Chapter 5

Summary and Conclusion

This chapter summarizes the results obtained from various characterizations performed on bulk and thin film samples of \((\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ag}_x\) \((0 \leq x \leq 4)\) system and conclusion drawn for the system under study. The outline of the future work that can be accomplished for better understanding and exploring technological importance of the material is also presented in the following section.

5.1 Summary and Conclusion

Bulk samples of \((\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ag}_x\) \((0 \leq x \leq 4)\) system were prepared by the conventional melt quenching technique and thin films were deposited by thermal evaporation technique. The following conclusions have been drawn from the present study.

1. Bulk samples of the \((\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ag}_x\) \((0 \leq x \leq 4)\) were prepared by melt quenching technique. The materials of high purity were sealed in the high vacuum of \(10^{-5}\) mbar in the quartz tube. The sealed quartz tube is kept at 1373K for 72h in the furnace. The quenching is done by putting the quartz tube in ice water. The bulk alloy thus obtained was used to grow the thin films on well cleaned corning glass substrate. Utmost care was taken to clean the ampoules used for preparing the bulk material and the slides for growing thin films.

2. The as-prepared bulk samples of \((\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ag}_x\) \((0 \leq x \leq 4)\) system were found amorphous from XRD studies. The bulk samples of \((\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ag}_x\) \((0 \leq x \leq 4)\) system were annealed at 348K and 398K for 12h show the sharp peaks in XRD patterns, which confirms the existence of different microcrystalline phases in the samples. The identified crystalline phases are \(\text{Se}_8\) and \(\text{Ag}_5\text{Te}_3\). Thin films of \((\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ag}_x\) \((0 \leq x \leq 4)\) system were annealed \(~15K\) above their \(T_g\) for 2h show the presence of sharp peaks in XRD spectra indicated the presence of \(\text{Se}_8\), \(\text{Te}, \text{Ag}_2\text{Se}, \text{Ag}_2\text{Te}\) and \(\text{Ag}_5\text{Te}_3\) crystalline phases. These microcrystalline phases have been identified from the JCPDS database (1998).

3. DSC studies were performed on the powder samples of \((\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ag}_x\) \((0 \leq x \leq 4)\) system at four different heating rates viz. 5, 10, 15 and 20K/min.
DSC thermograms shows only one glass transition temperature and one exothermic crystallization peak but two endothermic melting peaks. The presence of two peaks means that there are two phases with melting temperatures represented as $T_{m1}$ and $T_{m2}$. The analysis of XRD results using JCPDS database (1998) indicates the formation $\alpha$Ag$_5$Te$_3$ crystalline phase. This phase probably gives the peak at 294°C in DSC runs. DSC traces for $(Se_{80}Te_{20})_{98}$Ag$_2$ samples at different heating rates show the shift in glass transition temperature towards higher temperature with increase in the heating rate. However the glass transition and crystallization temperature decreases with the increase in Ag content. The reason behind the decrease in $T_g$ is decrease in number of long Se–Te polymeric chains and Se–Te mixed ring rings but increase in the Se$_8$ rings concentration. The values of $T_g$ are higher than room temperature which is a desirable result as it will avoid self transition at room temperature from amorphous to crystalline phase. The dependence of $T_g$ on the heating rate has been studied using Lasoka formulation. The apparent activation energy of glass transition ($E_t$) were calculated using Kissinger’s equation. The apparent activation energy of glass transition increase with increase in Ag content, which has been explained on the basis of average heat of atomization ($H_a$). The exothermic peaks on deconvolution gives two crystallization temperatures ($T_{c1}$ and $T_{c2}$) and two peak crystallization temperatures ($T_{p1}$ and $T_{p2}$) corresponding to the first and second peaks respectively. The apparent activation energy for crystallization ($E_c$) has been calculated using Kissinger’s formulation. Thermodynamic parameters i.e enthalpy, entropy, fragility, Gibbs free energy and specific heat are also determined from the DSC plots. From these thermodynamic parameters we observed that the stability of the sample is least for $x = 1$ and increase to maximum for $x = 3$. The viscosity calculations of the system have been undertaken by using Vogel–Tamman–Fulcher equation.

4. Thin films of $(Se_{80}Te_{20})_{100-x}$Ag$_x$ ($0 \leq x \leq 4$) system (Thickness ~943 to 962nm) and $(Se_{80}Te_{20})_{96}$Ag$_4$ composition of different thickness (~504 to 960nm) have been prepared by thermal evaporation technique. The optical properties have been determined by transmission (T) and reflection (R) spectra in the spectral range of 500–2500nm. XRD pattern of $(Se_{80}Te_{20})_{100-x}$Ag$_x$ ($0 \leq x \leq 4$) and
(Se$_{80}$Te$_{20}$)$_{0.96}$Ag$_4$ thin films of different thickness show the amorphous nature. The atomic percentage ratio of Se, Te and Ag present in (Se$_{80}$Te$_{20}$)$_{100-x}$Ag$_x$ ($0 \leq x \leq 4$) thin films is determined by EDX. The SEM micrograph of (Se$_{80}$Te$_{20}$)$_{0.96}$Ag$_4$ thin film shows the smooth surface with featureless background. The compositional dependent studies show that the maxima and minima of the fringes shift towards the shorter wavelength region (blue shift) with increase in Ag content. Thickness dependent studies show the red shift occurs in the interference free region with increase in thickness. The optical band gap ($E_g$) has been determined from the Tauc extrapolation. For compositional dependent studies $E_g$ increase with increase in Ag content and it has been explained on the basis of decrease in the density of defect states. However for thickness dependent studies the $E_g$ decrease with increase in thickness which has been explained on the basis of quantum sizes effect. For compositional and thickness dependent studies the refractive index (n) and extinction coefficient (k) decrease with increase in wavelength. The change in the value of n with Ag content may be due to the change in stoichiometry and internal strain of glassy alloy. The decrease in the n with Ag content is due to decrease in density of the (Se$_{80}$Te$_{20}$)$_{100-x}$Ag$_x$ ($0 \leq x \leq 4$) system. However for thickness dependent studies the n increase with increase in thickness, the results are explained on the basis of change in density and/or the polarizability of the (Se$_{80}$Te$_{20}$)$_{0.96}$Ag$_4$ thin films. The oscillator strength ($E_o$) and dispersive energy ($E_d$) increase with increase in Ag content, while the optical conductivity ($\sigma$), real ($\varepsilon_r$) and imaginary parts ($\varepsilon_i$) of dielectric constant decreases with the increase in Ag content. For thickness dependent studies, the $E_d$, $\sigma$, $\varepsilon_r$ and $\varepsilon_i$ increases with the increase in thickness. The results are explained on the basis of change in defects and disorder in system.

5. The measurement of the temperature dependence photoconductivity at different intensities (0–1200lux) indicates that photoconductivity is also thermally activated in the temperature range 263–333K in all the samples studied as in case of dark conductivity. Dark conductivity ($\sigma_d$) and photoconductivity ($\sigma_{ph}$) increase with the increase in Ag concentration and intensity. This indicates the shift in the Fermi level due to splitting of the Fermi level into the quasi-Fermi level.
levels. The measurements of intensity dependence of $\sigma_{ph}$ show that the $\sigma_{ph}$ increases with intensity as a power law where the power is found to be between 0.5 and 1.0 for the glassy alloys. This indicates that there is a continuous distribution of the localized states existing in the mobility gap of glassy system under study. From the transient photoconductivity measurements on the thin film of a-(Se$_{80}$Te$_{20}$)$_{98}$Ag$_2$ glassy system, it has been observed that the rise and decay of the photoconductivity show the similar behavior for the different intensities. It has been observed that the photoconductivity increases with time, reaches its maximum value and then decreases; the decrease may be due to the appearance of a negative Dember voltage and the interaction between the holes and the trapped electrons on the surface.

6. Ultra-thin films (Thickness~76 to 81nm) of (Se$_{80}$Te$_{20}$)$_{100-x}$Ag$_x$ ($0 \leq x \leq 4$) system were prepared by thermal evaporation technique. The effect of thermal annealing on the optical properties was investigated by studying the T and R spectra in spectral range 300–1100 nm for the as-prepared as well as for the annealed (Se$_{80}$Te$_{20}$)$_{100-x}$Ag$_x$ ($0 \leq x \leq 4$) ultra-thin films. The structure of the as-prepared (Se$_{80}$Te$_{20}$)$_{100-x}$Ag$_x$ ($0 \leq x \leq 4$) ultra-thin films has been studied by XRD. XRD pattern of the as-prepared (Se$_{80}$Te$_{20}$)$_{100-x}$Ag$_x$ ($0 \leq x \leq 4$) ultra-thin films show the amorphous nature of the sample. However the XRD spectra of (Se$_{80}$Te$_{20}$)$_{100-x}$Ag$_x$ ($0 \leq x \leq 4$) ultra-thin films annealed at 343K (in between $T_g$ and $T_c$) shows the existence of different micro-crystalline phases. According to the JCPDS database (1998) the identified crystalline phases are Se$_8$, Te, Ag$_2$Se and Ag$_2$Te. The T and R spectra show clear blue shift of interference-free region with increasing Ag content. An increase in the magnitude of the measured T accompanied by a decrease in the R is observed for fresh and annealed films against the increase in Ag content. The decrease in the transmittance upon annealing was considered to be due to the nucleation of scattering centers or crystal growth in the bulk of the material. The $E_g$ has been determined by the Tauc’s extrapolation. The increase in the $E_g$ with increase in Ag content and with annealing below $T_g$ may be due to a decrease in disorder and defects. During annealing temperature higher than $T_g$, the $E_g$ increases with increase in annealing temperature. These results can be interpreted by assuming the
production of surface dangling bonds around crystallites during the process of crystallization. $E_u$ often regarded as the disorder parameter is calculated for as-prepared as well as annealed ultra-thin films. The observed trend of $E_u$ with Ag content and with annealing supports the behavior of $E_g$ in the given system. SEM micrographs of the as-prepared $(\text{Se}_{80}\text{Te}_{20})_{98}\text{Ag}_2$ and $(\text{Se}_{80}\text{Te}_{20})_{96}\text{Ag}_4$ and annealed $(\text{Se}_{80}\text{Te}_{20})_{96}\text{Ag}_4$ ultra-thin film (below $T_g$) are also reported. These micrographs have stone-like crystals which are of different sizes and shapes. SEM micrographs give the clear indication of increase in size of stone-like crystals with increase in Ag content and with annealing. The existence of stone-like crystals of different shapes that may be attributed to the formation of Ag$_2$Se or Ag$_2$Te nanophases alone or collectively in Se–Te–Ag thin films. The optical parameters like $n$ and $k$ are also reported. The $n$ and $k$ decrease with increase in wavelength for as-prepared as well as annealed ultra-thin films. The variation in the value of $n$ and $k$ of annealed thin films from the as-deposited thin films is interpreted on the basis of increase in the reflection or decrease in the transmission of annealed $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ag}_x$ $(0 \leq x \leq 4)$ thin films, which may be due to the change in surface roughness of the films. The other optical parameters like the real and imaginary dielectric constant are also reported. The variation of dark conductivity ($\sigma_d$) with temperature of as-prepared and annealed $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ag}_x$ $(0 \leq x \leq 4)$ ultra-thin films in the temperature range 288–358K has also been reported. The increase in dark conductivity with increase in temperature is observed for all samples. The variation in value of activation energy with Ag content and with annealing is found to be associated with the shift in Fermi level. The studied system is found to obey the MN rule in as-prepared and annealed thin films. The pre-exponential factor $\sigma_0$ values suggested the conduction of charge carriers in tail states.

5.2 Scope for Future Work

A lot of information is gathered from the presented work but a lot more can be done for more detailed understanding of the selected system.

1. Local structure of the material and its changes on the atomic scale independent of the state of material can be investigated by X-Ray absorption fine-structure
spectroscopy (XAFS). X-ray absorption near edge structure (XANES) can also be performed for much better understanding of the local structure.

2. DSC studies for higher heating rates (up to 100 K/min) in order to have a better understanding of the dependence of $T_g$ and $T_p$ on heating rates.

3. The optical, electrical and thermal studies can be done at higher concentration of silver for better understanding of the system.

4. Raman spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR) studies can be done to have knowledge about the structure of the samples.

5. The ion irradiation of the samples should be done to measure the effects of irradiation on the films.

6. The a.c. conductivity of all the samples should be done for having an idea about the defects present in the system.

7. Photoluminescence studies should be performed on the samples.

8. The effect of annealing can be checked by keeping it for long duration of time.

9. The cyclic voltametry should be performed on the $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ag}_x$ $(0 \leq x \leq 4)$ films to better understand the polarization effects in the present system.