GeTe$_4$ tetrahedron [37]. The absorption band at 211 cm$^{-1}$ has been assigned to the vibrations of Se-Te bonds. Wang et al [38] also have reported the vibrations of Se-Te bonds at 210 cm$^{-1}$ in Ge$_2$Se$_3$Te$_2$ glassy alloy. Further Ohsaka [14] has reported the frequency of IR band in Se-Te alloy at 205 cm$^{-1}$ which does not vary with the Te content. Consequently he did not assign this band to Se$_{p,x}$Te$_x$ chains but to Se$_{8,x}$Te$_x$ mixed rings and is estimated to be due to Se$_{5}$Te$_3$ mixed rings. The absorption band at 217 cm$^{-1}$ observed for Te added Ge-Se system has been assigned to the vibrations of Se-Te bonds. Schottmiller et al [16] also showed that the Raman band at 216 cm$^{-1}$ found in Se-Te alloys was attributed to Se$_{8,x}$Te$_x$ rings probably Se$_{5}$Te$_2$ rings. Absorption peak at 237 cm$^{-1}$ which does not show its appearance in compositions with $x = 0, 10, 20$ at.% starts showing its existence for $x \geq 30$ at.% of Te content. Phillips [36] has also reported an absorption band at 230 cm$^{-1}$ in Ge-Te glass and attributed it to $v_3$ ($F_2$) vibrational mode for GeTe$_2$. In our case, the band at 237 cm$^{-1}$ appears as Te replaces Se for $x \geq 30$ at.% and this may be assigned to $v_3$ ($F_2$) vibrational mode for GeTe$_2$.

In order to understand the IR absorption spectra obtained above for Ge$_{10}$Se$_{90-x}$Te$_x$, where $x = 0, 10, 20, 30, 40, 50$ glasses the absorption spectra of these glasses have been compared with the IR studies of pure Se [10], binary Ge-Se [18], Ge-Te [37], Se-Te [14] and ternary Ge-Se-Te glasses [38]. As seen for Ge$_{10}$Se$_{90}$ glassy alloy the absorption bands appears at 84 cm$^{-1}$, 102 cm$^{-1}$, 150 cm$^{-1}$, 175 cm$^{-1}$, 220 cm$^{-1}$ and 280 cm$^{-1}$ along with three shoulders at $\sim$ 127 cm$^{-1}$, 137 cm$^{-1}$ and 193 cm$^{-1}$. On the
addition of Te to Ge-Se system the absorption peak for \(E_2\) mode of \(Se_8\) at 84 \(\text{cm}^{-1}\) splits into two bands at 79 \(\text{cm}^{-1}\) and 89 \(\text{cm}^{-1}\) leading to the formation of \(GeTe_2\) and \(Se_8\) structural units respectively. The other new absorption bands which appears at 113 \(\text{cm}^{-1}\), 117 \(\text{cm}^{-1}\), 163 \(\text{cm}^{-1}\), 211 \(\text{cm}^{-1}\) and 217 \(\text{cm}^{-1}\) shows the existence of tetrahedra of \(GeTe_4\) at 113 \(\text{cm}^{-1}\) and 117 \(\text{cm}^{-1}\) doublet, \(GeTe_2\) unit at 163 \(\text{cm}^{-1}\) while vibrations of \(Se-Te\) bonds in \(Se_{8-x}Te_x\) mixed rings at 211 \(\text{cm}^{-1}\) and 217 \(\text{cm}^{-1}\). Moreover it is found that the absorption band at 150 \(\text{cm}^{-1}\) for \(x = 0\) composition disappears for \(x = 10\) at.\% whereas it again appears at 150 \(\text{cm}^{-1}\) for \(x \geq 20\) at.\% showing the symmetric stretching vibrations of \(Te-Te\) bonds. Further for \(x \geq 30\) at.\% the band at 237 \(\text{cm}^{-1}\) appears due to \(GeTe_2\) molecular unit.

With the increase of \(Te\) content it has been observed that some of the \(Ge-Se\) and \(Se-Se\) bonds disappear leading to the formation of \(Se-Te\) and \(Ge-Te\) bonds. Further the existence of \(Te-Te\) bonds has also been observed at 150 \(\text{cm}^{-1}\). \(Ge-Se\) and \(Se-Se\) bonds remain in the \(Ge_{10}Se_{90-x}Te_x\) glassy alloy even on the addition of \(Te\) may be explained in terms of their higher relative probability of formation (table 4.2.1). The formation of \(Se-Te\) and \(Ge-Te\) bonds may be explained on the basis of supremacy of heteropolar on homopolar bonds [29]. The existence of \(Ge-Ge\) bonds has not been observed as the compositions under study were chalcogen rich. The absorption peaks at 150 \(\text{cm}^{-1}\) (for \(x \geq 20\) at.\%) confirms the formation of \(Te-Te\) bonds. However these appear for higher \(Te\) content compositions. The least formation of \(Te-Te\) bonds may be attributed to their lower relative probability of formation. The formation of \(Te-Te\) bonds may also be explained on the basis of chemical bond approach (CBA) method [29]. Among chalcogens (Se and Te) Te acts as 3-fold coordinated. Thus for \(x > 20\) at.\%, Te become excessive and remain unsatisfied producing \(Te-Te\) homopolar bonds and appears at 150 \(\text{cm}^{-1}\) due to symmetric stretching of \(Te-Te\) bonds.

### 4.2.4 Conclusion

The addition of \(Te\) to \(Ge_{10}Se_{90}\) shows that the far-IR transmission spectra shift a little towards the lower wavenumber side. The addition of \(Te\) in \(Ge_{10}Se_{90}\) has shown the appearance of \(GeTe_2\) and \(GeTe_4\) molecular units and vibrations of \(Se-Te\) bond in \(Se_{8-x}Te_x\) mixed rings. The results were explained in terms of the vibrations of the
isolated molecular units. This has been observed that some of the Ge-Se and Se-Se bonds disappear leading to the formation of Se-Te and Ge-Te bonds. The existence of Ge-Ge bonds has not been observed as the compositions under study were chalcogen rich. The absorption peaks at 150 cm$^{-1}$ (for $x > 20$ at. %) confirms the formation of Te-Te bonds. However, these appear for higher Te content compositions. The least formation of Te-Te bonds may be attributed to their lower relative probability of formation and also to excess of Te-Te bonds according to CBA. These results are supported by observation that optical band gap decreases with the addition of Te to Ge$_{10}$Se$_{90-x}$Te$_x$ system (section 4.3.3).

4.3 Optical properties

4.3.1 Introduction

Chalcogenide glasses recognized as promising materials for infrared optical elements, infrared optical fibres, xerography, switching and memory devices, photolithography and in the fabrication of inexpensive solar cells and more recently for reversible phase change optical records [39-52]. The influence of impurities on electrical, optical and the structural properties of chalcogenide glasses are of important concern with respect to their application. This influence can be widely different for different impurities. Many approaches were proposed to explain the compositional dependence of various physical properties of chalcogenide networks [39,53-56].

The chemical composition and energy band structure change on introducing the Ge atoms into the Se matrix. The variation of the Ge-Se structure is reflected in different properties such as the glass forming regions, glass transition temperature, photoluminescence, IR and Raman spectra and the optical properties [57-59]. Optical properties of IV-VI compounds have been studied by various researchers [60,61]. The optical band gap and the localized states width were found to depend on the composition.

The optical band gap and refractive index are the most significant parameters in amorphous semiconducting thin films. The optical behaviour of material is utilized to determine its optical constants. Films are ideal specimen for absorbance and
transmittance type measurements. Therefore, accurate measurements of the optical constants are extremely important. The optical properties of amorphous semiconductors have been extensively studied \cite{60,61} on Ge-Se system because of their wide range of applications and strong dependence on composition.

In Ge\textsubscript{10}Se\textsubscript{90} system the average coordination number \( \langle r \rangle \) is 2.2 \textit{i.e.} the system is in floppy mode. Alloying of Ge\textsubscript{10}Se\textsubscript{90} with a fourth element of group VI (Te) is very important from the basic as well as application point of view because for Ge\textsubscript{10}Se\textsubscript{90-x}Te\textsubscript{x} (\( x = 0, 10, 20, 30, 40, 50 \)) compositions \( \langle r \rangle \) varies from 2.2 to 2.7 \textit{i.e.} the system varies from floppy mode to rigid mode with a change in mode at 2.4 \cite{54,56}. In the present work, therefore, the effect of Te additive on the optical properties of such a technically important system Ge\textsubscript{10}Se\textsubscript{90} has been studied. The optical parameters refractive index (\( n \)), extinction coefficient (\( k \)), absorption coefficient (\( \alpha \)) and optical band gap (\( E_{\text{opt}}^g \)) of the amorphous thin films of Ge\textsubscript{10}Se\textsubscript{90-x}Te\textsubscript{x} (\( x = 0, 10, 20, 30, 40, 50 \)) have been calculated by analyzing their transmission spectra. The dielectric constant and optical conductivity has also been calculated using the other optical parameters.

### 4.3.2 Experimental details

The normal incidence transmission spectra in the transmission range 200-2400 nm for Ge\textsubscript{10}Se\textsubscript{90-x}Te\textsubscript{x} (\( x = 0, 10, 20, 30, 40, 50 \)) thin films (thickness 800 nm) were obtained by a double beam ultraviolet-visible-near infrared spectrophotometer \cite{Hitachi-330}. The spectrophotometer was set with a slit width of 1 nm. The normal incidence transmission spectra were also obtained by a double beam ultraviolet-visible-near infrared spectrophotometer \cite{Perkin Elmer Lambda-750}. In UV region no transmission has been observed. The results obtained from both the instruments are in good agreement.

### 4.3.3 Results

Figures 4.3.1, 4.3.2 and 4.3.3 show transmission spectra for Ge\textsubscript{10}Se\textsubscript{90-x}Te\textsubscript{x} (\( x = 0, 10, 20, 30, 40, 50 \)) thin films. The fringes in the spectra are due to interference
Figure 4.3.1 Transmission spectrum for Ge_{10}Se_{90} thin film.

Figure 4.3.2 Transmission spectra of Ge_{10}Se_{90-x}Te_{x} (x = 10, 20, 30) thin films.
Figure 4.3.3 Transmission spectra of $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 40, 50$) thin films.

Figure 4.3.4 Variation of refractive index with wavelength for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 10, 20$) thin films.
Figure 4.3.5 Variation of refractive index with wavelength for $Ge_{10}Se_{90-x}Te_x$ ($x = 30, 40, 50$) thin films.

Figure 4.3.6 Variation of extinction coefficient with wavelength for $Ge_{10}Se_{90-x}Te_x$ ($x = 0, 10, 20$) thin films.

Figure 4.3.7 Variation of extinction coefficient with wavelength for $Ge_{10}Se_{90-x}Te_x$ ($x = 30, 40, 50$) thin films.
at various wavelengths. The maxima and minima of these fringes are used to calculate the various optical parameters. This is found that maxima and the minima of the fringes shift towards higher wavelength region with the increase of Te content in Ge_{10}Se_{90-x}Te_x. This may be due to the influence of the absorption coefficient (a) and scattering of light by defects.

Refractive index (n) and extinction coefficient (k) have been calculated using the technique proposed by Swanepoel (chapter 2). The spectral distribution of refractive index is shown in figures 4.3.4 and 4.3.5 and extinction coefficient is shown in figures 4.3.6 and 4.3.7 respectively. The values of refractive index at 800 nm are given in table 4.3.1.

The values of thickness of the thin films under investigation have been calculated using equation (2.22) and are given in table 4.3.1. The difference in thickness measured from thickness monitor and calculated from equation (2.22) lies with in ± 45 nm for all investigated thin films.

The high frequency properties of thin films could be treated as single oscillator. According to the single-effective oscillator model proposed by Wemple and DiDomenico [62] the optical data could be described to an excellent approximation by the following relation

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

where \( h \nu \) is the photon energy, \( n \) is refractive index, \( E_0 \) is the oscillator strength also called average energy gap, \( E_d \) is the dispersion energy. The latter quantity measures the average strength of the interband optical transitions. Plotting \( (n^2 - 1)^{-1} \) against \( (h \nu)^2 \) allows us to determine the oscillator parameters by fitting a straight line to the points. Figure 4.3.8 shows the plot of \( (n^2 - 1)^{-1} \) versus \( (h \nu)^2 \). The values of \( E_0 \) and \( E_d \) can be directly determined from the slope \( (E_0 E_d)^{-1} \) and the intercept on the vertical axis \( (E_0/E_d) \) respectively. The values of static refractive indices (\( n_o \)) for thin films under investigation are calculated by extrapolating the Wemple-DiDomenico dispersion equation to \( h \nu \to 0 \) and are given in table 4.3.1. The high
**Figure 4.3.8** Plot of refractive index factor $(n^2 - 1)^{-1}$ vs. $(hv)^2$ for $Ge_{10}Se_{90-x}Te_x$ ($x = 0, 10, 20, 30, 40, 50$) thin films.
Figure 4.3.9 Plot of absorption coefficient ($\alpha$) vs. $h\nu$ for $Ge_{10}Se_{90-x}Te_x$ ($x = 0$, 10, 20, 30) thin films.
Figure 4.3.10 Plot of absorption coefficient (α) vs. hν for Ge_{10}Se_{90-x}Te_{x} (x = 40, 50) thin films.

Figure 4.3.11 Plot of (αhν)^{0.5} vs. hν for Ge_{10}Se_{90-x}Te_{x} (x = 0, 10, 20, 30, 40, 50) thin films.
frequency dielectric constants [64] \( \varepsilon' = (n_0)^2 \) for Ge\(_{10}\)Se\(_{90}\)Te\(_x\) thin films are also given in Table 4.3.1. Moreover, an important achievement of Wemple-DiDomenico model is that it relates the dispersion energy \( E_d \) to other physical parameters of the material through a simple empirical relation \( E_d = \beta N_e Z_a N_c \) where \( N_e \) is effective number of valence electrons per anion, \( N_c \) is effective coordination number of the cation nearest neighbour to the anion, \( Z_a \) is the chemical valency of the anion and \( \beta \) is a two valued constant with either an ionic or covalent value (for ionic materials \( \beta = 0.26 \pm 0.03 \) eV and for covalent materials \( \beta = 0.37 \pm 0.04 \) eV).

Figures 4.3.9 and 4.3.10 show the variation of absorption coefficient (\( \alpha \)) with energy for the Ge\(_{10}\)Se\(_{90}\)Te\(_x\) thin films. The absorption coefficient is measured in high and intermediate absorption regions, not in the weak absorption region. The values of \( \alpha \) are calculated using equation (2.23). The absorption coefficient has been observed to decrease with the decrease in energy or increase in wavelength for all the thin films.

Figure 4.3.11 shows the plot of \((\alpha h \nu)^{1/2} \) vs. \( h \nu \) for calculation of optical band gap (\( E_{opt} \)). The optical gap is determined by taking the intercept of the extrapolations to zero absorption with the photon energy axis \((\alpha h \nu)^{1/2} \to 0\) [65]. It is clear from the figure 4.3.11 that the optical gap decreases with increasing Te content. Figures 4.3.12 and 4.3.13 show the plots of real (\( \varepsilon_r \)) and imaginary (\( \varepsilon_i \)) parts of dielectric constants against photon energy respectively. The values \( \varepsilon_r \) and \( \varepsilon_i \) are calculated by using \( n \) and \( k \) values in the relations \( \varepsilon_r = n^2 - k^2 \) and \( \varepsilon_i = 2nk \) [66]. The optical conductivity (\( \sigma \)) has been determined from the relation \( \sigma = \alpha nc/4\pi \) [67]. Figure 4.3.14 shows the variation of \( \sigma \) vs. \( h \nu \).

### 4.3.4 Discussion

Addition of Te in Ge-Se shifts the transmission towards higher wavelength side (figures 4.3.1, 4.3.2 and 4.3.3). This may be due to the influence of absorption coefficient and scattering of light by heavier Te atoms replacing the Se atoms as size of atoms play a crucial role in the scattering of light.
Figure 4.3.12 Plot of real part of dielectric constant ($\varepsilon_r$) vs. $h\nu$ for $Ge_{10}Se_{90-x}Te_x$ ($x = 0, 10, 20, 30, 40, 50$) thin films.

Figure 4.3.13 Plot of imaginary part of dielectric constant ($\varepsilon_i$) vs. $h\nu$ for $Ge_{10}Se_{90-x}Te_x$ ($x = 0, 10, 20, 30, 40, 50$) thin films.
Figure 4.3.14 Plot of optical conductivity ($\sigma$) vs. $hv$ for $Ge_{10}Se_{90-x}Te_x$ ($x = 0, 10, 20, 30, 40, 50$) thin films.
Table 4.3.1 Values of thickness (d), refractive index (n at 800 nm), optical band gap ($E_g^{opt}$), oscillator strength ($E_0$), dispersion energy ($E_d$), static refractive index ($n_0$) and high frequency dielectric constant ($\varepsilon_{\infty}$) for Ge$_{x}$Se$_{80-x}$Te$_x$ ($x = 0, 10, 20, 30, 40, 50$) thin films

<table>
<thead>
<tr>
<th>x</th>
<th>d (nm)</th>
<th>n</th>
<th>$E_g^{opt}$ (eV)</th>
<th>$E_0$</th>
<th>$E_d$</th>
<th>$n_0$</th>
<th>$\varepsilon_{\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>798</td>
<td>2.69</td>
<td>1.87 ± 0.01</td>
<td>4.89</td>
<td>27.76</td>
<td>2.58</td>
<td>6.66</td>
</tr>
<tr>
<td>10</td>
<td>836</td>
<td>2.88</td>
<td>1.62 ± 0.01</td>
<td>3.43</td>
<td>22.13</td>
<td>2.73</td>
<td>7.45</td>
</tr>
<tr>
<td>20</td>
<td>829</td>
<td>3.12</td>
<td>1.46 ± 0.01</td>
<td>3.12</td>
<td>20.79</td>
<td>2.81</td>
<td>7.90</td>
</tr>
<tr>
<td>30</td>
<td>749</td>
<td>3.21</td>
<td>1.27 ± 0.01</td>
<td>2.72</td>
<td>20.42</td>
<td>2.94</td>
<td>864</td>
</tr>
<tr>
<td>40</td>
<td>813</td>
<td>3.52</td>
<td>1.12 ± 0.01</td>
<td>2.39</td>
<td>20.19</td>
<td>3.09</td>
<td>9.55</td>
</tr>
<tr>
<td>50</td>
<td>782</td>
<td>3.86</td>
<td>1.03 ± 0.01</td>
<td>2.20</td>
<td>20.17</td>
<td>3.19</td>
<td>10.18</td>
</tr>
</tbody>
</table>
Figures 4.3.4 and 4.3.5 show the variation of refractive index with wavelength. It is found that with the increase of wavelength there is a continuous decrease in refractive index showing the normal dispersion behaviour of the material. The refractive index is found to increase with the increase of Te content. This increase is large for the higher Te contents. This may be due to the change in stoichiometry [68] and internal strain [69] of the glassy alloy with large incorporation of the Te content. The addition of Te into Ge-Se system causes increase in the disorder which in turn may lead to increase of refractive index. Dispersion of refractive index has been studied in terms of Wemple-DiDomenico single oscillator model. This model leads to the calculation of oscillator strength ($E_o$) which, according to Tanaka [10], is related to optical band gap by the relation $E_o \approx 2 \times E_{opt}$. The values of oscillator strength observed in our case are in concordance with the Tanaka's relation showing the justification of our results.

Figures 4.3.9 and 4.3.10 show that the absorption coefficient lies in the range $10^3$ - $10^4$ cm$^{-1}$. The absorption around the absorption edge has been often found to increase suddenly rather than gradually as in the case of oxide glasses. Optical band gap has been determined using the Tauc's extrapolation method. It is clear from Figure 4.3.11 that the optical gap decreases with increasing Te content. This can be correlated with the character of the chemical order of chalcogenide amorphous semiconductors. According to the model described by Kastner [71], the dominant contribution for states near the valence band edge in materials having chalcogen atoms as major constituents, comes from chalcogen atoms, especially from their lone-pair p-orbital. The lone-pair electrons in these atoms adjacent to electropositive atoms will have higher energies than those close to electronegative atoms. Therefore, the addition of electropositive elements to the alloy may raise the energy of some lone-pair states sufficiently to broaden further the band inside the forbidden gap. The electronegativities of Ge, Se and Te are 2.01, 2.55 and 2.1 respectively. According to these values, it is noticed that Te is less electronegative than Se, so the substitution of Te for Se may raise the energy of some lone-pair states and hence broaden the valence band. This will give rise to additional absorption over a wider range of energy leading to band tailing and hence shrinking of the band gap. The optical gap decreases from
1.87 to 1.03 eV for $x = 0$ to $x = 50$ Te content as shown in table 4.3.1. The addition of Te in the glass structure causes deeper band tails extended in the gap and thereby leading to a decrease in the value of optical band gap. The decrease in optical band gap with increasing Te content may also be related to the increase in number of Ge-Te (37.4 kcal/bond), Se-Te (40.6 kcal/bond) and Te-Te (33.0 kcal/bond) bonds and decrease of Se-Se (44.0 kcal/bond) and Ge-Se (49.1 kcal/bond) bonds. The strength of Ge-Te, Se-Te and Te-Te bonds is lower as compare to Ge-Se and Se-Se bonds so the optical absorption edge shifts towards higher values of wavelength with the addition of Te. Tellurium enters into the tetrahedral structure of GeSe$_2$ forming units containing all the three elements (Ge, Se, Te) thus leading to the modification of the glassy network. Further, the optical band gap is strongly dependent on the fractional concentration of Te atoms. This may be due to the tendency of Te atoms to form chemical disordering and to create localized states in the forbidden gap [72] leading to lower the optical band gap.

In chalcogenide glassy semiconductors, there are a large number of charged defect states, which are due to dangling bonds or valence alteration. The addition of Te to Ge-Se system induces structural changes in the host network because in chalcogenide glasses among divalent atoms, Te acts as three fold coordinated leading to acceptors or holes and thus supplying holes in the valence band. The increase of Te content leads to the formation of composition with higher degree of disorder and hence higher densities of localized states. The change in the optical properties for Ge$_{10}$Se$_{50}$Te$_x$ compositions may be explained by assuming that Te atoms act as an impurity center in the mobility gap. For binary Ge-Se alloy $E_F$ is approximately pinned at the center of mobility gap where the charged defect centers have equal concentration. Thus the distribution and density of localized states are modified and even some new trap states may be created in the mobility gap leading to changes in the optical gap.

The other parameters i.e. dielectric constants and optical conductivity have been determined by making use of the refractive index ($n$), extinction coefficient ($k$) and absorption coefficient ($\alpha$). Figures 4.3.12 and 4.3.13 show the variation of real and imaginary parts of dielectric constants and found to increase with the photon energy. Figure 4.3.14 shows the plot of optical conductivity and it also increases with
photon energy. Since dielectric constants and optical conductivity depends on \( n, k \) and \( \alpha \), thus their variation can be explained similarly to \( n, k \) and \( \alpha \).

### 4.3.5 Conclusion

Different parameters related to optical properties were calculated for the thin films of \( \text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x \) glassy alloy. Transmission spectra show that with the addition of Te content there is red shift in the transmission. Refractive index has been found to decrease with the increase of wavelength. The refractive index increases sharply for higher content of Te addition. Absorption coefficient lies in the range \( 10^{-3} - 10^{-4} \text{ cm}^{-1} \). Optical band gap has been calculated from Tauc’s extrapolation method and found to decrease with the increase of Te content. The optical band gap changes from 1.87 eV to 1.03 eV for \( x = 0 \) to \( x = 50 \) respectively in \( \text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x \) thin films. The decrease of optical band gap has been explained on the basis of decrease of bond energy of the system and electronegativity concept.

### 4.4 Effect of deposition parameters on the optical properties

Thin films deposited under different conditions produce different results, whether it is the case of method of thin film deposition or the parameters considered while deposition. In this section we have considered three important parameters on which the properties of films may depend. These parameters contain variation of thickness of films, type of substrates used and the substrate temperature at which films are deposited. The optical properties, viz. refractive index and optical band gap, of films deposited under these three conditions were investigated in this section.

#### 4.4.1 Effect of thickness

The thickness dependent study has been performed for the optical properties of \( \text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x \) (\( x = 0, 10, 20, 30, 40, 50 \)) thin films. Thin films of three different thicknesses have been deposited on microscopic glass substrates for all the six samples of Ge-Se-Te glassy alloys. Thickness of the thin films was measured while deposition using thickness monitor (DTM-101) attached with coating unit (HINDHIVAC 12A4D). The temperature of substrate was kept at 303 K.
The transmission spectra of all the thin films have been obtained using UV-Vis-NIR spectrophotometer (Perkin Elmer Lambda-750) in the spectral range 200-1500 nm. In UV region no transmission has been observed. Figures 4.4.1 and 4.4.2 show the transmission spectra for 500 nm and 1100 nm thick films. Figures 4.3.1, 4.3.2 and 4.3.3 show transmission spectra for 800 nm thick films. Refractive index (n) has been determined from the envelope method proposed by Swanepoel using transmission data only (chapter 2). Optical band gap ($E_{opt}^c$) has been determined from the Tauc's extrapolation method (chapter 2). The accuracy in the values of thickness measured and calculated using equation (2.22) was within ± 45 nm.

The variation of refractive index with wavelength for 500 nm and 1100 nm thick films is shown in figure 4.4.3. Figures 4.3.4 and 4.3.5 show the variation of refractive index for $d = 800$ nm. Table 4.4.1 shows the refractive indices calculated at 800 nm wavelength for 500 nm, 800 nm and 1100 nm thick films.

This has been observed from table that there is almost no variation of refractive index with the change in thickness of the films from 500 nm to 1100 nm. The standard deviation in the results is almost 0.018 on the average for all compositions. So there is no change with in experimental error on the refractive index in the thickness range from 500 nm to 1100 nm. Concerning the variation of refractive index with composition, it increases with increasing Te ratio for all the thicknesses, which may be attributed to the compactness of the material and/or material aggregation leading to increase in disorder, as discussed earlier.

Figures 4.3.11 and 4.4.4 show the plots of $((ahv)^{0.5}$ versus $hv$ for the optical band gap estimation. The corresponding values of optical band gap for all composition for different $d$ values are listed in Table 4.4.1. This has been observed that the thicker films are accompanied with the larger optical band gap. This can be explained in terms of insufficient number of atoms deposited on the amorphous film, resulting in the existence of unsaturated bonds, which are responsible for the formation of some defects in the film. These, in turn, produce localized states in the band gap resulting in lowering of band gap. Thus thicker films are characterized by a homogeneous network, which minimizes the number of defects and the localized states, thereby increasing the optical band gap.
Table 4.4.1 Value of refractive index at 800 nm and optical band gap of Ge$_{10}$Se$_{50-x}$Te$_x$ ($x = 0, 10, 20, 30, 40, 50$) thin films for $d = 500$ nm, 800 nm and 1100 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Refractive Index (at 800 nm wavelength)</th>
<th>Optical Band Gap (eV) + 0.01 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500 nm</td>
<td>800 nm</td>
</tr>
<tr>
<td>0</td>
<td>2.67</td>
<td>2.69</td>
</tr>
<tr>
<td>10</td>
<td>2.85</td>
<td>2.88</td>
</tr>
<tr>
<td>20</td>
<td>3.10</td>
<td>3.12</td>
</tr>
<tr>
<td>30</td>
<td>3.25</td>
<td>3.21</td>
</tr>
<tr>
<td>40</td>
<td>3.49</td>
<td>3.52</td>
</tr>
<tr>
<td>50</td>
<td>3.84</td>
<td>3.86</td>
</tr>
</tbody>
</table>
Figure 4.4.1 Transmission spectra for 500 nm thick $Ge_{10}Se_{100-x}Te_x$ films.

Figure 4.4.2 Transmission spectra for 1100 nm thick $Ge_{10}Se_{99.5}Te_x$ films.
Figure 4.4.3 Variation of refractive index with wavelength for different thickness values ($d = 500$ nm and $1100$ nm).

Figure 4.4.4 Plots of $(\alpha h \nu)^{0.5}$ versus $h \nu$ for different thickness values ($d = 500$ nm and $1100$ nm).
4.4.2 Effect of substrate type

To study the effect of substrate material on the optical properties of thin films, three types of substrates have been used, (i) microscopic glass, (ii) quartz and (iii) mica. Films of Ge_{10-x}Se_{90-x}Te_{x} (x = 0, 10, 20, 30, 40, 50) glassy alloys were deposited on these three substrates keeping thickness at 800 nm. The normal incidence transmission spectra of films were obtained in the spectral range 200-2400 nm. In UV region no transmission has been observed. The spectrophotometer was set with a suitable slit width of one nm in the measured spectral range. Figures 4.4.5 and 4.4.6 show the transmission spectra for Ge-Se-Te films deposited on quartz and mica substrates respectively. Figures 4.3.1, 4.3.2 and 4.3.3 show transmission spectra for films deposited on microscopic glass. The refractive index (n) has been determined by the envelope method proposed by Swanepoel using transmission data only. The values of refractive indices used for three substrates are; s (microscopic glass) = 1.51, s (quartz) = 1.46, s (mica) = 1.56. The optical band gap \( E_{g}^{opt} \) has been determined from the Tauc's extrapolation method (chapter 2).

The spectral dependence of refractive index for the three substrates used is shown in figure 4.4.7. The values of refractive index at 800 nm are given in table 4.4.2. This is clear from the table that refractive index has maximum value for mica substrate while for quartz substrate it has minimum values. The trend for refractive index values is as \( n_{\text{mica}} > n_{\text{microscopic glass}} > n_{\text{quartz}} \). The higher values of refractive index for mica may be attributed to the increase of disorderness and the internal strain in the films [69]. The effect of the substrate becomes less significant with the increase in film thickness [73]. In terms of composition, refractive index increases (for all types of substrates) with the increase of Te content. This may be explained on the basis of polarizability. Larger the atomic radius of the atom larger will be its polarizability and consequently according to Lorentz- Lorenz relation of refractive index and polarizability [74] larger will be the refractive index.

Figures 4.3.11, 4.4.8 and 4.4.9 show the plots of \( (\alpha h \nu)^{0.5} \) versus \( h \nu \) for the optical band gap estimation corresponding to microscopic glass, quartz and mica substrates respectively. The values of optical band gap for all composition under investigations are also listed in table 4.4.2.
Figure 4.4.5 Transmission spectra for $Ge_{10}Se_{90-x}Te_x$ films deposited on quartz.

Figure 4.4.6 Transmission spectra for $Ge_{10}Se_{90-x}Te_x$ films deposited on mica.
Figure 4.4.7 Variation of refractive index for different substrates used for deposition of $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 10, 20, 30, 40, 50$) thin films.
Figure 4.4.8 Plots of $(\alpha h \nu)^{0.5}$ versus $h \nu$ for $\text{Ge}_{10-\alpha}\text{Se}_{\alpha}\text{Te}_{20}$ (x = 0, 10, 20, 30, 40, 50) thin films deposited on quartz substrates.
Figure 4.4.9 Plots of $(\alpha h \nu)^{0.5}$ versus $h \nu$ for Ge$_{10}$Se$_{90-\chi}$Te$_{\chi}$ ($\chi = 0, 10, 20, 30, 40, 50$) thin films deposited on mica substrates.
Table 4.4.2 Value of refractive index at 800 nm and optical band gap of Ge\textsubscript{10}Se\textsubscript{90-x}Te\textsubscript{x} (x = 0, 10, 20, 30, 40, 50) thin films deposited on different substrates.

<table>
<thead>
<tr>
<th>x</th>
<th>Refractive Index (at 800 nm)</th>
<th>Optical Band Gap (eV) ± 0.01 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Microscopic glass</td>
<td>Quartz</td>
</tr>
<tr>
<td>0</td>
<td>2.69</td>
<td>2.65</td>
</tr>
<tr>
<td>10</td>
<td>2.88</td>
<td>2.85</td>
</tr>
<tr>
<td>20</td>
<td>3.12</td>
<td>3.00</td>
</tr>
<tr>
<td>30</td>
<td>3.21</td>
<td>3.16</td>
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<tr>
<td>40</td>
<td>3.52</td>
<td>3.46</td>
</tr>
<tr>
<td>50</td>
<td>3.86</td>
<td>3.81</td>
</tr>
</tbody>
</table>
The films deposited on mica substrates have lower optical energy gap compared to films deposited on glass and quartz substrates. The low values of $E_{\text{opt}}^g$ of films grown on mica may be attributed to that there might be some dangling bonds on the mica which may further contribute to the defects at substrate film interface. These defects may lead to decrease in $E_{\text{opt}}^g$. In such systems the degree of chemical order has a considerable effect on the band-gap. The chemical order and structured features depend in principle on the composition and deposition parameters, such as substrate type. The effect of the substrate becomes less significant with the increase in film thickness. These results are in good agreement with the results reported for Ge-Se-Bi-S system [73].

4.4.3 Effect of substrate temperature

The effect of substrate temperature on the optical properties, optical band gap and refractive index, of thermally deposited Ge$_{10}$Se$_{90-x}$Te$_x$ ($x = 0, 10, 20, 30, 40, 50$) thin films have been reported using transmission data. Thin films of the glassy alloys were prepared on glass substrates by vacuum evaporation technique at three different substrate temperatures 303 K, 363 K and 423 K. Thickness of the films has been kept at 800 nm. XRD patterns of Ge$_{10}$Se$_{90-x}$Te$_x$ ($x = 0, 10, 20, 30, 40, 50$) thin films deposited at 303 K reveals the amorphous nature of the films as they do not show any spectacular peak (figure 4.1.2) while those deposited at 363 K (figure 4.4.10) and 423 K (figure 4.4.11) show the polycrystalline nature of films. The normal incidence transmission spectra in the spectral range 200-1500 nm of Ge$_{10}$Se$_{90-x}$Te$_x$ ($x = 0, 10, 20, 30, 40, 50$) thin films were obtained by a double beam ultraviolet-visible-near infrared spectrophotometer [Perkin Elmer Lambda-750]. All transmission spectra were obtained at room temperature (300 K). Transmission spectra of films deposited at 363 K and 423 K have shown in figures 4.4.12 and 4.4.13 respectively. Figures 4.3.1, 4.3.2 and 4.3.3 show transmission spectra for films deposited at 303 K.

Refractive index ($n$) has been determined from the envelope method and optical band gap ($E_{\text{opt}}^g$) from Tauc extrapolation method for all the films deposited at three different substrate temperatures. The spectral dependence of refractive index has been shown in figure 4.4.14. The values of refractive index at 800 nm are given in
**Figure 4.4.10** XRD pattern of Ge$_{10}$Se$_{90-x}$Te$_x$ films deposited at substrate temperature of 363 K.

**Figure 4.4.11** XRD pattern of Ge$_{10}$Se$_{90-x}$Te$_x$ films deposited at substrate temperature of 423 K.
Table 4.4.3 Value of refractive index at 800 nm and optical band gap of \( \text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x \) \((x = 0, 10, 20, 30, 40, 50)\) thin films deposited for different substrate temperatures.

<table>
<thead>
<tr>
<th>(x)</th>
<th>(303\text{ K})</th>
<th>(363\text{ K})</th>
<th>(423\text{ K})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_g^{\text{opt}}) (eV)</td>
<td>n</td>
<td>(E_g^{\text{opt}}) (eV)</td>
<td>n</td>
</tr>
<tr>
<td>0</td>
<td>1.87</td>
<td>2.69</td>
<td>1.82</td>
</tr>
<tr>
<td>10</td>
<td>1.62</td>
<td>2.88</td>
<td>1.59</td>
</tr>
<tr>
<td>20</td>
<td>1.46</td>
<td>3.12</td>
<td>1.40</td>
</tr>
<tr>
<td>30</td>
<td>1.27</td>
<td>3.21</td>
<td>1.21</td>
</tr>
<tr>
<td>40</td>
<td>1.12</td>
<td>3.52</td>
<td>1.09</td>
</tr>
<tr>
<td>50</td>
<td>1.03</td>
<td>3.86</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Figure 4.4.12 Transmission spectra of Ge$_{10}$Se$_{90-x}$Te$_{x}$ films deposited at 363 K.

Figure 4.4.13 Transmission spectra of Ge$_{10}$Se$_{90-x}$Te$_{x}$ films deposited at 423 K.
Figure 4.4.14 Variation of refractive index for different substrate temperatures of deposition for Ge$_{10}$Se$_{90-x}$Te$_x$ ($x = 0, 10, 20, 30, 40, 50$) thin films.
Figure 4.4.15 Plots of \((\alpha h \nu)^{0.5}\) versus \(h \nu\) for different substrate temperatures of deposition for Ge\(_{10}\)Se\(_{90-x}\)Te\(_x\) (\(x = 0, 10, 20, 30, 40, 50\)) thin films.
table 4.4.3 for comparison sake. It is seen from the table that there is almost no change in the refractive index with the increase of substrate temperature. According to Lorentz-Lorenz relation [75], refractive index depends on polarizability which further depends on the covalent radius (Ge = 122 pm, Se = 117 pm, Te = 137 pm [20]) of atom. So the refractive index shows its dependence on the composition of films (table 4.4.3). It does not show any dependence on the substrate temperature. The optical band gap \( (E_{g}^{opt}) \) has been estimated using the Tauc relation [65],

\[ a h \nu = B (h \nu - E_{g}^{opt})^{n} \]

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. This relationship allows us to estimate the value of optical band gap. For substrate temperatures 303 K, 363 K and 423 K the plots of \( (a h \nu)^{0.5} \) versus \( h \nu \) are shown in figure 4.4.15.

The values of the optical band gap for the thin films under investigation corresponding to different substrate temperatures are given in table 4.4.3. The optical gap has been found to decrease with the increase of substrate temperature for all the thin films. This reveals the increase in crystallinity of compositions [77]. Substrate temperature higher than room temperature may have enough vibrational energy to break some of the weaker bonds, thus introducing some translational degrees of freedom to the system. Consequently, increase in crystallinity via nucleation and growth becomes possible [78]. The area occupied by the crystallites increases, where some of them may be interconnected and some may be isolated, due to which there may be a decrease in optical gap. The decrease in energy gap and the increase in the width of localized state tails with the increase in substrate temperature can be interpreted by assuming it to be the product of surface dangling bonds around the crystallites during the process of crystallization. The obtained values of optical gap are in good agreement with that reported previously [79-81]. This is also observed that the optical gap decreases with the increase of Te content for all substrate temperatures. The shrinking of optical gap with increasing Te content can be correlated with increase in covalent character of glass network. Since Ge-Te bonds (~
99\% covalent) are more covalent than Ge-Se (\~90 \% covalent) so optical gap decreases with the increase in Te contents. A detailed discussion on the decrease of optical gap with Te content is given in section 4.3.4.

4.4.4 Conclusion

Optical properties of Ge\textsubscript{10}Se\textsubscript{90-x}Te\textsubscript{x} (x = 0, 10, 20, 30, 40, 50) thin films have been studied for different deposition conditions, i.e. thickness, type of substrate and substrate temperature. The concluding points are summarized below:

- With the increase of thickness (500 nm - 1100 nm) the optical band gap has been found to increase while no significant change has been observed for refractive index with in experimental errors.
- For different substrate used in deposition of thin films the refractive index follows the order as \( n_{\text{mica}} > n_{\text{microscopic glass}} > n_{\text{quartz}} \). The optical band gap for mica substrate is the smallest whereas no significant change has been observed for microscopic glass and quartz substrate.
- With the increase of substrate temperature (i.e. from 303 K – 423 K) refractive index remains unchanged while optical band gap decreases.
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