5. ELECTRONIC CONDUCTION

5.1. INTRODUCTION

Study of the conduction properties is one of the important ways of characterizing a semiconductor film. In this chapter a detailed analysis of the a.c and d.c electrical conduction in Ge, Se, Ge\textsubscript{x}Se\textsubscript{1-x} films prepared by vacuum evaporation and hot wall deposition is given. The variation of conductivity with temperature is studied for all films and the activation energy is calculated in each case.

5.2. A.C. Conduction

The charge transport measurements in disordered semiconductors and insulators have been of considerable interest because they can provide information regarding the electronic structure of the materials \[1,2\]. The study of a.c conductivity also yields information about the mechanism of conduction phenomena in the films. The chief advantage of a.c measurements is that it permits investigation of the interior of the insulator materials. Secondly, the a.c voltage bias being 0.05 V, the maximum field within the insulating film material is kept to a minimum and there is little danger of more than one conduction process being active.

The study of a.c conductivity ($\sigma_{ac}$) in disordered solids has attracted much attention in the last decade. One of the main
reasons for this interest is the assumption that this conductivity is dominated by the deep defect levels lying in the mobility gap of these materials; hence a study of a.c conductivity in these materials will throw light on the nature of these levels. The experimental results obtained on amorphous semiconductors, as well as on a variety of other materials, indicate that the observed a.c. conductivity commonly exhibits behaviour in the form \( \sigma(\omega, T) = B + A \omega^s \), where \( \omega \) is the angular frequency and \( B \) is the d.c. limit [3]. \( A \) and \( s \) have usually been found to be temperature-dependent parameters. This behaviour has been explained with various models. The customary approach has been to consider a.c. and d.c. conductions separately and attribute the former to the transfer of an electron between a pair of defect states. This is known as the "pair approximation" [4].

The earliest application of the pair approximation was by Pollak and Geballe to explain this type of behaviour observed on n-type crystalline Silicon at very low temperature [5]. Austin and Mott adopted this theory to amorphous semiconductors, assuming that the a.c. loss was mainly due to quantum mechanical tunnelling of an electron through a barrier separating two localised states within the mobility gap under the effect of an applied field [6,7]. An alternative method of improving the theoretical formulation of the frequency-dependent hopping problem has been proposed by Summerfield and Butcher [8,9].
5.2.1. THEORY

A variation of $\sigma$ with frequency ($\omega$) is expected if the conductivity of the material is inhomogeneous on a macroscopic scale. For example it has been reported that a material of bulk conductivity $\sigma_0$ contains barrier with bulk conductivity $\sigma_B$ occupying a fraction 'f' of the volume. An elementary analysis show that, for $\omega < 16 \pi^2 \sigma_0 \sigma_B$ conductivity is proportional to $\sigma_B$, for $\omega > \sigma_0$ the conductivity is $\sigma_0$ and between these limits it increases as $\omega^2$.

Pollack [2] has observed that the a.c. conductivity studies carried out on materials such as $AS_2Se_3$ [10-13], $AS_2Te_3$ [14], $Al_2O_3$ [15], $CS_2$ [16], $V_2O_5$ [17], GeTe [18] and Ge [18] reveals that,

1. The conductivity is a non-decreasing function of frequency which indicates hopping conduction by electrons or ions.

2. In all the materials there exist a range of frequency in which $\sigma(\omega)$ varies as the first power of frequency or slightly less rapidly.

3. In certain materials there is a region in which $\sigma(\omega)$ varies as second power of $\omega$ and this appears at the higher frequencies.

4. In certain materials at high frequencies $\sigma(\omega)$ varies very slowly with $\omega$. Such a slowly varying region can occur also near $\omega = 0$. 

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5. The temperature dependence of $\sigma(\omega)$ is more pronounced where $\sigma$ varies as $\omega^2$ than it is where $\sigma$ varies as $\omega$ and

6. The changeover from linear to quadratic regions of $\sigma(\omega)$ occur approximately at $10^6$ Hz.

Pollack has proposed a theory suitable for hopping conduction in the pseudogap of amorphous semiconductors and derived expressions applicable under various conditions. It has been pointed out by Mott and Davis [19] that all the three mechanisms that contribute to direct current in amorphous semiconductors can contribute also to the a.c. conductivity. Three mechanisms of a.c. conductivity as given by Mott and Davis are given below,

(a) Transport by carriers in the extended states near $E_C$ or $E_V$. For this $\sigma(\omega)$ is given by the formula,

$$
\sigma(\omega) = \frac{\sigma(0)}{(1-\omega^2 \tau^2)} \quad \text{(5.1)}
$$

Since the relaxation time $\tau$ is of the order of $10^{-15}$ s, equation (5.1) is not really applicable for such small values of $\tau$. Even when $\tau$ is large, deviation from this formula is expected if the density of states varies with energy over a range of $\hbar/\tau$. So it can be said that upto $10^7$ Hz no frequency dependence of the conductivity due to carriers in the extended states is expected.
(b) Transport by carriers excited into the localised states at the band edges can be a possibility when the conductivity varies approximately as $\omega^{0.8}$. The temperature dependence of this component of the a.c. conductivity should be the same as that for the part of d.c. conductivity involving excitation to the band edges. For the valence band it must vary as,

$$\exp \left( -\frac{E_F-E_B}{kT} \right)$$

where $E_B$ is the energy at the band edge.

(c) The third mechanism is the hopping by carriers near the Fermi level. The frequency dependence will be the same as that for process (b) but the temperature dependence will be proportional to $T$, if $kT$ is small compared to the width of the occupied part of the defect band and independent of $T$ otherwise. Accordingly $\sigma(\omega)$ is obtained by Austin and Mott [6] as,

$$\sigma(\omega) = \frac{1}{3} \pi e^2 kT \left[ N(E_F) \right]^2 \alpha^{-5} \omega^4 \left[ \ln(\gamma_{ph}/\omega) \right]^4$$

Here $N(E_F)$ is the density of states at the Fermi level and $\alpha^{-1}$ is the measure of the spatial extension of the wave function $\exp(-\alpha \tilde{\gamma})$ associated with localized states. $\gamma_{ph}$ is the phonon frequency.


According to Elliott's theory an electrical conductivity
having a frequency dependence $\tilde{\omega}^{s}$, where $s < 1$ can occur due to the hopping of two electrons over a potential barrier between defect sites, the height of the barrier being correlated with the intersite separation. The hopping process is explained as follows.

Carriers are ejected from a $D^{-}$ site (fig. 5.1(a)) into one of the excited levels designated as $E$ in fig. 5.1(b). Assuming that a two electron wave function can exist within the potential spanning both centres, the carriers may transfer to the neighbouring site without recourse to tunnelling. The carriers ejected from the initial $D^{-}$ centre drop into the $D^{+}$ centre, converting it to a $D^{-}$. The energy $W_{m}$, assumed to be a constant here, is the energy that would be required to take two electrons from the $D^{-}$ state to the conduction band in the absence of a nearby $D^{+}$ centre. The energy is the difference in energies between two $D^{-}$ sites owing to randomness. The potential barrier $W$ over which carriers must hop is the random variable in the problem. Variations in $W$ arise from variations in the distance $R$ separating the two centres.

The final expression for the a.c. conductivity is given by

$$\sigma_{a.c.}(\tilde{\omega}) = \frac{\pi^{2} N^{2} \varepsilon}{24} \left[ \frac{8e^{2}}{K W_{m}} \right] \frac{\tilde{\omega}^{s}}{\tau} \quad (5.4)$$

where $N$ is the density of states at the Fermi level, $\varepsilon$ is the dielectric constant, $e$ is the electronic charge, $\tilde{\omega}$ is frequency.
Fig. 5(a) Schematic diagram of the potentials experienced by carriers a distance $R$ apart. $W_M$ is the energy required to remove two electrons from a $D^-$ centre to form a $D^-$; $W$ is the height of the barrier over which the carriers must hop. The potential wells are assumed to be Coulombic; bound states which form the intermediate stage of the hopping process are designated by $E$. (b) Schematic diagram of the hopping process considered in this paper. Two electrons transfer from a $D^-$ to a $D^-$ centre, which thereby exchange places (represented by the dotted line).
of measurement and \( \beta = (1-s) \). \( W_m \), the thermal energy required to remove two electrons from a D\(^-\) states is given by

\[
W_m = E_g - W_1 + W_2 \tag{5.5}
\]

where \( E_g \) is the band gap energy of the material and \( W_1 \) and \( W_2 \) are approximately the distortion energies associated with the \( D^0 \) and \( D^+ \) states respectively. It is assumed that no distortion energy is associated with the \( D^- \) state since it does not bond with a lone pair orbital.

The slope \( S \) of the \( \ln(\sigma_{a,c}) \) versus \( \ln(\omega) \) plot is related to \( \beta \), the power of the relaxation time \( \tau_a \), in equation (5.4) by the relation,

\[
S = (1-\beta)
\]

\( \beta \) is given by

\[
\beta = \frac{6kT}{W_m} \tag{5.6}
\]

where \( k \) is the Boltzmann constant and \( T \) is the absolute temperature.

Substituting this value of \( \beta \) in the equation for \( S \) we get,

\[
S = 1 - \frac{6kT}{W_m} \tag{5.7}
\]

Equation (5.7) predicts that as \( T \) increases \( S \) decreases as is often found in experiments. The density of states calculated using this model for so many chalcogenides agree well with those derived by other methods. Even though the theory is well suited
for chalcogenide glasses there arise certain serious problems when it is employed for other amorphous semiconductors. These are given below.

1. As pointed out by Elliot himself the approximation of the binding energy \( W_0 \) as the band gap energy is not possible in the case of non-chalcogenide amorphous materials. This is due to the reason that the top of the valance band in chalcogenides is derived from the lone-pair orbitals of the chalcogen \([22]\). Hence significant rearrangements in chemical bonding may take place within the glass and utilizing the lone-pair orbitals, the chalcogen atoms can become overcoordinated. It is these arrangements that can be responsible for doubly occupied defect states. Such a bipolaron formation could be expected to be much less prevalent in tetrahedrally bonded materials, since no lone-pair orbitals exist in them. However, David Emin \([23]\) has suggested that formation of bipolarons is possible in the case of certain amorphous semiconductors.

2. The slope \( S \) of the \( \ln(\sigma) \) versus \( \ln(w) \) is given by equation (5.7). From this equation we can see that the maximum value \( S \) can assume is only 1 corresponding to \( T = 0 \) or \( W_0 = \bar{\omega} \). Hence in the practical cases \( S \) can assume a maximum value just below 1.

5.2.2. Experimental

\( \text{Ge, Se and Ge}_x\text{Se}_{1-x} \) films were prepared on glass substrates pre-coated with aluminium electrodes. Top aluminium electrodes were deposited with an electrode overlapping area of \( 3-5 \times 10^{-6} \text{ m}^2 \).
The a.c. conductivity of the films were determined by knowing capacitance (C), loss factor (\(\tan \delta\)) and frequency.

As-deposited metal-semiconductor-metal (MSM) sandwich structures with Ge or Se or Ge\(_x\)Se\(_{1-x}\) as an intermediate layer were subjected to number of annealing cycles to achieve stabilization. The a.c. conductivity of these stabilized films were studied as a function of frequency in the range 1 kHz - 1 MHz and temperature in the range 303 - 483 K. The measurement details are given in section 4.3.

5.2.3. RESULTS AND DISCUSSION

The frequency dependence of \(\sigma_{a.c}(\omega)\) of vacuum evaporated and hot wall deposited Ge films are given in figs. 5.2 and 5.3. The thicknesses of the films are 247 and 350 nm with electrode overlapping areas of \(4.83 \times 10^{-6}\) m\(^2\) and \(5 \times 10^{-6}\) m\(^2\) respectively. It can be seen from fig. 5.2 that there are three well defined regions. The slope in the frequency region of 1 - 20 kHz varies from 1.2 to 0.92 in the temperature region 303 - 423 K. From 20 - 300 kHz the slope varies from 0.87 to 0.83 in the temperature region given as above. In the last region i.e. from 300 kHz to 1 MHz the variation of the slope is from 1.41 to 1.36 with the change in temperature.

In the case of hot wall deposited Ge film [fig. 5.3], once again the three dispersive regions are observed. In the low frequency region the slope varies from 1.3 to 0.67 in the
Fig. 5.2 Frequency dependence of conductivity $\sigma$ of vacuum evaporated Ge film.

$d = 247 \text{nm}$

$A = 483 \times 10^{-6} \text{m}^2$

423K
323K
303K
Fig. 5.3 Frequency dependence of $\sigma_{a.c}$ of hot wall deposited Ge film.

$d = 350 \text{ nm}$

$A = 5 \times 10^{-6} \text{ m}^2$

$423 \text{ K}$

$403 \text{ K}$

$303 \text{ K}$
temperature region 303 to 423 K, whereas in the second and third regions the variation of the slopes are from 0.67 to 1.2 and 1.4 to 0.7 respectively.

In the case of vacuum evaporated Se films, only two dispersive regions are observed [fig. 5.4], with slope values varying from 0.55 to 0.36 in the first region (below the frequency of 30 kHz) and the slope value of 0.8 to 0.7 in the second region (above 30 kHz) in the temperature range 303 to 423 K.

In hot wall deposited Se films, [fig. 5.5] temperature independent phenomena of the conductivity is observed in the frequency range 1 - 30 kHz with the slope value around 2. Above 30 kHz the slope values for all temperature are more than 2.

In fig. 5.6 the log $\sigma_{a.c}$ versus log $f$ curve for vacuum evaporated Ge$_x$Se$_{1-x}$ film of typical thickness 160 nm is presented in the frequency range 1 kHz-1 MHz and in the temperature region 303 - 463 K. At 303 K three dispersive regions are observed, but above that temperature only two are observed. The slope in the middle region at 303 K is measured as 1.4, whereas for higher temperatures, the slope values are found to be less than 1. In the higher frequency region the slope values are found to be more than 2.

In hot wall deposition Ge$_x$Se$_{1-x}$ film a linear variation of conductivity with frequency is observed at 303 K with a slope value of 1.2, but at higher temperatures two regions are observed
d=160nm
A=3.58×10^{-6}m^2

Fig. 5.4 Frequency dependence of vacuum evaporated Se film.
Fig. 5.5 Dependence of frequency with $\omega_{a.c}$ for hot wall deposited Se film.

$d=447\,\text{nm}$

$A=3.45\times10^{-6}\,\text{m}^2$
Fig. 5.6 Plot of log $\sigma_{a,c}$ versus frequency curve for vacuum evaporated Ge$_x$Se$_{1-x}$ film.

$d=160\,\text{nm}$

$A=4.4\times10^{-6}\,\text{m}^2$
with a change in slope values taking place at 100 kHz. The slope value varies from 0.88 to 0.80 in the temperature region 323 - 423 K in the first region. The slope varies from 1.2 to 0.7 in the second region [fig. 5.7].

The important observations of the present study on the three films can be summarised as follows,

1. Three dispersive regions are observed in both vacuum evaporated and hot wall deposited Ge films, while that of Se and Ge$_x$Se$_{1-x}$ films have only two dispersive regions.

2. Almost one order difference in the conductivity of vacuum evaporated and hot wall deposited Ge film is observed at 303 K, throughout the frequency range studied.

3. At 303 K, $\sigma_{a.c}$ increases as $\omega^{1.2}$ in the first region, $\omega^{0.87}$ in the second region and $\omega^{1.4}$ in the third region for vacuum evaporated Ge film with almost similar trend for hot wall deposited films.

4. In vacuum evaporated Se films $\sigma_{a.c}$ varies as $\omega^{0.55}$ in the first region and as $\omega^{0.8}$ in the second region at 303 K.

5. $\sigma_{a.c}$ of hot wall deposited films are practically independent of temperature in the first region and increases as $\omega^2$ with frequency and in the second region as $\omega^{\gamma}$.

6. At higher temperatures, the conductivity of HWD films are two orders higher than that of vacuum evaporated films. At lower temperature region, the difference in conductivity for the films prepared by the two methods is reduced.
Fig. 5.7 Conductivity versus frequency plot of hot wall deposited Ge$_x$Se$_{1-x}$ film.
7. $\sigma_{a.c}$ of vacuum evaporated $\text{Ge}_x\text{Se}_{1-x}$ film shows three dispersive regions.

8. At 303 K $\sigma_{a.c}$ of HWD $\text{Ge}_x\text{Se}_{1-x}$ films show a linear variation as $\omega^{1.2}$. At higher temperatures, $S$ varies from 0.88 to 0.80.

9. As in the case of Se films, the conductivity of HWD are higher by more than two orders than that of vacuum evaporated films at higher frequencies.

10. As the measuring temperature is increased the slope of the $\log(\sigma_{a.c})$ versus $\log(f)$ curve decreases for all Ge, Se and $\text{Ge}_x\text{Se}_{1-x}$ films prepared by both techniques.

From the above observations and discussions it becomes clear that neither Astin-Mott nor Elliott's theory (both discussed in section 5.2.1) can be used to fully explain the a.c conduction behaviour of the semiconducting films used in the present study. Indeed such high value for the slope was reported earlier, like $S = 1.08$ for a-Se by Lakatos and Abkowitz [24], $S = 1.2$ for $\text{CdAs}_2+\text{Si}_x$ and $\text{CdAs}_2+\text{Sb}_x$ by Kocka et al. [25] and $S = 1.4-1.7$ for hydrogenated Silicon films by Rajeev Kumar and Sathianandan [26], but such values were ruled out by Elliott as unreasonable. In the present case also, all other observations including that on vacuum evaporated Se films strongly support the Elliott's model. The occurrence of higher slope values may be due to a lower cut off relaxation time($\tau$) of hopping as suggested by Pollack [2].

5.3. D.C. CONDUCTION

Various mechanisms are attributed to explain the d.c
conduction in thin films. A brief review of each mechanism is given below.

5.3.1. THEORY

5.3.1.1. Tunnelling

Electrons, even though their initial energy is smaller than the potential barrier, can pass through thin layers of insulating materials by the quantum mechanical process called tunnelling. In a thin film MIM structure there is a probability for electron from one electrode to tunnel through the insulator forbidden gap to the other electrode. This probability decreases exponentially with the width of the barrier and also decreases as the barrier height increases. If the insulator is sufficiently thin (> 5 nm) the predominant contribution to the current is derived from electrons in the cathode by tunneling through the insulator potential barrier [27-32].

5.3.1.2. Impurity conduction

The mechanism involved in this process is electronic hopping. The availability of impurity (trap) levels enables the electron to move from one trap to another without going into the conduction band and hence take part in current flow. The effect of many electrons in the conduction band is to mask impurity conduction if the hopping electrons have low mobility. An insulator has a lower density of thermally generated carriers in
the conduction band than a narrow gap semiconductor. So, impurity conduction is more likely in an insulator.

5.3.1.3. Space charge limited conduction (SCLC)

When the rate of carrier injection from the contact exceeds the rate at which the carriers can be transported across the film, a space charge will be built up in the conduction band. This will oppose the applied voltage and impede the flow of electrons. If an ohmic contact is made to the insulator, the space charge injected into the conduction band of the insulator is capable of carrying current. This process is termed as space charge limited conduction.

For the simple case of single carrier trap-free SCLC, the well known Mott-Gurney [33] relation gives,

\[ J = \frac{9 \mu \varepsilon_0 \varepsilon'}{8 d^3} V^2 \]

\[ \text{(5.8)} \]

Where \( \mu \) is the drift mobility of the charge carriers, \( \varepsilon' \) is the dielectric constant, \( \varepsilon_0 \) is the dielectric constant of free space, \( V \) is the applied voltage and \( d \) is the thickness of the insulator. However, the above equation (5.8) predicts much higher currents than are observed in practice, and also after that, space-charge limited currents are temperature insensitive, which is also contrary to observations. These deviations from the simple trap free theory are readily accounted for when a more realistic insulator, i.e., one containing traps, is concerned.
The theory of SCL current in defect insulators has been proposed initially by Rose [34]. When the insulator contains traps, a large fraction of the injected space charge condenses therein, which means that the free-carrier density is much lower than in a trap-free insulator. Furthermore, since the occupancy of traps is a function of temperature, the SCL current is temperature dependent. If the insulator contains $N_t$ shallow traps positioned an energy $E_t$ below the conduction band, the ratio of free-to-trapped charge is [35]

$$\theta = \frac{N_c}{N_t} \exp \left(-\frac{E_t}{kT}\right) \quad \text{------- (5.9)}$$

where $N_c$ is the density of states approximately equal to $10^{25}$ m$^{-3}$ at room temperature. Thus the SCL current for an insulator with shallow traps is given by,

$$J = \frac{9}{8} \mu \varepsilon' \varepsilon_0 \theta \frac{v^2}{d^3} \quad \text{------- (5.10)}$$

5.3.1.4. Schottky effect

When the potential barrier is sufficiently thick to permit tunneling to occur, the current flowing through the insulator is limited principally by the rate at which electrons are thermally excited over the interfacial potential barrier into the insulator conduction band. This is known as Schottky emission [36,37].

The current density in the Richardson thermionic equation is
given by,
\[ J = AT^2 \exp \left[ - \frac{\Phi_o}{kT} \right] \] ------- (5.11)

where \( A = \frac{4\pi m e k^2}{h^3} \), \( m \) is the mass of the electron, \( e \) the electronic charge, \( \Phi_o \) interfacial barrier height and \( T \) the absolute temperature. Here \( \Phi_o \) varies with applied field because of the attendant image forces due to the electrode from which they were ejected. Thus current does not saturate but is a function of the applied voltage.

The potential energy of the electron due to the image force is,
\[ \Phi_{im} = -\frac{e^2}{16\pi\epsilon\epsilon_0 x} \] ------- (5.11)

where \( x \) is the distance of the electron from the electrode surface and \( \epsilon' \) the high frequency dielectric constant. The potential step with respect to the Fermi level at a neutral barrier with attendant image potential as a function of the distance \( x \) from the interface of an electron is given by

\[ \Phi(x) = \Phi_o + \Phi_{im} \] ------- (5.13)

and thus in the presence of an uniform field \( F \)
\[ \Phi(x) = \Phi_o - \frac{e^2}{16\pi\epsilon\epsilon_0 x} - e F x \] ------- (5.14)

This equation has a minimum at
The attenuation \( \Delta \Phi_S \ [= \Phi_O - \Phi(x_m)] \) of the barrier height due to the interaction of the applied field with the image potential is given by,

\[
x_m = \left[ \frac{e}{16\pi \varepsilon' \varepsilon_0 F} \right]^{1/2}
\]

\[------------- (5.15)\]

where \( \beta_S \) is the Schottky constant. Substituting

\[
\Phi(x_m) = \Phi_O - \Phi_S \quad \text{for } \Phi \text{ in equation (5.11)}
\]

\[
J = A T^2 \exp \left[ \frac{\beta_S F^{1/2} - \Phi_O}{kT} \right]
\]

\[------------- (5.17)\]

which is just the Richardson-Schottky equation.

5.3.1.5. Poole-Frenkel effect

The physical basis for the occurrence of the Poole-Frenkel effect is the lowering of the coulombic potential barrier surrounding a localized charge under the influence of an external electric field. This is otherwise the bulk analogue of the Schottky effects at an interfacial barrier. Since the potential energy of an electron in a coulombic field \([-e^2 / (4\pi \varepsilon' \varepsilon_0 x)]\) is four times that due to image force effects, the Poole-Frenkel attenuation of a coulombic barrier \( \Phi_{PF} \) in an uniform electric field is twice that due to the Schottky effect at a neutral barrier.
\[ i.e. \Phi_{PF} = \left( \frac{3e}{\pi \epsilon' \epsilon_0} \right)^{1/2} F^{1/2} = \beta_{PF} F^{1/2} \quad \text{(5.18)} \]

where \( \beta_{PF} \) is the Poole-Frenkel coefficient.

This mechanism was applied to a number of atoms in bulk semiconductors and insulators by Frenkel. It was also argued that the ionization potential \( V_a \) of the atoms in a solid are lowered by an amount given by the equation (5.18), in the presence of a uniform field. Then the conductivity will be field dependent and of the form,

\[ \sigma = \sigma_0 \exp \left[ \frac{\beta_{PF} F^{1/2}}{2kT} \right] \quad \text{------ (5.19)} \]

where \( \sigma_0 \) is the low field conductivity. The equation (5.18) may be written in the form,

\[ J = J_0 \exp \left[ \frac{\beta_{PF} F^{1/2}}{2kT} \right] \quad \text{------ (5.20)} \]

where \( J_0 \) is the current density at low fields. Though the quantity \( \Delta \Phi_{PF} \) is equal to \( 2\Delta \Phi_s \), the coefficient of \( F^{1/2} \) in the exponential is the same for both the Richardson-Schottky and Poole-Frenkel current field characteristics, i.e., \( \beta_{PF} = 2\beta_s \).

Accordingly to Mead [38] in an insulator when the traps are in abundance, a trap having a coulombic type barrier would experience the Poole-Frenkel effect at high fields. This enhances the probability of escape of an electron immobilized therein. The
current density in thin film insulators having shallow traps is given by,

$$J = J_0 \exp \left[ \frac{\beta_{PF} F^{1/2}}{kT} \right]$$

Now the coefficient of $F^{1/2}$ is twice that in equation (5.20). Mead [39] has also reported field dependent conductivity apparently of the form given by equation (5.20) and for this reason equation (5.21) is usually the form of Poole-Frenkel equation associated with thin film insulators than equation (5.8).

5.3.2. MEASUREMENTS

Initially all the films (Ge, Se and Ge_xSe_{1-x}) of both vacuum evaporated and hot wall deposited were stabilized by repeated annealing cycles. The a.c. conduction parameters have been evaluated from the measured values of capacitance (C) and loss factor (tanδ), the measurements of which have been described in section 4.3. In d.c. conduction studies the current through the capacitors as a function of applied voltage has been measured in a rotary vacuum at different temperatures using an electrometer amplifier (ECIL-EA8155) and a FET nanoammeter (Aplab, India).

5.3.3. RESULTS

5.3.3.1. Germanium

Fig. 5.8 and 5.9 shows the variation of current with applied
**Fig. 5.8** Variation current with applied voltage of vacuum evaporated Ge film.

\[
d = 150 \text{ nm} \\
A = 5.52 \times 10^{-6} \text{ m}^2
\]
Fig. 5.9 Current-voltage characteristic of hot wall deposited Ge film.

\[ \begin{align*} 
&d = 350 \text{ nm} \\
&A = 5 \times 10^{-6} \text{ m}^2 
\end{align*} \]
voltage of vacuum evaporated and hot wall deposited Ge films. In vacuum evaporated Ge films, the current (I) exhibits a voltage (V) dependence of the form $I \propto V^n$, where $n$ is found to be 1.25 at low fields and attains values around 4 at high fields. The two regions observed tend to disappear as the temperature increases. In hot wall deposited Ge films the two regions are well defined at all temperatures. At low fields $n$ has a value of 2.0 and at high fields, the value is more than 5.0. When comparing the current voltage characteristics of vacuum evaporated and hot wall deposited Ge films it can be seen that the current in vacuum evaporated Ge films are higher at least by an order of 5 to 6 at any temperature in the low field region. In the higher field region, the current in vacuum evaporated films are still higher but the order of difference is reduced.

The field dependence ($F^{1/2}$) of the current of vacuum evaporated and hot wall deposited Ge films are given in figs. 5.10 and 5.11. Linear plots with decreasing slopes are observed in both figures, such linear plots indicate that the conduction mechanism in both cases may be of either Schottky or Poole-Frenkel type. The experimental values of the field lowering coefficient ($\beta$) are calculated [Eqn. 5.21] from the slopes of the log I versus $F^{1/2}$ plots and are found to be $2.17 \times 10^{-5}$ and $6.68 \times 10^{-5}$ eV(V$^{-1}$m$^{-1}$)$^{1/2}$ for vacuum evaporated and hot wall deposited Ge films respectively. The theoretical values of $\beta$ are calculated [Eqs. 5.16 and 5.18] by
Fig. 5.10 Field dependence ($F^{1/2}$) versus current plot of vacuum evaporated Ge film.

- $d = 150 \text{ nm}$
- $A = 5.52 \times 10^6 \text{ m}^2$

$\text{Log I (Amps)} \rightarrow$

$F^{1/2}(\text{V/m})^{1/2} \rightarrow$

$403 \text{ K}$
$383 \text{ K}$
$363 \text{ K}$
$343 \text{ K}$
$303 \text{ K}$
Fig. 5.11 $F^{1/2}$ versus log I plot for hot wall deposited Ge film.
taking the high frequency (1MHz) dielectric constant (\(\varepsilon\)) values for both cases from the results of chapter IV. Activation energies of Ge film prepared by two methods are calculated using the relation,

\[
I = I_0 \exp \left(-\frac{\Delta E}{kT}\right)
\]

by plotting the log current against the inverse absolute temperature \(\text{[fig. 5.12 and 5.13]}\). The activation energies calculated at different applied voltages are given in table 5.1.

5.3.3.2. Selenium

The current, voltage characteristics of vacuum evaporated and hot wall deposited Se films are given in figs. 5.14 and 5.15. In vacuum evaporated Se film two regions are observed, one in the temperature region 303 - 323 K and the other above 323 K. The slope values vary from 3.0 - 4.5 in the two regions. At high temperatures (>323 K) only one region is observed with the slope value of 3.0. Also in the case of hot wall deposited films, only single region is observed with slope values around 4.0.

From the figs. 5.14 and 5.15 it can be observed that hot wall deposited films posses higher values of current at any given voltage and temperature than vacuum evaporated Se films. This observation is quit contrary to that of Ge films.

Figs. 5.16 and 5.17 shows the variation of the current with \(F^{1/2}\) for Se films prepared by the two methods. The field lowering
Fig. 5.12 Plot of log I versus inverse absolute temperature of vacuum evaporated Ge film

- d = 150 nm
- $A = 5.52 \times 10^{-6} \text{m}^2$

Log I (Amps) vs. $\frac{1000}{kT}$
Fig. 5.13 Plot of log I versus inverse absolute temperature of hot wall deposited Ge film

\[ d = 350 \text{nm} \]

\[ A = 5 \times 10^{-6} \text{m}^2 \]
d = 160 nm
A = 3.58 \times 10^{-6} \text{ m}^2

Fig. 5.14 Current-voltage characteristics of vacuum evaporated Se film.
Fig. 5.15 Current-voltage characteristics of hot wall deposited Se film.

\[ d = 44.7 \text{ nm} \]
\[ A = 3.45 \times 10^{-6} \text{ m}^2 \]
Fig. 5.16 Variation of current with $F^{1/2}$ for vacuum evaporated Se film.

$d = 160\text{nm}$

$A = 3.58 \times 10^{-6}\text{m}^2$
Fig. 5.17 Variation of current with $F^{1/2}$ for hot wall deposited Se film.
coefficients (β) are calculated as $7.82 \times 10^{-5}$ and $7.22 \times 10^{-5}$ eV(V$^{-1}$m)$^{1/2}$ for vacuum evaporated and hot wall deposited films respectively. The high frequency dielectric constant values used for the theoretical calculation of β are 13 and 18.6 for Se films prepared by the two methods respectively.

The variation of log I versus inverse of temperature at different applied voltages for vacuum evaporated and hot wall deposited Se films are given in figs. 5.18 and 5.19. The activation energies of Se films calculated from the above figures are given in table 5.1.

5.3.3.3. Ge$_x$Se$_{1-x}$

Figs. 5.20 and 5.21 shows the log-log plot of current-voltage characteristics, of vacuum evaporated and hot wall deposited films. The relation $I \propto V^n$ holds good in this material also. The values of n varies from 5-4 in the temperature range 303-403 K. In hot wall deposited films, two regions are observed one in the low fields and another in the high field at all temperatures. The first is having slope value of 4.3, whereas in the second region $n > 5$. Like in Se films the current values in hot wall deposited Ge$_x$Se$_{1-x}$ films are higher at any given voltage and temperature than vacuum evaporated Ge$_x$Se$_{1-x}$ films as seen in figs. 5.20 and 5.22.

Figs.5.22 and 5.23 represent the log I versus $F^{1/2}$ for vacuum evaporated and hot wall deposited Ge$_x$Se$_{1-x}$ films. The β values
Fig. 5.18 Variation of log I versus inverse of temperature for vacuum evaporated Se film.
Fig. 5.19 Variation of log I versus inverse of temperature for hot wall deposited Se film.

d = 447 nm

A = 3.45 x 10^{-6} m^2
Fig. 5.20 Current-voltage characteristics of vacuum evaporated Ge_xSe_1-x film.

\[ d = 160 \text{ nm} \]
\[ A = 44 \times 10^{-6} \text{ m}^2 \]
Fig. 5.21 Current-voltage characteristics of hot wall deposited Ge$_x$Se$_{1-x}$ film.

$\text{d} = 2.25 \text{nm}$

$A = 4.4 \times 10^{-6} \text{ m}^2$
Fig. 5.22 Plot represent the log I versus $F^{1/2}$ for vacuum evaporated $Ge_xSe_{1-x}$ film.
Fig. 5.23 Variation of \( \log I \) with \( F^{1/2} \) for hot wall deposited Ge\(_x\)Se\(_{1-x}\) film.

\[
\begin{align*}
d &= 225\text{nm} \\
A &= 4 \times 10^6 \text{m}^2
\end{align*}
\]

- 423 K
- 403 K
- 383 K
- 363 K
- 343 K
- 303 K
calculated from the slopes of the two graphs are $7.04 \times 10^{-5}$ and $7.52 \times 10^{-5}$ eV(V$^{-1}$ m)$^{1/2}$ respectively. Dielectric constant values of 22 and 23.3 for vacuum evaporated and hot wall deposited films are used for the theoretical calculation. Activation energies of Ge$_x$Se$_{1-x}$ films are calculated from the figures 5.24 and 5.25 and are given in table 5.1.

5.3.4. DISCUSSION

When referring to power law dependence of current upon voltage in all the films studied in the present work, a natural tendency is to think of space charge limited conduction [40]. But the field dependence of current of these films show that the conduction mechanism may be of either Schottky or Poole-Frenkel type. Comparison of the experimental and theoretically calculated values of the field lowering coefficient ($\beta$) indicate that in vacuum evaporated Ge films, the dominating conduction mechanism may be of Schottky type and in hot wall deposited Ge films and in Se and Ge$_x$Se$_{1-x}$ films prepared by both methods Poole-Frenkel type is the predominant mechanism. Table 5.2 gives the comparative data of the films. Similar type of conduction mechanism have been observed in numerous insulators [41-45] and semiconductors [46-50].

D.C. electrical conductivity in HWD Ge films is lower than in vacuum evaporated Ge films, which indicates the higher band gap energy in hot wall deposited films. In the structural
Fig. 5.24 Plot of log I versus inverse absolute temperature vacuum evaporated Ge$_x$Se$_{1-x}$ film.

- $d=160\text{nm}$
- $A=4.4\times10^{-6}\text{m}^2$
Fig. 5.25 Plot of log I versus inverse absolute temperature hot wall deposited $\text{Ge}_x\text{Se}_{1-x}$ film.

$d = 225\, \text{nm}$

$A = 4.4 \times 10^{-6}\, \text{m}^2$
analysis of Ge films (chapter III) it has been found that vacuum evaporated Ge films possess amorphous structure while hot wall deposited films have real amorphous (near defect free) structure. Also an increase in optical band gap value in hot wall deposited film is observed while studying the optical properties of these films, (chapter VI). Hence, the reduction of electrical conductivity, in hot wall deposited film is justified.

In Se and Ge\textsubscript{x}Se\textsubscript{1-x} materials it is observed that the conductivity in hot wall deposited films is higher than in vacuum evaporated films. The structural studies reveal that both Se and Ge\textsubscript{x}Se\textsubscript{1-x} vacuum evaporated films possess amorphous structure while hot wall deposited films are crystalline in nature. The optical studies presented in the next chapter shows that the optical band gaps of hot wall deposited Se and Ge\textsubscript{x}Se\textsubscript{1-x} films are lower than that of vacuum evaporated films. The phenomenon of increased conductivity in crystalline Se and Ge\textsubscript{x}Se\textsubscript{1-x} films may be explained on the basis of a model proposed by Chopra and Bahl [47]. According to this model the tails of conduction and valance bands extend into the crystalline forbidden gap. By assuming exponential tailing of the valance band [that is, density of states falling as \( \exp(-E/\Delta) \), where \( \Delta \) is the inverse of the slope of the exponential trap distribution] and the magnitude of tailing inside the forbidden gap, the observed increase in conduction can be understood. Exponential tailing is a common characteristic of a number of materials such as
amorphous Se [51] and GeTe [52] films and intrinsic bulk materials of ZnS [53], CdS [54,55], and AgBr [56].

It can be seen from the table 5.1 that the activation energies of all the films studied decreases with increasing applied voltage. The zero field activation energies may be associated with traps in the energy gap. Also the linear dependence of these curves along with the significant variations in the slope between the curves obtained for different voltage levels implied the existence of an exponential distribution of trapping levels (tailing) rather than of a single discrete hopping level below the conduction band edge. This fact is in confirmation with the discussion given above.
### Table 5.1

**Variation of activation energies with applied voltages for vacuum evaporated and hot wall deposited Ge, Se and Ge$_x$Se$_{1-x}$ films**

<table>
<thead>
<tr>
<th>Applied Voltages (Volts)</th>
<th>Vacuum evaporated</th>
<th></th>
<th></th>
<th>Hot wall deposited</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ge</td>
<td>Se</td>
<td>Ge$<em>x$Se$</em>{1-x}$</td>
<td>Ge</td>
<td>Se</td>
<td>Ge$<em>x$Se$</em>{1-x}$</td>
</tr>
<tr>
<td>0</td>
<td>0.50</td>
<td>1.69</td>
<td>0.99</td>
<td>0.25</td>
<td>1.49</td>
<td>1.24</td>
</tr>
<tr>
<td>1</td>
<td>0.35</td>
<td>1.55</td>
<td>0.84</td>
<td>0.21</td>
<td>1.36</td>
<td>0.84</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>1.49</td>
<td>0.70</td>
<td>0.18</td>
<td>1.24</td>
<td>0.55</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>0.99</td>
<td>0.49</td>
<td>0.13</td>
<td>0.99</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Table 5.2

Comparative data values of $\beta$ for Ge, Se and $\text{Ge}_x\text{Se}_{1-x}$ films

<table>
<thead>
<tr>
<th>Material</th>
<th>Method of preparation</th>
<th>Theoretical $-\beta$ $x 10^{-5}$ eV[(Vm)$^{1/2}$]</th>
<th>Experimental $-\beta$ $x 10^{-5}$ eV[(Vm)$^{1/2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\beta_{PF}$</td>
<td>$\beta_S$</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------------</td>
<td>-------------------------------------------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>Ge</td>
<td>Vacuum Evaporation</td>
<td>3.986</td>
<td>1.993</td>
</tr>
<tr>
<td></td>
<td>HWD</td>
<td>5.108</td>
<td>2.554</td>
</tr>
<tr>
<td>Se</td>
<td>Vacuum Evaporation</td>
<td>7.989</td>
<td>3.995</td>
</tr>
<tr>
<td></td>
<td>HWD</td>
<td>6.679</td>
<td>3.340</td>
</tr>
<tr>
<td>$\text{Ge}<em>x\text{Se}</em>{1-x}$</td>
<td>Vacuum Evaporation</td>
<td>6.141</td>
<td>3.071</td>
</tr>
<tr>
<td></td>
<td>HWD</td>
<td>5.967</td>
<td>2.984</td>
</tr>
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</table>
REFERENCES


42. H. HIROSE AND Y. WADA, ibid, 4 (1965) 639.
43. K.L. CHOPRA, ibid, 36 (1965) 184.
54. F. URBACH, ibid, 93 (1953) 1324.