EFFECT
OF
SILVER DISSOLUTION
ON
ELECTRICAL PROPERTIES
OF
\( a-\text{Ge}_x\text{Se}_{100-x} \)

Chapter 4
4.1 INTRUCTION

Development of modern technology led to the appearance of new family of materials. Chalcogenide Glasses Semiconductors are one of these families due to their interesting properties. Amorphous semiconductors from Se-based system such as Ge$_x$Se$_{100-x}$ have attracted much attention in recent years. This family of chalcogenide glasses can provide an ideal system for investigation. The melts of many IV-VI substances can be cooled sufficiently fast, to bypass crystallization and form the glassy state. The variation of the Ge$_x$Se$_{100-x}$ structure is reflected in different studies like photo luminescences, IR and optical properties [141-146]. Changing the physical properties of these materials at a specific composition reflects the most interesting information. The glass transition has been treated by various theoretical approaches. It is suggested that this property shows a first, second or even third-order transition [147]. Some others have claimed that there is no true phase transition at all [148]. According to Phillips et al [149], the glass forming difficulty with x undergoes a minimum at x $\approx$ 50. Also, a maximum glass transition temperature has been observed at the stoichiometric composition, at x = 20 (Ge$_x$Se$_{100-x}$) [144]. Optical properties of IV-VI compounds have been studied by many investigators [142-146, 151-153]. Experimental data have been reported on the electrical conductivity and refractive index depending on the Ge content in the Ge$_x$Se$_{100-x}$ alloy prepared by different techniques.

Ge$_{15}$Se$_{100-x}$ (x = 15, 20 and 25) is being actively investigated as high efficiency semiconductors for xerography, switching and memory
devices and reversible phase change optical recording [154-159]. Exposure to light or heat that excites electron-hole pairs produces structural changes in nearly all chalcogenide glasses. The results change with atomic configuration, and a subsequent change in the physical properties such as structure, optical and electrical properties of the material [160-162].

4.1.1 Mechanism of Silver Photo Doping in Ge-Se System

The process termed as photodoping, photodissolution, photo enhanced diffusion or photo dissociation, has been found in a wide class of amorphous chalcogenide semiconductors when contacted with a metal such as Silver.

The role of Silver as a dopant in chalcogenide glasses is of technical interest, although the basic issue remains unresolved. The mechanism of photodoping has been controversial for more than a quarter of a century [163-168]. Despite the universality and the technological importance of photodoping, the understanding of its mechanism remains unresolved.

Photodoping results from photoinduced migration of metallic ions in chalcogenide glasses [169]. Detailed studies on electrical properties, of Ag-Ge-Se glasses suggest that diffusion and drift of photo excited holes induce migration of Ag$^+$ ions [170]. It should be noted that in the chalcogenide glasses of interest, holes are more mobile than electrons in marked contrast to the electron-dominated characteristic of Ag-halide crystals [171]. Ag-Ge-Se glasses also exhibit photo surface deposition [172-175] and photo chemical modification [176]. The mechanism of these phenomena can also be understood in a similar way to that of the photo doping phenomenon [171, 175 and 176]. Having understood the motive force behind Ag$^+$ ion migration, scientists in this field would like to see single-ion motion so that atomic manipulation will be possible.
In general, we can say that, the mechanism responsible for photodoping phenomenon is photoinduced Ag\(^+\) motion. The defect states in real non-crystalline semiconductors control the electronic properties of disordered semiconductors. The defects in chalcogenide amorphous semiconductors corresponding to deviations from normal bonding configurations control the electronic properties. Mott et al [177] proposed that the defect states D\(^+\), D\(^0\), D\(^-\) (having no electron, one electron and two electrons respectively) are responsible for pinning the Fermi level in these semiconductors which are generally always p-type and are relatively insensitive to the additions of foreign impurity atoms.

However, if the addition of impurity is able to alter the ratio of the charged dangling bonds, the conductivity may be increased by many orders of magnitude and even reversal of conduction type may occur [122].

### 4.1.2 Electrical Properties of Pure and Silver Doped Ge\(_x\)Se\(_{100-x}\)

As already mentioned, generally, dc conductivity in chalcogenide glasses is a linear function of 1/T and near room temperature it has an Arrhenius type of temperature variation. Hauser et al [178 and 179] reported deviation from linearity at low temperatures for some chalcogenides. Mott and Street [180] suggested that this deviation may be due to close proximity of D\(^+\) and D\(^-\) centres, forming a dipole, whose concentration depends on the rate of cooling. Ac conductivity has been reported for a wide variety of amorphous chalcogenides. The temperature and frequency dependence of ac conductivity has been reported for a wide range of operating temperatures/frequencies.

In lower temperature range (<100K), the ac conductivity in chalcogenide glasses is relatively temperature independent but the
frequency dependence is linear at the lowest temperatures. The experimental ac conductivity in these glasses at low temperatures is not explained by making use of “CBH” model as the transition mechanism tends towards quantum limit. The atomic tunnelling model may be used to explain the anomalous behaviour of these glasses at low temperatures. But experimentally, various atomic tunnelling parameters, i.e. asymmetry energy band width, the width $\lambda_0$ of the distribution function, dipole moment $P_0$, are not yet known with certainty. Hence, it is difficult to estimate the density of atomic sites responsible for conduction, although work done at low temperatures on glassy As$_2$S$_3$ [181] gives density of states ($1.6\times10^{18}\text{cm}^{-3}$) which matches with the value at high temperatures.

In the intermediate temperatures (100K-300K), the frequency exponent “$s$” is temperature dependent (in which case it takes value near unity), or it decreases from unity with increasing temperature. Figure 1.8 (described earlier) clearly depict that this behaviour of QMT model and Small Polaron Tunnelling model. Further according to QMT model, the ac conductivity should be linearly dependent on temperature but such a sample Temperature dependence is not observed in case of chalcogenides. Therefore, there is significant evidence that rules out the QMT or small polaron formation being the leading mechanisms in case of chalcogenides. The fact that frequency exponent “$s$” of $\sigma(\omega)$ is temperature dependent, is a signature of the fact that the hopping length at a particular frequency is a function of temperature. This behaviour of chalcogenides can be well accounted for by using the CBH model. Most of the properties of these glasses, in the intermediate range of temperatures, are accounted for by using CBH model.

At high temperatures (>300 K), the temperature dependence of ac conductivity appears to become much stronger than at low temperatures. The high temperatures behaviour of chalcogenides has been accounted
for by using the Correlated Barrier Hopping of single polaron centres [182]. For Chalcogenide glasses, it is assumed that an electron (or hole) hops between \( D^- \) and \( D^0 \) (or \( D^+ \) and \( D^0 \)) centres. For materials with large negative correlation energy “\( U_{\text{eff}} \)” at intermediate temperatures, the equilibrium (2 \( D^0 \rightarrow D^- + D^+ \)) (equation 1.46) will lie well over to the right, and so bipolaron hopping between \( D^- \) and \( D^+ \) centre is dominant, as has been assumed so far. Therefore, at high temperatures, particularly for materials having small values of “\( U_{\text{eff}} \)” number of thermally generated \( D^0 \) centres will be produced with a temperature dependent concentration given as:

\[
N_0 = N_s \exp \left( -\frac{U_{\text{eff}}}{KT} \right) \tag{4.1}
\]

Where \( N_s \) is the concentration of \( D^- \) or \( D^+ \) centres at \( T = 0\)°K (i.e. in the absence of \( D^0 \) centres). It is assumed that half of the \( D^0 \) centres created by the reaction ([\( D^- \]) + [\( D^+ \]) \rightarrow 2 [\( D^0 \]) mentioned in (1.46)) contribute relaxation between \( D^0 \) and \( D^- \) (shown as Process II in Fig. 1.9) and other half to relaxation between \( D^0 \) and \( D^+ \) (shown as Process III in Fig. 1.9). The defect concentration \( N_{NP} \) is given as:

\[
N_{NP} = \frac{N_s}{2} \tag{4.2}
\]

For bipolaron hopping, process II, Fig. 1.9)

\[
N_{NP} = \frac{N_s^2}{2} \exp \left( -\frac{W_1}{kT} \right) \tag{4.3}
\]

(For single polaron hopping, process III Fig. 1.9)

Where the maximum barrier height “\( W_M \)” is equal to “\( W_1 \)” for process II and “\( W_2 \)” for Process III.

Therefore, as already mentioned in section (1.2.3) the total conductivity as a function of temperature and frequency can be written as:

\[
\sigma(\omega) = \sigma_{ac}(b) + \sigma_{ac}(s) + \sigma_{dc} \tag{1.50}
\]
The ac behaviour of chalcogenide glasses have been therefore studied both experimentally and theoretically by using CBH model where bipolaron hopping dominates in the intermediate temperature range and single polaron hopping dominates at higher temperatures.

### 4.1.3 Aim of this work

Germanium Selenium compound exhibits properties which are unusual, and possibly unique, relative to other semiconductors and these unusual characteristics have obviously added much flavour to the stimulated study. However, interest in the basic properties of this amorphous semiconductor has been the reason for many investigations of scientists as well as engineers.

Chalcogenide glasses are materials having short range order with sharp mobility edge and charged defect states. Unique properties of these glasses can be studied by using the concept of charged dangling bonds, (D+ and D') but the role of impurities and defect states in these materials are yet not clearly understood.

Indeed, Ag-Ge₅Se₁₀₀₋ₓ is an important glass for which a large number of investigations have been made on its electrical properties. The application of photodoping of transition metals in Ge₅Se₁₀₀₋ₓ glass, have been studied by many workers [183-185]. One of the remarkable developments is to the photolithography technique [183-185]. It is therefore, desirable to study the effect of transition metals such as Ag on electrical properties of Ge₅Se₁₀₀₋ₓ.

In present work, the effect of Ag-doping in electrical properties of a-Ge₅Se₁₀₀₋ₓ has been studied.
4.2 EXPERIMENTAL RESULTS

Electrical conductivity, which is the ability to conduct electrical current under the application of a voltage, has one of the widest ranges of values of any physical properties of matter. The increase in conductivity with temperature, light or impurities arises from an increase in the number of conduction electrons which are the carriers of the electrical current. To produce conduction electrons, temperature or light is used to excite the valence electrons out of their bonds, having them free to conduct current.

Deficiencies or holes are left behind that contribute to the flow of electricity. This is the physical origin of the increase in electrical conductivity of semiconductors with temperature.

A method to produce free carriers of electricity is to add impurities to, or to dope the semiconductors. The difference in the number of valence electrons between the doping material or doping and host gives rise to negative or positive carriers of electricity.

4.2.1 Preparation of Germanium Selenium Glass (Pure and Silver Doped)

Amorphous Ge\textsubscript{x}Se\textsubscript{100-x} prepared by quenching the melt, are ingots which are hard solid pieces of materials having irregular shapes. Obviously, these ingots have to be processed to make sample for different measurements.

Different investigators have either carried out their reported measurements on bulk samples (compressed pellets) or thin films. It means that, the observed behaviour of conductivity has not been found to depend on the form of sample used for measurements. One could, therefore, safely use a compressed pellets or a thin film which ever is acceptable to the measuring instrument.
Compressed pellets are prepared by grinding the bulk-ingots into fine powder and compressing the powder in a die under a hydraulic pressure. While making compressed pellets, one must ensure that the powder is compressed to maximum compaction so that there are no voids in the sample. Obviously, the amount of compression (pressure) is decided by the size of the sample and nature of the material.

Hundreds of strong pellets (diameter = 0.68 cm and thickness ~ 0.07 cm) have been prepared in our laboratory and it has been experienced that a hydraulic pressure of about 10^6 Kg/m is good enough for providing maximum compaction.

The users of compressed pellets claim that such samples can obtain precisely of the required dimensions having uniform surface and sharp edges. However, diffusion of the electrode-elements cannot be eliminated in pellets as well.

4.2.2 DC Conductivity Behaviour of Amorphous Ge_xSe_100-x

The measurements of dc conductivity in case of amorphous semiconductors have yielded valuable information about the transport mechanism. The majority of amorphous semiconductors (chalcogenides and tetrahedrals, annealed at high temperatures) show activated temperature dependence according to the relation (σ = σ₀ exp (-ΔE₀/kT) (3.2)), Where ΔE₀ and σ₀ are the activation energy and pre-exponential factors respectively. These parameters are of significance to differentiate the various conduction mechanisms. The high value of ΔE₀ (of the order of half the mobility gap) suggests that condition occurs either in the extended states beyond the mobility edge or in the localized states at the band edge. However, Mott has shown that the magnitude of σ₀ is about 10^1.
two to three orders higher for extended states conduction than that associated with the localized states conduction. Most of the tetra-hedral films, exhibit variable range hopping conduction amongst the localized states near the Fermi level which helps in determining the density of localized states at the Fermi level. The effect of annealing on dc conductivity also provides information about the charge transport.

Figure 4.1 shows temperature dependence of dc conductivity for different compositions of undoped Germanium Selenium in the temperature range of 273K - 373 K. It can be observed from this figure that the dc conductivity is singly activated in the entire temperature range investigated. From the figure, it is evident that dc conductivity decreases with decreasing temperature.

The activation energies for Ge$_{15}$Se$_{85}$, Ge$_{20}$Se$_{80}$ and Ge$_{25}$Se$_{75}$ were 0.93 eV, 0.76 eV and 0.90 eV respectively.

![Fig. 4.1, Temperature dependence of dc Conductivity for different percentages of undoped Ge$_x$Se$_{100-x}$.](image)
4.2.3 AC Conductivity Behaviour of Amorphous Ge\textsubscript{x}Se\textsubscript{100-x}

The results of ac conductivity for Ge\textsubscript{x}Se\textsubscript{100-x} system at different temperatures and frequencies have been shown in Figs 4.2, 4.3 and 4.4. From these figures it is clear that \( \sigma_{ac} = A\omega^s \), where “s” is frequency exponent and “A” is a constant. The decrease in slope with increasing temperature clearly indicates that, the value of “s” decreases with increasing temperature for all samples.

Shimakawa [59] through data fitting could somehow explain temperature dependence of ac conductivity at lower temperatures (below room temperature).

Measurements have been made at different frequencies and different temperatures for the bulk samples of Ge\textsubscript{x}Se\textsubscript{100-x}. For these measurements, the procedure which discussed earlier in section 2.1.7 has been used. Using a modified Correlated Barrier Hopping Model (CBH) [8, 9], the above results can be easily explained.

![Log of ac Conductivity versus log of frequency for Undoped a-Ge\textsubscript{15}Se\textsubscript{85}](image)

*Fig. 4.2, Log of ac Conductivity versus log of frequency for Undoped a-Ge\textsubscript{15}Se\textsubscript{85}.*
Fig. 4.3, Frequency dependence of ac conductivity at different temperatures for Undoped a-Ge$_{20}$Se$_{80}$.

Fig. 4.4, Log of ac Conductivity versus log frequency for Undoped a-Ge$_{25}$Se$_{75}$. 

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This model is the most widely accepted model to describe the approximately frequency independent behaviour of "s" as observed by the author. The temperature dependence of "s" for Ge$_x$Se$_{100-x}$ (x = 15, 20 and 25) is given in fig. 4.5. The figure indicates that with increasing percentage of Ge in the system, the value of "s" increases. The value of "s" is correlated with the value of "W_M", maximum barrier height through the relation given by equation (1.40). Therefore, an increase in the value of "s" predicts an increase in value of "W_M". The temperature dependence of ac conductivity for Ge$_x$Se$_{100-x}$ (x = 15, 20 and 25) is given in figures 4.6, 4.7 and 4.8.

The Correlated Barrier Hopping "CBH" model has been used to get the best possible fits for these graphs (calculations have been made using equation 1.40 to calculate conductivity at different temperatures and frequencies). Theoretically calculated values of ac conductivity are plotted along with experimental points in Figs. 4.6, 4.7 and 4.8.

![Fig. 4.5, Temperature dependence of frequency exponent "s" for different Undoped samples of Ge$_x$Se$_{100-x}$ system.](image-url)
Figure 4.6. Temperatures dependence of ac Conductivity at (a) 5 KHz, (b) 10 KHz and (c) 20 KHz for a-Ge_{15}Se_{85}.
Fig. 4.7, Temperatures dependence of ac Conductivity at (a) 5 KHz, (b) 10 KHz and (c) 20 KHz for $a$-Ge$_{20}$Se$_{80}$. 

O Experimental  Bipolaron Hopping
--- Single Polaron Contribution  Sum of all
**Fig. 4.8.** Temperatures dependence of ac Conductivity at (a) 5 KHz, (b) 10 KHz and (c) 20 KHz for $\text{a-Ge}_{25}\text{Se}_{75}$. 

![Graphs showing ac Conductivity](image_url)
The figures clearly indicate that the theoretical calculations fit well with the experimental results. The different values of parameters used for these calculations are given in Table 4.1.

### Table 4.1

Parameters used for CBH Model Fitting for Undoped Ge<sub>x</sub>Se<sub>100-x</sub>

<table>
<thead>
<tr>
<th>GLASS</th>
<th>W&lt;sub&gt;M&lt;/sub&gt; (eV)</th>
<th>W&lt;sub&gt;1&lt;/sub&gt; (eV)</th>
<th>W&lt;sub&gt;2&lt;/sub&gt; (eV)</th>
<th>U&lt;sub&gt;eff&lt;/sub&gt; (eV)</th>
<th>N&lt;sub&gt;T&lt;/sub&gt; (cm&lt;sup&gt;-3&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge&lt;sub&gt;15&lt;/sub&gt;Se&lt;sub&gt;85&lt;/sub&gt;</td>
<td>1.55</td>
<td>0.50</td>
<td>0.50</td>
<td>0.55</td>
<td>2.40E18</td>
</tr>
<tr>
<td>Ge&lt;sub&gt;20&lt;/sub&gt;Se&lt;sub&gt;80&lt;/sub&gt;</td>
<td>1.76</td>
<td>0.60</td>
<td>0.60</td>
<td>0.56</td>
<td>7.00E18</td>
</tr>
<tr>
<td>Ge&lt;sub&gt;25&lt;/sub&gt;Se&lt;sub&gt;75&lt;/sub&gt;</td>
<td>1.80</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>9.00E18</td>
</tr>
</tbody>
</table>

Table clearly indicates that the value of maximum barrier height "W<sub>M</sub>" as well the density of defect states "N<sub>T</sub>" increases with increase in Ge content. The value of U<sub>eff</sub> (Correlation energy) is minimum for Ge<sub>15</sub>Se<sub>85</sub> and is maximum for Ge<sub>25</sub>Se<sub>75</sub>.

The value of U<sub>eff</sub> is known as a measure of the D<sup>0</sup> states and lower is the value of U<sub>eff</sub>, higher will be the number of D<sup>0</sup> states. The graphs, (figures 4.6, 4.7 and 4.8) which show the theoretically calculated contributions from bipolaron hopping and single polaron hopping, clearly indicates that the single polaron hopping dominates over bipolaron hopping above a certain temperature only, in case of Ge<sub>15</sub>Se<sub>85</sub>. However, in case of Ge<sub>20</sub>Se<sub>80</sub> and Ge<sub>25</sub>Se<sub>75</sub>, the bipolaron hopping dominates over single polaron hoping in the studied temperature range.
In fact the sharper decrease in the value of frequency exponent “s” in case of Ge_{15}Se_{85} (figure 4.5) can be attributed to the dominance of single polaron hopping at higher temperatures which is not the case for Ge_{20}Se_{80} and Ge_{25}Se_{75}.

4.2.4 Effect of Silver Dissolution on Electrical properties of a-Ge_{15}Se_{85}

Two different categories as dc and ac conductivity have been studied for effect of Silver dissolution on electrical properties of a-Ge_{15}Se_{85} in.

4.2.4 (a) DC Conductivity

Figure 4.9 shows the temperature dependence of dc conductivity for undoped, thermaldoped and photodoped of Ge_{15}Se_{85}.

*Fig. 4.9, Temperature dependence of dc Conductivity for Undoped, Thermaldoped and Photodoped a-Ge_{15}Se_{85}.*
From the figure, it is clear that activation energy increases with doping. DC conductivity indicates maximum activation energy for thermaldoped Ge$_{15}$Se$_{85}$ showing that the band gap is probably increasing with doping and is maximum for thermaldoped Ag-Ge$_{15}$Se$_{85}$.

4.2.4 (b) AC Conductivity

The results of ac conductivity for Ag-Ge$_{15}$Se$_{85}$ system at different temperatures and frequencies have been shown in Figs. 4.10 and 4.11.

From these figures it is clear that, $\sigma_{ac} = A\omega^s$, where $s$ is frequency exponent and $A$ is a constant. The decrease in slope with increasing temperature clearly indicates that, the value of $s$ decreases with increasing temperature for all samples.

![Figure 4.10](image)

*Fig. 4.10, Log of frequency versus log of ac conductivity at different temperatures for Thermaldoped Ag-Ge$_{15}$Se$_{85}$.***
Fig. 4.12 shows the temperature dependence of frequency exponent “s” for undoped, thermodoped and photodoped Ag-Ge$_{15}$Se$_{85}$. It is evident from the figure that the value of “s” decreases with increasing the temperature, but increases with doping at same temperature.

Figure 4.13 indicates the temperature dependence of ac conductivity in three different frequencies. It is clear from the figure that ac conductivity for Ge$_{15}$Se$_{85}$ increases with photodoping but decreases with thermal doping.

*Fig. 4.11.* Log of frequency versus log of ac conductivity at different temperatures for Photodoped Ag-Ge$_{15}$Se$_{85}$.
Fig. 4.12, Temperature dependence of frequency exponent "s" for Undoped, Thermaldoped and Photodoped $a^{-}\text{Ge}_{15}\text{Se}_{85}$ samples.
Fig. 4.13, Temperature dependence of ac Conductivity for Undoped, Thermaldoped and Photodoped $Ge_{1+x}Se_{8-x}$ at (a) 1 KHz, (b) 20 KHz and (c) 50 KHz.
4.2.5 Effect of Silver Dissolution on Electrical properties of 
\textit{a-Ge}_{20}\textit{Se}_{80}

Effect of dissolution of Silver on electrical properties of 
\textit{Ge}_{20}\textit{Se}_{80} has been studied in the same manner as that of \textit{Ge}_{15}\textit{Se}_{85}.

4.2.5 (a) DC Conductivity

Fig. 4.14 shows the temperature dependence of dc conductivity 
for \textit{Ge}_{20}\textit{Se}_{80}. The results clearly show that \textit{AE}_0 increases with doping.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.14.pdf}
\caption{Log of dc Conductivity versus 1000/T for Undoped, Thermaldoped and 
Photodoped \textit{a-Ge}_{20}\textit{Se}_{80}.}
\end{figure}

4.2.5 (b) AC Conductivity

Figs. 4.15 and 4.16 show the frequency dependence of ac 
conductivity for Silver doped \textit{Ge}_{20}\textit{Se}_{80}. The results are similar to \textit{Ag-Ge}_{15}\textit{Se}_{85}. The value of \textit{“s”} is calculated from the slopes of these graphs 
and the temperature dependent of \textit{“s”} is plotted in fig. 4.17. The
behaviour of Ge$_{20}$Se$_{80}$ is similar to what has been observed in case of Ag-Ge$_{15}$Se$_{85}$ and other chalcogenide systems.

**Fig. 4.15.** Log of ac Conductivity versus log of frequency at different temperatures for Thermaldoped Ag-Ge$_{20}$Se$_{80}$.

**Fig. 4.16.** Log of ac Conductivity versus log of frequency at different temperatures for photodoped Ag-Ge$_{20}$Se$_{80}$.
Figure 4.17, Temperature versus frequency exponent "s" for Undoped, Photodoped and Thermaldoped Ge$_{20}$Se$_{80}$ samples.

Figure 4.18 (a, b and c) shows temperature dependence of ac conductivity of undoped, thermaldoped and photodoped Ge$_{20}$Se$_{80}$ at different frequencies. It is clear from the figure that, ac conductivity decreases with doping. It has already been observed that the number of defect states is larger for Ge$_{20}$Se$_{80}$ samples as compared to Ge$_{15}$Se$_{85}$ samples.
Fig. 4.18, Temperature dependence of ac Conductivity for Undoped, Thermaldoped and Photodoped Ge$_2$OSe$_8$ at (a) 1 KHz, (b) 2 KHz and (c) 10 KHz.
4.2.6 Effect of Silver Dissolution on Electrical properties of a-Ge$_{25}$Se$_{75}$

Under this title two different categories has been studied, dc and ac conductivity same manner as that of Ge$_{15}$Se$_{85}$ and Ge$_{20}$Se$_{80}$.

4.2.6 (a) DC Conductivity

Fig. 4.19 represents temperature dependence of dc conductivity for undoped, thermaldoped and photodoped Ge$_{25}$Se$_{75}$.

It is found from the figure that dc conductivity decreases with doping; moreover dc conductivity shows that for thermaldoped samples band gap is maximum, because the maximum activation energy “$\Delta E_0$” is maximum as that of Ge$_{15}$Se$_{85}$ and Ge$_{20}$Se$_{80}$.

![Fig. 4.19, Temperature dependence of dc Conductivity for Undoped, Thermaldoped and Photodoped a-Ge$_{25}$Se$_{75}$](image)
4.2.6 (b) AC Conductivity

The results are shown in figs. 4.20 and 4.21 as a plot of ac conductivity versus log frequency for thermaldoped and photodoped Ge\textsubscript{25}Se\textsubscript{75} respectively at various temperatures. The results are similar to that of Ge\textsubscript{15}Se\textsubscript{85} and Ge\textsubscript{20}Se\textsubscript{80}. The temperature dependence of frequency exponent “s” is plotted in Fig. 4.22. The results are similar to Ge\textsubscript{20}Se\textsubscript{80}, showing that with doping, the value of “s” increases.

Fig. 4.23 shows the temperature dependence of ac conductivity for undoped and Silver doped Ge\textsubscript{25}Se\textsubscript{75} system. The ac conductivity increases with doping.

*Fig. 4.20, Log of ac Conductivity versus log of frequency at different temperatures for Thermaldoped Ag-Ge\textsubscript{25}Se\textsubscript{75}.*
**Fig. 4.21**. Frequency dependence of ac Conductivity at different temperatures for photodoped $\text{Ag-Ge}_{25}\text{Se}_{75}$.

**Fig. 4.22**. Temperature dependence of frequency exponent "$s$" for Undoped, Photodoped and Thermaldoped $\text{Ge}_{25}\text{Se}_{75}$ samples.
Fig. 4.23, Log of ac Conductivity versus 1000/T for Undoped, Thermaldoped and Photodoped Ge$_{25}$Se$_{75}$ at (a) 2 KHz, (b) 5 KHz and (c) 50 KHz.
4.3 Discussion

The increase in ac conductivity of Ge$_{15}$Se$_{85}$ and Ge$_{25}$Se$_{75}$ is contrary to what has been observed in case of Silver doped As$_2$S$_3$ where conductivity decreases with Silver doping. On the other hand a behaviour similar to that of As$_2$S$_3$ has been observed for Ge$_{20}$Se$_{80}$. The observed contradiction can be explained in the following manner. In case of As$_2$S$_3$ the density of states is quite large ($N_T = 2.00$E$19$ for As$_2$S$_3$) as compare to Ge$_{15}$Se$_{85}$ ($N_T = 2.40$E$18$).

In that case:

$$D' + Ag' \rightarrow [D'Ag']^0 \quad (4.2)$$

$$D^0 + e^- \rightarrow D' \quad (4.3)$$

These reactions explain that the number of neutral D$^0$ centres decreased because of the capture of electron by D$^0$ centres.

However, in the present case when the density of states is small and moreover the larger value of $U_{\text{eff}}$ results in very small number of D$^0$ centres in the undoped Ge$_{15}$Se$_{85}$. In case of photodissolution which is performed at room temperature, the number of D$^0$ centres is going to be smaller than the number of D$^0$ centres for thermaldoped samples, where dissolution is performed at enhanced temperatures as per equation (1.47).

It is expected that the number of free electrons of Silver is much more than D$^0$ centres for photodoped Ge$_{15}$Se$_{85}$. Therefore, all electrons are not captured by D$^0$ centres. Free electrons which are available because of Silver doping start contributing to ac conductivity resulting in the overall increase in ac conductivity after Silver dissolution. However, for thermaldoped Ge$_{15}$Se$_{85}$, enough number of D$^0$ centres is available for capturing the free electrons and therefore its behaviour is similar to As$_2$S$_3$. 

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In case of Ge$_{20}$Se$_{80}$ and the number of defect states are quite large as compared to Ge$_{15}$Se$_{85}$ (see table 4.1). There is hardly any change in the value of $U_{\text{eff}}$ from that of Ge$_{15}$Se$_{85}$. Therefore, it is expected that large number of D$^0$ centres are available for capturing all the free electrons. It is expected that after Silver doping, the electrons given by Silver are captured by D$^0$ centres, making them D$^-$. The contribution from D$^0$ centres is expected to decrease and dominance of bipolaron hopping is expected to increase. The decrease in ac conductivity with doping can be attributed to the decrease in D$^0$ centres.

In case of Ge$_{25}$Se$_{75}$, the value of $U_{\text{eff}}$ is more than that of Ge$_{15}$Se$_{85}$ and Ge$_{20}$Se$_{80}$. An increase in the value of $U_{\text{eff}}$ can decrease the value of D$^0$ centres exponentially. Therefore, although the value of density of defect states increases marginally from that of Ge$_{20}$Se$_{80}$. The increase in the value of $U_{\text{eff}}$ decrease the number of D$^0$ centres, making its behaviour similar to that of Ge$_{15}$Se$_{85}$, where the conductivity increases with doping. A calculation for D$^0$ centres (4.1) for these samples at 373K has been made. The numbers of D$^0$ centres for Ge$_{15}$Se$_{85}$, Ge$_{20}$Se$_{80}$ and Ge$_{25}$Se$_{75}$ are 1.3E9, 3.2E9 and 1.07E9 respectively at 373K. This clearly indicates that the available D$^0$ centres are maximum for Ge$_{20}$Se$_{80}$. 

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