Chapter 4
Electrical Properties

4.1 D. C. Electrical Conductivity

Study of electrical and photo-electrical properties of disordered materials has been the subject of extensive investigations for the best part of the century. Inspite of large number of applications, fundamentally, the understanding of these materials is yet not complete. The analysis of disordered systems is complicated because of their complex structure and diverse nature of electrical and photo-electrical properties. A systematic study of electrical and photo-electrical properties provides useful information about the band gap, density of states, mechanism of conduction, type of dominant charge carriers, recombination kinetics and defect states etc. of the material.

In general, the electrical properties of amorphous semiconductors depend either on the motion of carriers in the extended states beyond the mobility edge or in the localized states near the band edge. In materials with high density of states in the energy gap and at low temperature, conduction takes place due to tunneling between localized states at the Fermi Level. Hence, the contribution to conductivity, in general is given as [1],

$$\sigma = e \int g(E) \mu(E) f(E)(1 - f(E))dE$$  \hspace{1cm} (4.1)

where $g(E)$ is the density of extended or localized states, $\mu(E)$ is the mobility of carriers, $f(E)$ is the Fermi distribution function, which can be written as

$$f(E) = \frac{1}{\exp \left[ \frac{(E-E_F)/kT}{1} \right]}$$  \hspace{1cm} (4.2)

Using these basic equations, one can discuss the mechanism of d.c. and a.c. conduction in amorphous semiconductors.

Various models have been proposed to explain the conduction in amorphous semiconductors. In the proceeding chapter 1 (section 1.1.3), a brief description of some of these models have been discussed. Further, a review on electrical and photo-electrical properties of chalcogenides semiconductors has been presented.
Assuming sharp mobility edges, \( \mu = 0 \) for \( E_V < E_F < E_C \), where \( E_V, E_F \) and \( E_C \) are energies of valence, Fermi and conduction levels respectively, the conductivity can be written as [1]

\[
\sigma = e\mu_h g(E_r) kT \left[ \frac{E_C - E_F}{kT} \right] + e\mu_e g(E_v) kT \left[ \frac{E_F - E_V}{kT} \right]
\]

(4.3)

where \( \mu_h \) and \( \mu_e \) are the mobilities of holes and electrons respectively. Amorphous semiconductors are extrinsic in nature because the defect states control the position of fermi level. Conduction in these materials is found to be p-type [2, 3-6] and \( \mu_h \gg \mu_e \). Therefore, the contribution of electrons to the conductivity in these materials is negligible as compared to holes. Hence, Eq. (4.3) can be modified as

\[
\sigma = e\mu_h g(E_r) kT \exp \left[ -\frac{E_F - E_V}{kT} \right]
\]

(4.4)

putting \( e\mu_h g(E_r) kT = \sigma_0 \) we get,

\[
\sigma = \sigma_0 \exp \left[ -\frac{E_F - E_V}{kT} \right]
\]

(4.5)

The D.C. conductivity \( (\sigma_{dc}) \) of amorphous semiconductors has been extensively investigated by many researchers [7-11]. A generalized plot of \( \ln \sigma_{dc} \) versus \( 1/T \) found to consist of more than one segment [9], as shown in Fig. 4.1.

These segments can be classified as the temperature segments. Fundamentally, for amorphous materials, the temperature dependence of conductivity is determined by three mechanisms [7]:

1. Conduction in extended state,
2. Conduction in band tails,
3. Conduction in localized sites.

In case of conduction in the extended state, it is assumed that beyond the mobility edge, the mean free path for conduction is short and nearly equal to the average separation between atoms. The conduction in this case is an activated process and the conductivity is given as

\[
\sigma = \sigma_{\text{min}} \exp \left[ -\frac{E_C - E_F}{kT} \right]
\]

(4.6)

where \( \sigma_{\text{min}} \) is minimum metallic conductivity and \( k \) is Boltzmann constant. In the second mechanism i.e., conduction in the band tails, the conduction occurs due to the tunneling of the carriers to the unoccupied levels of the nearest neighbour. Since the tunneling process involves the emission or absorption of phonons, it requires a
tunneling energy $\Delta W_i$, in addition to the thermal activation energy $E_F - E$, to raise the charge carriers to the levels $E$. The conductivity due to this mechanism is given as

$$\sigma = \sigma_1 \exp \left[ -\frac{E_1}{kT} \right]$$  \hspace{1cm} (4.7)

where the activation energy $E_1$ is given by $E_A - E_F + \Delta W_i$, where $E_A$ is acceptor energy level. The conduction in localized states at Fermi-energy is analogous to impurity conduction in heavily doped semiconductors. The carriers can move between the states via phonon assisted hoping (tunnelling) process. The conductivity due to this mechanism can be written as

$$\sigma = \sigma_2 \exp \left[ -\frac{(\Delta W_i)}{kT} \right]$$  \hspace{1cm} (4.8)

As the temperature is lowered, the number and the energy of phonons decreases, hence the hopping between the nearest neighbour will become less probable and instead the carrier will hop to larger distances i.e., to the sites within the range $kT$. For such conduction, Mott [8] proposed the Variable Range Hopping (VRH) in which the conductivity is proportional to $T^{-1/4}$.

Figure 4.1 Illustration of three modes of electrical conduction as a function of temperature in amorphous semiconductors: (a) Extended state conductivity (b) Conduction in band tails and (c) Conduction in localized sites.
At low temperatures, transport near $E_F$ becomes dominant, since the number of carriers in the extended and tail states decrease significantly. Instead, hopping transport near $E_F$ may occur. Since there are $(4 \pi /3) R^3 N(E_F)$ states available in a spherical region of radius $r$, where $N(E_F)$ is the density of states (DOS) at $E_F$, the average separation of these energy levels can be expressed as

$$W = \left[ \frac{4 \pi}{3} R^3 N(E_F) \right]^{-1} \quad (4.9)$$

This suggests that the hopping distance $R$ is correlated with the energy difference $W$. Using Eq. (4.9), an optimal distance $R$ [8] may be defined, at which the hopping rate will be maximum. Thus, hopping rate $\Gamma$ is called the variable-range hopping (VRH) and has been applied to electronic transport in many disordered materials, Mott [10].

However, tunneling from a lower to a higher energy state within the conduction tail states will have to be thermally activated and hence phonon assisted. The rate $\Gamma$ of such hopping or tunneling from a state of energy $E_i$ to $E_f$, such that $E_i < E_f$, is given as [11]

$$\Gamma = \nu_{ph} \exp \left( - \frac{2R}{a} \frac{W}{kT} \right) \quad (4.10)$$

where $\nu_{ph}$ is usually taken to be the phonon frequency, $W = E_f - E_i$. The radius of localization is: $a \approx 10 \text{Å}$ [11]. Using Eq. (4.9) in Eq. (4.10), and then optimizing the hopping rate with respect to $R$, we obtain $R$ as

$$R = \left( \frac{9a}{8\pi N(E_F)kT} \right)^{1/4} \quad (4.11)$$

Using Eq. (4.11) in (4.9) gives

$$W = 0.2k(T_o T^3)^{1/4} \quad (4.12)$$

where

$$T_o = \frac{18.1}{a^4 k N(E_F)} \quad (4.13)$$

Using Eqs (4.11) and (4.12) in Eq. (4.10), the optimal hopping rate is then obtained as

$$\Gamma_{opt} = \nu_{ph} \exp \left( - \left( \frac{T_o}{T} \right)^{1/4} \right) \quad (4.14)$$

The hopping conductivity [11] can be expressed as
\[ \sigma = \frac{N_c (eR)^2 \Gamma}{6kT} \]  \hspace{1cm} (4.15)

where \(N_c\) is the number of carriers. Substituting Eq. (4.14) in Eq. (4.15) and using \(N_c = N(E_f) kT\), we get

\[ \sigma = \sigma_o \exp \left[ -\left( \frac{T_a}{T} \right)^{1/4} \right] \]  \hspace{1cm} (4.16)

where

\[ \sigma_o = e^{3/2} \nu_o \left[ \frac{N(E_f) a}{32 \pi kT} \right]^{1/2} \]  \hspace{1cm} (4.17)

Equation (4.17) has been applied to many amorphous semiconductors [11], doped crystalline semiconductors [12] and even high-Tc superconducting materials [13]. Also, percolation approach supports the VRH concept [14].

4.1.1 Experimental:

**Electrical properties of In\(_x\)Se\(_{1-x}\) (x = 0.4, 0.5, 0.6) thin films**

DC conductivity measurements of In\(_x\)Se\(_{1-x}\) (x = 0.4, 0.5, 0.6) thin films have been measured by computer controlled Keithley 6517A electrometer. The current (A) is recorded at different temperatures varying from (100 to 400K) in steps of 10K for a-\(\text{In}_2\text{Se}_3\), a-InSe, c-\(
\text{In}_3\text{Se}_2\) deposited at room temperature and c-\(\text{In}_2\text{Se}_3\) thin film annealed at 393K for 30min. The calculation of activation energy depends on the range of temperatures from low temperature (100K) to high temperature (400K). Activation energy has been calculated from the slope of \(\ln \sigma\) vs. 1000/T curves. We have found three activation energies as shown in the figure 4.2.

We have found three temperature regions (three different activation energies). The first \((E_{a1})\), second \((E_{a2})\) and third \((E_{a3})\) thermal activation energies of conduction along with the temperature range for each region are given in table 4.1 for these thin films. The first region of thermal activation energy of conduction is due to the excitation of holes to the extended valence band. The conductivity in this region is associated with the transport of carriers through the extended states of the relative transport band according to Eq. (4.6). The second region of thermal activation energy of conduction is due to carrier excitation from localized states to extended states according to Eq. (4.7). The third region is due to the hopping conduction near the Fermi level \(E_F\), which is matching for low activation energy, and \(\sigma\) varies...
exponentially with $T^{-1/4}$ according to Eq. (4.8), following the model proposed by Mott [8]. The phonons do not have enough energy for transferring to a nearest neighbour atom and the charge carrier hops from a neutral atom to another neutral atom situated at the same energy level, which can be many interatomic distance away [15]. It is clear from Fig. 4.2, that at high temperatures, $\sigma$ obeys the law: $\ln \sigma \propto 1/T$ and at low temperatures, obey the law $\ln \sigma \propto T^{-1/4}$, indicating variable range hopping in localized states near the Fermi level in the later case [16, 17].

The temperature dependence of the DC conductivity ($\sigma$) of In$_x$Se$_{1-x}$ ($x = 0.4, 0.5, 0.6$) thin films, prepared by thermal evaporation technique, have been studied and plotted in Fig. 4.2. The curves indicate a thermally activated process for DC conduction in these samples. The incorporation of In atoms in Se matrix leads to an increase in the electrical conductivity for a-InSe from $1.93 \times 10^{-6}$ ($\Omega \cdot cm$)$^{-1}$ to 29 ($\Omega \cdot cm$)$^{-1}$ for annealed c-In$_3$Se$_2$ at 393K. Whereas the thermal activation energy decreases from 0.37eV to 0.074eV for conduction in extended state and from 0.12eV to 0.03eV for conduction in band tails and from 0.026eV to 0.01eV for conduction in localized sites for a-InSe and c-In$_3$Se$_2$ thin films respectively and all the values are listed in table 4.1.

We have calculated carrier concentration and the nature of the charge carriers at room temperature (300K), by using Hall effect from the slope of current vs. hall voltage as shown in the figure 4.3. By using the relation $p = (I/Vh)(B/qt)$, where B is magnetic field in (tesla), q electronic charge (coul) and t is the thickness of thin film (~0.5um), we have found that the incorporation of In atoms in Se matrix leads to an increase in carrier concentration. Its value for a-InSe is $4.38 \times 10^{11}$ cm$^{-3}$ and increases to $5.62 \times 10^{19}$ cm$^{-3}$ for annealed c-In$_3$Se$_2$ thin film. On the other hand, we have found the nature of the charge carriers change from p-type to n-type for In$_x$Se$_{1-x}$ at $x = 0.6$ then we have calculated mobility ($\mu$) for all these InSe thin films by using the relation $\sigma = p\mu$.

Figure 4.4 shows the plot of the conductivity in the region below 170 K. The experimental data for different compositions are plotted in figure 4.4 on $T^{-1/4}$ scale. In accordance with relation (4.16), $\sigma$ obeys the $T^{-1/4}$ law. In the present set of glasses, the $T^{-1/4}$ law applies for temperatures $T < 170$ K, which can be clearly seen from the plots in figure 4.4, have also been observed to be linear in this temperature range, which proves the insensitivity of the conductivity on temperature [18-19].

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Fig. 4.2 Dependence of Ln (σ) vs. 1000/T in the range 100K-400K for as deposited (a) a-In$_2$Se$_3$ thin films (b) a-InSe thin films (c) c-In$_3$Se$_2$ thin films and (d) annealed c-In$_3$Se$_2$ thin films at 393K for 30 min.
Fig. 4.3 Hall voltage vs. current at room temperature for as deposited (a) a-In$_2$Se$_3$ thin films (b) a-InSe thin films (c) c-In$_3$Se$_2$ thin films and (d) annealed c-In$_3$Se$_2$ thin films at 393K for 30 min.
From figure 4.4, we have evaluated the constant $T_0$ from the slope of the $\ln (\sigma T^{1/2})$ vs. $T^{-1/4}$ by using the relation (4.16) and then we have calculated the density of states $N(E_F)$ at the Fermi level by using the Eq. (4.13). The density of states for a-In$_2$Se$_3$ is $9.09 \times 10^{19} \text{cm}^3\text{eV}^{-1}$ and increases to $9.8 \times 10^{21} \text{cm}^3\text{eV}^{-1}$ for c-In$_3$Se$_2$ thin films and then decrease to $5.39 \times 10^{20} \text{cm}^3\text{eV}^{-1}$ for annealed c-In$_3$Se$_2$ in the temperature range of 100-160K. The values have been listed in the table 4.1 for all the four InSe alloys. The hopping distance ($R$) of the charge carriers have been calculated by using the Eq. (4.11) and its value decrease as we increase the In concentration. For a-In$_2$Se$_3$ its value is $4.33 \times 10^{-7} \text{cm}$ and decreases to $1.34 \times 10^{-7} \text{cm}$, for c-In$_3$Se$_2$ thin films and then increase to $2.77 \times 10^{-7} \text{cm}$ for annealed c-In$_3$Se$_2$ thin films at 130K as shown in the table 4.1 [20]. In addition the energy differences between the localized states ($W$) have been calculated by using the Eq. (4.12). The hopping energy for a-In$_2$Se$_3$ is $0.032 \text{eV}$ and decreases to $0.01 \text{eV}$ for c-In$_3$Se$_2$ thin films and then increase to $0.02 \text{eV}$ for annealed c-In$_3$Se$_2$ in the temperature 130K. Thus, from the experimental results in the present system, one can clearly see that the charge transport in the low temperature range can be attributed to the hopping of the charge carriers at the localized states.

Viswanathan et al. [21] have reported the variable range hopping in the InSe thin films, the conductivity was behaving like that of Mott's variable-range hopping (VRH) type in the temperature range 210–290 K. Watanabe et al [22] carried out the measurements in the In$_x$Se$_{100-x}$ system over a wide range of compositions from $x = 6\%$ to $x = 53 \%$ and could observe only activated type conduction in all the samples. However, in their later communication [23] they repeated their measurements of dc conductivity on $x = 37$, 40 and 43 % samples over a wider temperature range and could observe the variable range hopping conduction in these samples.

Shigetomi et al. [24] have made the Hall measurements on crystalline InSe in the temperature range of 300K with the hole concentration $10^{13}$ to $10^{15} \text{cm}^{-3}$. Chaiken et al [25] have done the Hall measurements on polycrystalline $\gamma$-In$_3$Se$_3$ thin films namely n-type carriers with carrier concentration of $< 10^{13} \text{cm}^{-3}$ and mobility $20 \leq \mu \leq 60 \text{cm}^{2}/\text{Vsec}$. 
Fig. 4.4 Dependence of \( \ln (\sigma T^{1/2}) \) vs. \( T^{1/4} \) in the range 100K-160K for as deposited (a) a-In\(_2\)Se\(_3\) thin films (b) a-InSe thin films (c) c-In\(_3\)Se\(_2\) thin films and (d) annealed c-In\(_3\)Se\(_2\) thin films at 393K for 30 min.
Table 4.1 Electrical parameters like activation energy ($E_a$), carrier concentration (n or p), conductivity ($\sigma$) and Hall mobility ($\mu$), density of localized states at the fermi level $N(E_f)$, hopping distance (R) and hopping energy (W) for InSe thin films.

<table>
<thead>
<tr>
<th>Thin films Materials</th>
<th>a-In$_2$Se$_3$</th>
<th>a-InSe</th>
<th>c-In$_3$Se$_2$</th>
<th>c-In$_3$Sc$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{a1}$ (eV)</td>
<td>0.37</td>
<td>0.36</td>
<td>0.27</td>
<td>0.074</td>
</tr>
<tr>
<td></td>
<td>(270-400) K</td>
<td>(270-400) K</td>
<td>(280-400) K</td>
<td>(170-400 K)</td>
</tr>
<tr>
<td>$E_{a2}$ (eV)</td>
<td>0.12</td>
<td>0.104</td>
<td>0.030</td>
<td>0.030</td>
</tr>
<tr>
<td></td>
<td>(160-270) K</td>
<td>(180-270) K</td>
<td>(160-280) K</td>
<td>(130-170 K)</td>
</tr>
<tr>
<td>$E_{a3}$ (eV)</td>
<td>0.026</td>
<td>0.021</td>
<td>0.0034</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>(100-160) K</td>
<td>(100-180) K</td>
<td>(100-160 K)</td>
<td>(100-130 K)</td>
</tr>
<tr>
<td>$\sigma$ ($\Omega.cm)^{-1}$</td>
<td>1.93x10^{-6}</td>
<td>3.15x10^{-6}</td>
<td>3.30x10^{-3}</td>
<td>29</td>
</tr>
<tr>
<td>at 300K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carrier concentration (cm$^{-3}$) at 300K</td>
<td>p=4.38x10^{11}</td>
<td>p=2.25x10^{11}</td>
<td>n=3.45x10^{16}</td>
<td>n=5.62x10^{19}</td>
</tr>
<tr>
<td>$\mu$ (cm$^2$/Vsec)</td>
<td>28</td>
<td>87</td>
<td>0.59</td>
<td>3.33</td>
</tr>
<tr>
<td>at 300K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_s$ (100-160K)</td>
<td>2.31x10^{6}</td>
<td>1.20x10^{6}</td>
<td>2.14x10^{4}</td>
<td>3.90x10^{5}</td>
</tr>
<tr>
<td>$N(E_f)$ (cm$^{-3}$eV$^{-1}$)</td>
<td>9.09x10^{19}</td>
<td>1.75x10^{20}</td>
<td>9.80x10^{21}</td>
<td>5.39x10^{20}</td>
</tr>
<tr>
<td>R (cm) at 130K</td>
<td>4.33x10^{-7}</td>
<td>3.67x10^{-7}</td>
<td>1.34x10^{-7}</td>
<td>2.77x10^{-7}</td>
</tr>
<tr>
<td>W (eV) at 130K</td>
<td>0.032</td>
<td>0.027</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The first phase semiconductor transition in as deposited In$_x$Se$_{1-x}$ thin films occurs at x=0.6 from amorphous to hexagonal crystalline phase as discussed in chapter 3 (section 3.5.1). Above this transition point, the electrical conductivity change drastically as we increase the In metal concentration in the same range of temperature. This increase in activation energy of crystallization may be explained by considering the structural change in the binary sample due to the addition of In. The
addition of In would considerably modify the host amorphous network. At lower concentrations of In, it dissolves in the Se chains, and makes bonds with Se in amorphous phase. As the In concentration is increased, some kind of atomic arrangements are developed and In favours the formation of bonds with Se and In.

It is evident that the thermal treatment reduces the disorder present in c-In$_3$Se$_2$ film, and that the transition from the amorphous to the polycrystalline state, which appears with the formation of grains forming more or fewer grain boundaries, produces changes in electrical properties. Such arrangements lead to an increase in the chain length and a decrease in the mobility of molecular species and, hence, much energy is required to complete the disorder-order transformation to change in hexagonal structure [25, 26].

**Electrical properties of Ga$_x$Se$_{1-x}$ (x = 0.4, 0.5, 0.6, 0.7) thin films**

DC conductivity measurements of Ga$_x$Se$_{1-x}$ (x = 0.4, 0.5, 0.6, 0.7) thin films have been measured by computer controlled Keithley 6517A electrometer. The current (A) is recorded at different temperatures varying from (100 to 400K) in steps of 10K for a-Ga$_2$Se$_3$, a-GaSe, a-Ga$_3$Se$_2$, a-Ga$_7$Se$_3$ as deposited at room temperature and c-Ga$_7$Se$_3$ thin film annealed at 453K for 30min. The calculation of activation energy depends on the range of temperatures from low temperature (100K) to high temperature (400K). Activation energy has been calculated from the slope of ln$\sigma$ vs 1000/T curves. We have found two activation energies as shown in the figure 4.5, which depends on Eq. (4.6) for extended state conductivity mechanism and on Eq. (4.8) for conduction in localized sites. We have calculated all the electrical parameters for a- Ga$_2$Se$_3$, a-GaSe, a-Ga$_3$Se$_2$, a-Ga$_7$Se$_3$ as deposited at room temperature and c-Ga$_7$Se$_3$ thin film annealed at 453K for 30min and the values are inserted in table 4.2. The incorporation of Ga atoms in Se matrix leads to an increase in the electrical conductivity and decrease in the thermal activation energy in the temperature range (100-400 K).

We found two temperature regions (two different activation energies). The first ($E_{a1}$) and second ($E_{a2}$) thermal activation energies of conduction along with the temperature range for each region are given in table 4.2 for these thin films. The first region of thermal activation energy of conduction is due to the excitation of holes to the extended valence band with activation energy. The conductivity in this region is
associated with the transport of carriers through the extended states of the relative transport band (according to Eq. (4.6)). The second region is due to the hopping conduction near the Fermi level $E_f$, which is matching for low activation energy, and $\sigma$ varies exponentially with $T^{-1/4}$ (according to Eq. (4.8)), following the model proposed by Mott [8]. The phonons do not have enough energy for transferring to a nearest neighbour atom and the charge carrier hops from a neutral atom to another neutral atom situated at the same energy level, which can be many interatomic distance away [15]. It is clear from Fig. 4.5 that at high temperatures $\sigma$ obeys the law: \( \ln \sigma \propto 1/T \) and at low temperatures, obey the law $\ln \sigma \propto T^{-1/4}$, indicating variable range hopping in localized states near the Fermi level.

Figure 4.5 shows the plot of the DC electrical conductivity of GaSe thin films in the temperature range 100-400K increases with increase in concentration of Ga metal, the electrical conductivity for a-Ga$_2$Se$_3$ is $1.9 \times 10^{-9}$ ($\Omega$.cm)$^{-1}$ increases to $0.51$ ($\Omega$.cm)$^{-1}$ for annealed c-Ga$_2$Se$_3$ at 453K. Whereas the thermal activation energy decreases from 0.79eV to 0.0374eV for conduction in extended state and from 0.041eV to 0.002eV for conduction in localized sites for a-GaSe and c-Ga$_2$Se$_3$ thin films respectively and all the values are listed in table 4.2.

Sakr et al [27] have measured the dc conductivity on GaSe thin films in the temperature range 130–475 K. The conduction in the low temperature range (below 350 K) exhibits relatively less thermal activation energy 0.063 eV and was found to be due to variable range hopping. While in the high temperature range 350–475K, it was 0.32 eV. The conductivity increases with increasing temperature according to the ordinary semiconductor behaviour.

We have calculated carrier concentration and the nature of the charge carriers at room temperature (300K), by using Hall measurements from the slope of current vs. Hall voltage as shown in the figure 4.6. By using the relation $p = (I/V_h) * (B/qt)$, where B is magnetic field in (tesla), q electronic charge (coul) and t is the thickness of thin film (~0.5um), we have found that the incorporation of Ga atoms in Se matrix leads to an increase in carrier concentration. Its value for a-GaSe is $4.1 \times 10^9$ cm$^{-3}$ and increases to $2.6 \times 10^{16}$ cm$^{-3}$ for annealed c-Ga$_2$Se$_3$ thin film. On the other hand, we have found the nature of the charge carriers was p-type for all Ga$_x$Sc$_{1-x}$ (x=0.4, 0.5, 0.6, 0.7) thin films. We have also calculated carrier mobility ($\mu$) for all these GaSe thin films by using the relation $\sigma = pq\mu$
Figure 4.5 Dependence of \( \ln(\sigma) \) vs. \( 1000/T \) in the range 100K-400K for as-deposited (a) a-Ga\(_2\)Se\(_3\) thin films (b) a-GaSe thin films (c) a-Ga\(_3\)Se\(_2\) thin films (d) a-Ga\(_7\)Se\(_3\) thin films and (e) annealed c-Ga\(_7\)Se\(_3\) thin films at 453K for 30 min.
Fig. 4.6 Hall voltage vs. current at room temperature for as deposited (a) a-Ga$_2$Se$_3$ thin films (b) a-GaSe thin films (c) a-Ga$_3$Se$_2$ thin films (d) a-Ga$_7$Se$_3$ thin films and (e) annealed c- Ga$_7$Se$_3$ thin films at 453K for 30 min.
Figure 4.7 Dependence of \(\ln(\sigma T^{1/2})\) vs. \(T^{-1/4}\) in the range 100K-160K for as-deposited (a) \(a\)-Ga\(_2\)Se\(_3\) thin films (b) \(a\)-GaSe thin films (c) \(a\)-Ga\(_3\)Se\(_2\) thin films (d) \(a\)-Ga\(_7\)Se\(_3\) thin films and (e) annealed \(c\)-Ga\(_5\)Se\(_3\) thin films at 453K for 30 min.
Figure 4.7 shows the experimental data of the conductivity for different compositions of GaSe thin films in the region below 250 K. In accordance with relation (4.16), $\sigma$ obeys the $T^{-1/4}$ law. We have evaluated the constant $T_0$ from the slope of the $\ln(\sigma T^{1/2})$ vs. $T^{-1/4}$ by using the relation (4.16) and then we have calculated the density of states $N(E_F)$ at the Fermi level by using the Eq. (4.13). The density of states for a-Ga$_2$Se$_3$ is $1.7 \times 10^{19}$ cm$^{-3}$ eV$^{-1}$ and increases to $2.97 \times 10^{20}$ cm$^{-3}$ eV$^{-1}$ for a-Ga$_3$Se$_2$ thin films and then decreases to $4.11 \times 10^{19}$ cm$^{-3}$ eV$^{-1}$ for a-Ga$_7$Se$_3$ and then increases to $5.12 \times 10^{22}$ cm$^{-3}$ eV$^{-1}$ for annealed c-Ga$_7$Se$_3$ in the temperature range of 100-250K. The values have been listed in the table 4.2 for all the four GaSe alloys. The hopping distance ($R$) of the charge carriers have been calculated by using the Eq. (4.11) and its value decreases as we increase the Ga concentration. For a-Ga$_2$Se$_3$, its value is $6.55 \times 10^{-7}$ cm and decreases to $3.22 \times 10^{-7}$ cm for a-Ga$_3$Se$_2$ thin films and then increases to $5.28 \times 10^{-7}$ cm for a-Ga$_7$Se$_3$. It again decreases to $8.88 \times 10^{-8}$ cm for annealed c-Ga$_7$Se$_3$ thin films at 130K as shown in the table 4.2.

In addition, the energy difference between the localized states ($W$) have been calculated by using the Eq. (4.12). The hopping energy for a-Ga$_2$Se$_3$ is 0.049 eV and decreases to 0.024 eV for a-Ga$_3$Se$_2$ thin films and then increases to 0.039 eV for a-Ga$_7$Se$_3$. It again decreases to 0.0066 for annealed c-Ga$_7$Se$_3$ in the temperature 130K. Thus, from the experimental results, one can clearly see that the charge transport in the low temperature range can be attributed to the hopping of the charge carriers at the localized states. In addition, the hopping distance ($R$) and the energy difference between the localized states ($W$) between which the hopping takes place decreases with increase in the concentration of Ga [27, 28].

Thmilsevan et al [28] have reported the variable range hopping in amorphous and poly-GaSe films at low field conduction. The amorphous and polycrystalline GaSe thin films have localized states density values of $N(E_F) = 1.686 \times 10^{17}$ cm$^{-3}$ eV$^{-1}$ and $1.257 \times 10^{15}$ cm$^{-3}$ eV$^{-1}$ respectively. The experimental results have been interpreted in terms of variations in the density of localized states due to progressive decrease of the unsaturated bonds during deposition.

In polycrystalline materials, at low temperatures, the carriers can not be transferred into the grain by thermionic-emission as they do not have enough energy to cross the grain barrier potential. In the grain boundary-trapping model, the trapping states created by the disordered atoms and the incomplete bonding among them are distributed in the band gap. Depending on the temperature and also on the distribution
of these states in the gap, some of the trapping states are filled with carriers. The empty states may capture an electron from the charged state under favourable energy condition. Then a possibility for conduction is by the hopping of charge carriers from filled trap states to the empty trap states [29].

Table.4.2. Electrical parameters like activation energy ($E_a$), carrier concentration ($n$ or $p$), conductivity ($\sigma$) and Hall mobility ($\mu$), density of localized states at the Fermi level $N(E_f)$, hopping distance ($R$) and hopping energy ($W$) for GaSe thin films.

<table>
<thead>
<tr>
<th>Thin films materials</th>
<th>a-Ga$_2$Se$_3$</th>
<th>a-GaSe</th>
<th>a-Ga$_3$Se$_2$</th>
<th>a-Ga$_2$Se$_3$</th>
<th>e-Ga$_3$Se$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{a1}$ (eV)</td>
<td>0.79</td>
<td>0.74</td>
<td>0.312</td>
<td>0.089</td>
<td>0.037</td>
</tr>
<tr>
<td>(250-400K)</td>
<td></td>
<td>(250-400K)</td>
<td></td>
<td>(220-400K)</td>
<td>(220-400K)</td>
</tr>
<tr>
<td>$E_{a2}$ (eV)</td>
<td>0.041</td>
<td>0.034</td>
<td>0.018</td>
<td>0.033</td>
<td>0.002</td>
</tr>
<tr>
<td>(100-250K)</td>
<td></td>
<td>(100-250K)</td>
<td></td>
<td>(100-220K)</td>
<td>(100-220K)</td>
</tr>
<tr>
<td>$\sigma$ (\Omega.cm)$^{-1}$ at 300K</td>
<td>1.9x10$^9$</td>
<td>1.8x10$^9$</td>
<td>5.04x10$^6$</td>
<td>0.26</td>
<td>0.51</td>
</tr>
<tr>
<td>$\mu$ (cm$^2$/V.sec) at 300K</td>
<td>2.88</td>
<td>2.04</td>
<td>0.62</td>
<td>1.67</td>
<td>0.12</td>
</tr>
<tr>
<td>$T_e$ (100-160K)</td>
<td>12.1x10$^6$</td>
<td>3.17x10$^6$</td>
<td>0.70x10$^6$</td>
<td>5.11x10$^6$</td>
<td>4.10x10$^3$</td>
</tr>
<tr>
<td>$N(E_f)$ (cm$^{-3}$eV$^{-1}$)</td>
<td>1.74 x10$^{19}$</td>
<td>6.63 x10$^{19}$</td>
<td>2.97 x10$^{20}$</td>
<td>4.11 x10$^{19}$</td>
<td>5.12 x10$^{22}$</td>
</tr>
<tr>
<td>$R$ (cm) at 130K</td>
<td>6.55x10$^{-7}$</td>
<td>4.68x10$^{-7}$</td>
<td>3.22x10$^{-7}$</td>
<td>5.28x10$^{-7}$</td>
<td>8.88x10$^{8}$</td>
</tr>
<tr>
<td>$W$ (eV) at 130K</td>
<td>0.049</td>
<td>0.035</td>
<td>0.024</td>
<td>0.039</td>
<td>0.0066</td>
</tr>
</tbody>
</table>
Electrical properties of Sb$_x$Se$_{1-x}$ (x = 0.4, 0.5, 0.6, 0.7) thin films

DC conductivity measurements of Sb$_x$Se$_{1-x}$ (x = 0.4, 0.5, 0.6, 0.7) thin films have been measured by computer controlled Keithley 6517A electrometer. The current (A) is recorded at different temperatures varying from (100 to 400K) in steps of 10K for a-Sb$_2$Se$_3$, a-SbSe, a-Sb$_3$Se$_2$, a-Sb$_7$Se$_3$ deposited at room temperature and c-Sb$_7$Se$_3$ thin film annealed at 453K for 30min. The calculation of activation energy depends on the range of temperatures from low temperature (100K) to high temperature (400K). Activation energy has been calculated from the slope of ln$\sigma$ vs 1000/T curves. We have found two activation energies as shown in the figure 4.6, which depends on Eq (4.6) for extended state conductivity mechanism and on Eq. (4.8) for Conduction in localized sites. We have calculated all the electrical parameters for a-Sb$_2$Se$_3$, a-SbSe, a-Sb$_3$Se$_2$, a-Sb$_7$Se$_3$ as deposited at room temperature and c-Sb$_7$Se$_3$ thin film annealed at 453K for 30min and the values are inserted in table 4.2. The incorporation of Sb atoms in Se matrix leads to an increase in the electrical conductivity and decrease in the thermal activation energy in the temperature range (100-400 K).

We have found two temperature regions (two different activation energies). The first (E$_{a1}$) and second (E$_{a2}$) thermal activation energies of conduction along with the temperature range for each region are given in table 4.3 for these thin films. The first region of thermal activation energy of conduction is due to the excitation of holes to the extended valence band. The conductivity in this region is associated with the transport of carriers through the extended states of the relative transport band (according to Eq. (4.6)). The second region is due to the hopping conduction near the Fermi level $E_F$, which is matching for low activation energy, and $\sigma$ varies exponentially with $T^{-1/4}$ (according to Eq. (4.8)), following the model proposed by Mott [8]. The phonons do not have enough energy for transferring to a nearest neighbour atom and the charge carrier hops from a neutral atom to another neutral atom situated at the same energy level, which can be many interatomic distance away [15]. It is clear from Fig. 4.8 that at high temperatures, $\sigma$ obeys the law: $\ln \sigma \propto 1/T$ and at low temperatures, $\ln \sigma \propto T^{-1/4}$, indicating variable range hopping in localized states near the Fermi level.
Fig. 4.8 Dependence of $\ln(\sigma)$ vs. $1000/T$ in the range 100K-400K for as-deposited (a) a-Sb$_2$Se$_3$ thin films (b) a-SbSe thin films (c) a-Sb$_3$Se$_2$ thin films (d) a-Sb$_7$Se$_3$ thin films and (e) annealed c-Sb$_7$Se$_3$ thin films at 453K for 30 min.
Fig. 4.9 Hall voltage vs. current at room temperature for as deposited (a) a-Sb$_2$Se$_3$ thin films (b) a-SbSe thin films (c) a-Sb$_3$Se$_2$ (d) a-Sb$_7$Se$_3$ and (e) annealed c- Sb$_7$Se$_3$ at 453K for 30 min.
Figure 4.10 Dependence of $\ln(\sigma T^{1/2})$ vs. $T^{-1/4}$ in the range 100K-160K for as-deposited (a) a-Sb$_2$Se$_3$ thin films (b) a-SbSe thin films (c) a-Sb$_3$Se$_2$ (d) a-Sb$_7$Se$_3$ and (e) annealed c- Sb$_7$Se$_3$ at 453K for 30 min.
Figure 4.8 shows the plot the DC electrical conductivity of SbSe thin films, in the temperature range 100-400K, increases with increase in concentration of Sb metal. The electrical conductivity for a-Sb$_2$Se$_3$ is $1 \times 10^{-9}$ (Ω.cm)$^{-1}$ increases to 0.98 (Ω.cm)$^{-1}$ for annealed c-Sb$_7$Se$_3$ at 453K. Whereas the thermal activation energy decreases from 0.63eV to 0.117eV for conduction in extended state and from 0.074eV to 0.0037eV for conduction in localized sites for a-SbSe and c-Sb$_7$Se$_3$ thin films respectively. All these values are listed in table 4.3.

We have calculated carrier concentration and the nature of the charge carriers at room temperature (300K), by Hall measurements from the slope of current vs. Hall voltage as shown in the figure 4.9. By using the relation $p = (I/V_{H})*(B/qt)$, where B is magnetic filed in (tesla), q electronic charge (coul) and t is the thickness of thin film (~0.5um), we have found that the incorporation of Sb atoms in Se matrix leads to an increase in carrier concentration. Its value for a-SbSe is $1.3 \times 10^{10}$ cm$^{-3}$ and increases to $3.1 \times 10^{19}$ cm$^{-3}$ for annealed c-Sb$_7$Se$_3$ thin film. On the other hand, we have found the nature of the charge carriers change from p-type to n-type for SbxSe$_{1-x}$ at $x=0.6$. We have calculated carrier mobility for all SbSe thin films by using the relation $\mu = \frac{p}{q \mu}$.

Figure 4.10 shows the experimental data of the conductivity for different compositions of SbSe thin films in the region below 250 K. In accordance with relation (4.16), $\sigma$ obeys the T$^{-1/4}$ law. We have evaluated the constant $T_0$ from the slope of the Ln ($\sigma T^{1/2}$) vs. T$^{-1/4}$ by using the relation (4.16) and then we have calculated the density of states N (E_F) at the Fermi level by using the Eq. (4.13).

The density of states for a-Sb$_2$Se$_3$ is $5.39 \times 10^{18}$ cm$^{-3}$eV$^{-1}$ and decreases to $1.94 \times 10^{18}$ cm$^{-3}$eV$^{-1}$ for a-Sb$_3$Se$_2$ thin films and then increases to $5.62 \times 10^{22}$ cm$^{-3}$eV$^{-1}$ for annealed c-Sb$_7$Se$_3$ in the temperature range of 100-250K. The values have been listed in the table 4.3 for all the four SbSe alloys. The hopping distance (R) of the charge carriers have been calculated by using the Eq. (4.11) and its value decreases as we increase the Sb concentration. For a-Sb$_2$Se$_3$, its value is $8.78 \times 10^{-7}$cm and increases to $1.13 \times 10^{-6}$cm for a- Sb$_3$Se$_2$ thin films and then decreases to $8.68 \times 10^{-8}$cm for annealed c-Sb$_7$Se$_3$ thin films at 130K as shown in the table 4.3. In addition the energy difference between the localized states (W) have been calculated by using the Eq. (4.12). The hopping energy for a-Sb$_2$Se$_3$ is 0.065eV and increases to 0.084eV for a-Sb$_3$Se$_2$ thin films and then decreases to 0.006eV for annealed c-Sb$_7$Se$_3$ in the temperature 130K. Thus, from the experimental results in the present system, one can
clearly see that the charge transport in the low temperature range can be attributed to the hopping of the charge carriers at the localized states. In addition, the hopping distance (R) and the energy difference between the localized states (W) between which the hopping takes place decreases with increase in the concentration of Sb.

From table 4.3, we see that the density of localized states at the Fermi level $N(E_f)$ increases as the concentration of antimony metal increases. In addition, the hopping distance (R) and the energy difference between the localized states (W) between which the hopping takes place of the charge carriers decreases with increase in the concentration of Sb.

Table 4.3 Electrical parameters like activation energy ($E_a$), carrier concentration ($n$ or $p$), conductivity ($\sigma$) and Hall mobility ($\mu$), density of localized states at the Fermi level $N(E_f)$, hopping distance (R) and hopping energy (W) for SbSe thin films

<table>
<thead>
<tr>
<th>Thin films materials</th>
<th>a-Sb$_2$Se$_3$</th>
<th>a-SbSe</th>
<th>a-Sb$_3$Se$_2$</th>
<th>a-Sb$_7$Se$_3$</th>
<th>c-Sb$_7$Se$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{a1}$ (eV)</td>
<td>0.638</td>
<td>0.659</td>
<td>0.316</td>
<td>0.133</td>
<td>0.117</td>
</tr>
<tr>
<td></td>
<td>(250-400K)</td>
<td>(250-400K)</td>
<td>(170-400K)</td>
<td>(220-400K)</td>
<td>(220-400K)</td>
</tr>
<tr>
<td>$E_{a2}$ (eV)</td>
<td>0.074</td>
<td>0.075</td>
<td>0.071</td>
<td>0.0051</td>
<td>0.0037</td>
</tr>
<tr>
<td></td>
<td>(100-250K)</td>
<td>(100-250K)</td>
<td>(100-170K)</td>
<td>(100-220K)</td>
<td>(100-220K)</td>
</tr>
<tr>
<td>$\sigma$ (\Omega.cm)$^{-1}$ at 300K</td>
<td>1 x10$^{-8}$</td>
<td>2.4x10$^{-8}$</td>
<td>9.2x10$^{-4}$</td>
<td>2.5x10$^{-3}$</td>
<td>0.98</td>
</tr>
<tr>
<td>Carrier concentration (cm$^{-3}$) at 300K</td>
<td>p=1.38x10$^{10}$</td>
<td>p=5.3x10$^{10}$</td>
<td>n=3.7x10$^{14}$</td>
<td>n=9.3x10$^{16}$</td>
<td>n=3.1x10$^{19}$</td>
</tr>
<tr>
<td>$\mu$ (cm$^2$/Vsec) at 300K</td>
<td>4.8</td>
<td>2.8</td>
<td>16</td>
<td>0.16</td>
<td>0.19</td>
</tr>
<tr>
<td>$T_o$ (100-160K)</td>
<td>3.9x10$^7$</td>
<td>6.8x10$^7$</td>
<td>10.8x10$^7$</td>
<td>1.8x10$^4$</td>
<td>3.74x10$^3$</td>
</tr>
<tr>
<td>$N(E_f)$ (cm$^{-3}$eV$^{-1}$)</td>
<td>5.39 x10$^{18}$</td>
<td>3.09 x10$^{18}$</td>
<td>1.94 x10$^{18}$</td>
<td>1.16 x10$^{22}$</td>
<td>5.62 x10$^{22}$</td>
</tr>
<tr>
<td>R (cm) at 130K</td>
<td>8.78x10$^{-7}$</td>
<td>1.01x10$^{-6}$</td>
<td>1.13x10$^{-6}$</td>
<td>1.28x10$^{-7}$</td>
<td>8.68x10$^{-8}$</td>
</tr>
<tr>
<td>W (eV) at 130K</td>
<td>0.065</td>
<td>0.075</td>
<td>0.084</td>
<td>0.009</td>
<td>0.006</td>
</tr>
</tbody>
</table>
4.2 Photoconductivity

Photoconductivity is the incremental change in the electrical conductivity of a substance upon illumination with white light. It is especially apparent for semiconductors and insulators, which have low conductivity in the dark. Significant information can be derived for the electronic states in the semiconductor material, the exciting photon energy and the intensity of the illumination are the important factors on the carrier generation and recombination processes from the dependence of the photoconductivity. These results can in turn be used to investigate optical absorption coefficients and distribution of defects. Methods involving either steady state currents under constant illumination or transient methods involving pulsed excitation can be used to study the electronic density of states as well as the recombination. The transient time-of-flight technique also allows carrier drift mobilities to be determined.

Two types of photoconductions are defined in solids. One is called the transient photoconduction (TPC) and the other steady state photoconduction (SSPC). The time of flight technique (TOF) is a part of TPC. Photocarriers transit from the illuminated electrode to the counter electrode with blocking contacts, and the technique is used for deducing the drift velocity (mobility). In the secondary photoconduction, the whole sample is illuminated and the photocurrent is measured between two electrodes with ohmic contacts.

In general, photoconductivity depends on both the mobility of carriers $\mu$ and their recombination time $\tau$ and hence product of these two i.e.: $\mu \tau$ becomes a very important factor. The photoconduction depends very strongly on the temperature and excitation intensity. Bube [30] has study of photoconductivity has attracted much attention in a wide range of semiconductors. Charge carriers are generated both by thermal excitation and by absorbed photons that have $E \geq E_g$. As a result, the conductivity comprise of two components:

$$\sigma = \sigma_{th} + \sigma_{ph}$$

(4.18)

where $\sigma_{th}$ the thermally induced component and $\sigma_d$ represents the dark conductivity. Photoconductivity comes from the light source to generate equal excess densities of free electrons and holes, $\Delta n = \Delta p$, that lead to a change in the conductivity by

$$\sigma_{ph} = e(u_n \Delta n + u_p \Delta p)$$

(4.19)
When transport occurs in the extended states the photoconductivity, denoted by $\sigma_{ph}$, is defined as

$$\sigma_{ph} = \mu G \tau$$

(4.20)

where $G$ is the generation rate of photocarriers measured in the units of $\text{cm}^{-3}\text{s}^{-1}$, $\tau$ is recombination time (lifetime) measured in seconds (s), and $\mu$ is the free-carrier mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$). However, if transport occurs in the tail states, the $\mu$ represents the hopping mobility, which is very much smaller than the free-carrier mobility. $G \tau$ is the excess number of photogenerated charge carriers under steady-state illumination.

For a thin film of thickness $d$, neglecting multiple reflections, $G$ can be written

$$G = r_j N_0 (1 - R) \{1 - \exp(-\alpha d)\} / d$$

(4.21)

where $r_j$ is the quantum efficiency of generation of photocarriers, $N_0$ is the number of incident photons per unit area ($\text{cm}^{-2}\text{s}^{-1}$), $R$ reflectivity, and $\alpha$ absorption coefficient ($\text{cm}^{-1}$). For $a d < 1$, photons are uniformly absorbed throughout the films and then $\sigma_{ph}$ become:

$$\sigma_{ph} \approx e \eta N_0 (1 - R) \mu \tau \alpha$$

(4.22)

The photoconductivity can be obtained by both DC (steady-state illumination) and AC (chopping illumination) measurements.

The simplest rate equation for the change of the density of photo-excited carriers ($n$) can be expressed as

$$\frac{dn}{dt} = G - \frac{n}{\tau}$$

(4.23)

which gives $n = G \tau$ in the steady state. The rise and decay curves of the density of photo-excited carriers are described by

$$n(t) = G \tau \left[1 - \exp\left(-\frac{t}{\tau}\right)\right]$$

(4.24)

and

$$n(t) = G \tau \exp\left(-\frac{t}{\tau}\right)$$

(4.25)
Such a simple rise or decay curve is usually not observed in amorphous semiconductors, because of the involvement of electron and hole traps in the recombination processes. In the presence of traps, additional processes of trap filling during the rise and trap emptying during the decay get involved and hence the response time becomes longer than the recombination time \( \tau \). Furthermore, the response time is distributed around some peak value, which creates additional complications in the decay and rise curves in amorphous semiconductors. In this situation, \( n(t) \) is given by either a stretched exponential, \( \exp \left[ -\left( \frac{t}{\tau^\alpha} \right) \right] \) or a power law, \( t^\beta \).

### 4.2.1 Photoconductivity measurements of MSe (M=In, Ga, Sb) alloys

Photoconductivity (PC) technique will be used to measure the photosensitivity and photodecay in glassy semiconductor thin films. We have deposited semiconductor thin film (~1 um thickness) over clean glass substrate and then deposit Aluminum electrodes (~ 0.2um) over it for electrical contact with 0.8 mm gap between two electrodes on the surface of thin film. Experimentally we measured the photoconductivity of all the thin films alloys of M\(_x\)Se\(_{1-x}\) (M = In, Ga, Sb and \( x=0.4, 0.5 \) and 0.6). We observed that all thin films except for \( x=0.6 \), exhibits photoconductivity when illuminated for ~3 sec by white light tungsten halogen bulb.

If the energy of absorbed photons is more than optical energy gap of thin films (\( hv > E_g \)), every photon creates electron hole pair in the thin film, and these are separated by external biasing circuit. Electrons move to anode and holes move to negative electrode. The measured current is the sum of dark current and photocurrent. We plotted photocurrent response vs. time for In\(_2\)Se\(_3\), InSe, Ga\(_2\)Se\(_3\), GaSe, Sb\(_2\)Se\(_3\) and SbSe thin films as shown in the figures 4.11, 4.12 and 4.13.

From Fig. 4.11 it is clear that, the photosensitivity for a-In\(_2\)Se\(_3\) thin films is 9.8 and decreases to 3.2 for InSe thin films. The difference between these values is due to two parameters; the quantum efficiency and the trap defects. The photosensitivity for a-Ga\(_2\)Se\(_3\) thin film is 5.8 and decreases to 2.2 for GaSe thin films as shown in figure 4.12. The photosensitivity for a-Sb\(_2\)Se\(_3\) thin films is 2.6 and decreases to 2 for SbSe thin films as shown in figure 4.13, which have been listed in table 4.4. From table 4.4, it is clear that for all thin films alloys, the photoconductivity is higher for thin films in which percentage of Se is 40% than 50%.
Fig. 4.11 Photocurrent response with time for $\text{In}_2\text{Se}_3$ and InSe thin films
Fig. 4.12 Photocurrent response with time for Ga$_2$Se$_3$ and GaSe thin films
Fig. 4.13 Photocurrent response with time for Sb$_2$Se$_3$ and SbSe thin films
When the energy of absorbed photons is lower than the band gap energy $E_g$, the photoconductive effect does not occur in crystalline materials. But in disordered materials due to the existence of defect centers in the band tails, the phenomenon of photoconductivity can take place. Practically, we have evaluated the spectral response of our thin films by two ways: First, the spectral response range from energy gap of thin films by using the limiting wavelength $\lambda_{\text{(cut-off)}}$ which can be expressed in terms of energy gap ($E_g$) as follows: $\lambda_{\text{(cut-off)}} (\text{nm}) = 1240/E_g(\text{eV})$, is listed in table 4.4. Second, we have measured spectral response range of the In$_2$Se$_3$, InSe, Ga$_2$Se$_3$, GaSe, Sb$_2$Se$_3$ and SbSe thin films by using spectrophotometer SOLAR-TII MS2004 system. We have got monochromatic wavelengths from white light source, we have plotted spectral response vs. wavelength as shown in figure 4.14.

Fig 4.14 Spectral response vs. wavelength of In$_2$Se$_3$, InSe, Ga$_2$Se$_3$, GaSe, Sb$_2$Se$_3$ and SbSe thin films at room temperature
Daman et al [31] have measured the spectral response for InSe thin film in range 450-1100 nm. Shigetomi et al [32] have showed the spectral response of the short-circuit current of GaSe (Cu)/InSe photocells with the p-GaSe layer thickness as a parameter in the range (600-1000) nm. Qasrawi et al [33] measured the photocurrent of the polycrystalline β-GaSe thin films studied as function of incident illumination-intensity and temperature 80-300 K. Anis et al [34] measured the photoconductivity of GaSe thin films grown by the flash evaporation technique in the temperature region of 77-300K. Iovu et al [35] studied the steady-state photocurrent spectral response of Sb₂Se₃ and Sb₂Se₅: Sn films in the wavelength range from 500 to 1200 nm. We have got the similar type of photoresponse in our samples also.

Table 4.4 Photoconductivity data for In$_2$Se$_3$, InSe, Ga$_2$Se$_3$, GaSe, Sb$_2$Se$_3$ and SbSe thin films at room temperature.

<table>
<thead>
<tr>
<th>Thin films</th>
<th>σ dark (Ω.cm)$^{-1}$</th>
<th>σ Light (Ω.cm)$^{-1}$</th>
<th>Photosensitivity $\sigma_{ph}/\sigma_d$</th>
<th>$E_g$ (eV)</th>
<th>$\lambda$(cut-off) nm</th>
<th>Spectral response Range(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$Se$_3$</td>
<td>5.0 x10$^{-6}$</td>
<td>5.4x10$^{-5}$</td>
<td>9.8</td>
<td>1.44</td>
<td>~0.86</td>
<td>400-1000</td>
</tr>
<tr>
<td>InSe</td>
<td>1.4 x10$^{-5}$</td>
<td>6.0 x10$^{-5}$</td>
<td>3.2</td>
<td>1.16</td>
<td>~1</td>
<td>400-1100</td>
</tr>
<tr>
<td>Ga$_2$Se$_3$</td>
<td>6.0 x10$^{-7}$</td>
<td>4.1 x10$^{-6}$</td>
<td>5.8</td>
<td>2.05</td>
<td>~0.6</td>
<td>400-700</td>
</tr>
<tr>
<td>GaSe</td>
<td>2.0 x10$^{-5}$</td>
<td>6.4 x10$^{-5}$</td>
<td>2.2</td>
<td>1.43</td>
<td>~0.86</td>
<td>400-900</td>
</tr>
<tr>
<td>Sb$_2$Se$_3$</td>
<td>1.8 x10$^{-8}$</td>
<td>6.5 x10$^{-8}$</td>
<td>2.6</td>
<td>1.26</td>
<td>~0.98</td>
<td>400-950</td>
</tr>
<tr>
<td>SbSe</td>
<td>2.0 x10$^{-8}$</td>
<td>6.0 x10$^{-8}$</td>
<td>2.0</td>
<td>1.03</td>
<td>~1.2</td>
<td>400-1000</td>
</tr>
</tbody>
</table>

4.3 Time of flight (TOF)

In a crystal, defects formed by vacancies, dislocations and grain boundaries can scatter charge motions. In disordered chalcogenides, charges are “trapped” at lower energy sites, and moves through hopping: either phonon-assisted or tunneling. The phonon-carrier interaction is highly field and temperature sensitive. The effective mobility changes in the presence of traps. An example of a simple trap distribution is shown in figure 4.15. Let $\mu_0$ and $n_0$ be the mobility and carrier density in the
conduction band. $N_t$ carriers are trapped, with trap depth energy $E_t$. Then the situation can be divided into two cases: shallow traps and deep traps. Let us first consider shallow traps [41], which are characterized by the condition $\tau < T_t$. During the transit time ($T_t$), the average mobility is related to the trap-free value by

$$n_0 \mu_0 = (n_0 + n_t) \mu$$  \hspace{1cm} (4.26)

where $n_t$ is the density of trapped charge. In thermal equilibrium, we have,

$$\frac{n_t}{n_c} = \frac{N_t}{N_c} \exp \left( \frac{E_t}{kT} \right)$$  \hspace{1cm} (4.27)

where $N_t$ and $N_c$ are the total trap density (at $E_t$) and density of conduction states (at the band edge), respectively. Equation (4.26) and (4.27) lead to the effective mobility,

$$\mu = \mu_0 \left[ 1 + \frac{N_t}{N_c} \exp(E_t / kT) \right]^{-1}$$  \hspace{1cm} (4.28)

At sufficiently high temperature, $\mu \approx \mu_0$. At low temperature, the exponential term in eq. (4.28) dominates and

$$\mu = \mu_0 \exp \left( -\frac{E_t}{kT} \right)$$  \hspace{1cm} (4.29)

The second group of traps is “deep” trap defined by the condition: $\tau > T_t$. With the existence of deep traps, some of the carriers will be delayed and we would expect a more complicated dependence of mobility on temperature. If the shallow and deep traps dominate, all the carriers are trapped at least once or even the carriers are transported from trap directly. We encounter the so-called dispersive transport which has been studied by several researchers [42-44].
Time-of-Flight (TOF) technique is used to study the behaviour of photogenerated charge carriers in the case of low conductivity semiconductors. Using TOF technique, we can estimate the parameters of these materials like charge carrier mobility, charge carrier concentration, extracted charge, charge carrier bimolecular recombination coefficient, monomolecular carrier lifetime, quantum efficiency, density of states, mobility-lifetime product, charge carrier drift distance, sample resistance, diffusion coefficient and current of photogenerated charge carriers.

TOF method allows us to study the nature of photogenerated charge carriers and the experimental setup is rather simple: external electric voltage pulse is applied on the sandwich-type semiconductor sample and after the $\tau_{ac}$ relaxation time the short laser light pulse is applied to photogenerate charge carriers of the semiconductor. The photogeneration can be surface or volume, depending on the absorption coefficient of the material: If $ad > 1$, then surface photogeneration takes place and if $ad < 1$, then volume photogeneration takes place, where $\alpha$ is the absorption coefficient and $d$ is the sample thickness.

The TOF experiment is completely different from the photoconduction experiment described earlier. In the TOF technique, photocarriers transit from the illuminated electrode to the counter electrode with blocking contacts and carriers are far from thermal equilibrium. So, this type of transport is called the transient photoconduction and a sample of sandwich configuration is used in the experiment as shown in Fig 4.16. Both electrons and holes are created as a thin sheet below the illuminated transport electrode using a flash of highly absorbable illumination. Therefore, light of energy much larger than band gap is required. One of the carriers, electron or holes, drifts across the sample under the external applied voltage $V$.

Fig. 4.16 TOF circuit diagram.
While these carrier packets are moving through the sample, a current is induced in the external circuit. The drift mobility is then estimated by

\[ \mu_d = \frac{v_d}{E} = \frac{v_d}{V/d} = \frac{d/T_t}{V/d} = \frac{d^2}{VT_t} \]  

(4.30)

where \( T_t \) is called the transit time, \( v_d \) drift velocity, \( E \) an applied electric field, \( V \) biasing voltage and \( d \) thickness of the sample. For carriers which move exclusively in extended states, the dispersion results from statistical variations in scattering processes, which described in terms of a diffusion coefficient \( D \) which is related to the carrier mobility via the Einstein relation

\[ D = \left( \frac{kT}{e} \right) \mu \]  

(4.31)

The photoconductive gain has an interesting physical significance. Let \( T_t \) be the transit time for a charge carrier to drift from one detector electrode to the other,

\[ G = \frac{\tau}{T_t} \]  

(4.32)

\( G \) is thus the ratio of carrier lifetime to carrier transit time, and \( \eta G \) is the probability that a photon incident on the detector will produce a charge carrier that will penetrate to an electrode. And \( \eta \) is the quantum efficiency of generation of photocarriers, \( \eta=1 \) that's mean every generated carrier from one photon [36].

4.3.1 Time of flight measurements of MSe (M=In, Ga, Sb) alloys

We deposit thin film alloy (thickness > 1 \( \mu m \)) on the pre-deposited Al electrode (back contact) on glass substrate followed by the deposition of semitransparent layer of metal (usually Al) over this film. Biasing circuit consists of load resistance (\( \approx 1000 \) ohms) and power supply (3 volt) as shown in figure 4.16. The TOF method in disordered materials is limited to moderate electric fields, representative values ranging between 4\( \times 10^4 \) \( V \ cm^{-1} \) to 1\( \times 10^6 \) \( V \ cm^{-1} \).

The thin film was illuminated using the second harmonic double frequency KTP crystal (532 nm) of a Nd:YAG laser pulse 1064 nm with 10 ns pulse durations to generate electron hole pair with the condition that photon energy \( h\nu \geq E_g \). Carriers drift to opposite electrodes depending on the majority carriers in the samples. All samples are p-type as is investigated by Hall measurements. The photogenerated charges drift through the sample under the external electric field applied by a voltage
supply and were recorded by a digitizing oscilloscope using a low-noise current amplifier. The devices were kept under the constant applied bias between the light pulses to ensure extraction of all the photogenerated carriers between the measurements. The transit time of charge carriers was defined as the intersection point of the asymptotes of the two linear regimes in the photocurrent versus time plots as schematically illustrated in Fig. 4.17. The incident-light intensity was adjusted by power supply.

Carrier types were selected by applying a bias using regulated power supply. The current transient signal produced by the laser pulse in presence of the applied electric field was recorded using digital storage oscilloscope. Mobility ($\mu$) was then calculated from Eq (4.30), where $d$ is the thickness of thin film, $V$ is the applied voltage, $T_t$ is the charge carrier transit time.

The analysis of signal shape recorded from TOF for thin films are represented in figure (4.17), where

- **Rise time** ($t_r$) : Value from 10% to 90% of output signal storage from TOF.
- **Fall time** ($t_f$) : Value from 90% to 10% of output signal storage from TOF.
- **Transit time** ($T_t$) : Time required moving all carriers from one electrode to another by applied electric field and incident laser pulse.
- **Life time** ($\tau$) : Average time for a free carrier to be captured (shallow or deep traps by localized state)
- **Gain** ($G$) : is the ratio of carrier lifetime to carrier transit time,

![Fig 4.17 Shape of electrical pulse from semiconductor material.](image-url)
Fig. 4.18 Photocurrent response with time for In$_2$Se$_3$ and InSe thin films
Fig. 4.19 Photocurrent response with time for $\text{Ga}_2\text{Se}_3$ and GaSe thin films
Fig. 4.20 Photocurrent response with time for Sb\textsubscript{2}Se\textsubscript{3} and SbSe thin films.
Figures 4.18, 4.19 and 4.20 shows the experimental data of the photocurrent response with time from TOF technique with computerized digital oscilloscope for In$_2$Se$_3$, InSe, Ga$_2$Se$_3$, GaSe, Sb$_2$Se$_3$ and SbSe thin films respectively. We have calculated signal data parameters like rise time ($t_r$), transit time ($T_t$), life time ($\tau$) and fall time ($t_f$), by analyzing the diagram of figure 4.17. Mobility for all these samples are calculated with positive biasing circuit by using Eq. 4.30, and calculated gain by using Eq. 4.32, and all the values are inserted in table 4.5.

From figure 4.18 and the results shown in table 4.5, it is clear that the rise time, transit time, life time, fall time and gain for In$_2$Se$_3$ thin film are 14μsec, 56μsec, 230μsec, 740μsec, 4.1 and increases to 21μsec, 170μsec, 1550μsec, 3760μsec, 9.1 whereas the values of mobility reduce from 5.89x10$^{-5}$ cm$^2$/Vsec to 1.94x10$^{-5}$ cm$^2$/Vsec respectively for InSe thin films. It implies that when we increase the In metal concentration, the transit time increases and leads to decrease in mobility. It is due to the increase in the defects with dangling bonds and trapping centers between valence and conduction bands.

From figure 4.19 and the results shown in table 4.5, the rise time, transit time, life time and fall time for Ga$_2$Se$_3$ thin film are 13μsec, 24μsec, 143μsec and 435μsec and increase to 16μsec, 36μsec, 188μsec and 465μsec, and except gain and mobility which decrease from 5.9 and 1.37x10$^{-4}$ cm$^2$/Vsec to 5.2 and 9.16x10$^{-5}$ cm$^2$/Vsec respectively for GaSe thin films. It may be due to the reason that when we increase the Ga metal concentration, the transit time increases and lead to decrease of mobility. It is due to the increase of defects with dangling bonds and trapping center between valence and conduction bands.

From figure 4.20 and the results shown in table 4.5, the transit time, life time, fall time and gain for Sb$_2$Se$_3$ thin film are 42μsec, 320μsec, 740μsec and 7.6 and decrease to 28μsec, 135μsec, 660μsec and 4.8 whereas rise time and mobility increase from 15 and 7.85x10$^{-5}$ cm$^2$/Vsec to 18 and 1.17x10$^{-4}$ cm$^2$/Vsec respectively for SbSe thin films. It implies that when we increase the Sb metal concentration, the transit time decreases and lead to increase of mobility. It is due to the increase in the defects with dangling bonds and trapping center between valence and conduction bands.

The most interesting result is that the Hall mobility ($\mu_H$) differs significantly from the time-of-flight mobility ($\mu_{TOF}$). Although, based on transport theory, the conductivity and photoconductivity mechanism processes are the main difference between Hall mobility ($\mu_H$) and time-of-flight mobility ($\mu_{TOF}$). The experimental
evidence indicates that the value of Hall mobility ($\mu_H$) is more than from time-of-flight mobility ($\mu_{TOF}$) because it is determined by scattering processes while time-of-flight mobility ($\mu_{TOF}$) is influenced by both scattering and trapping into localized states [8].

Table 4.5 signal data like rise time ($t_r$), transit time ($T_t$), life time ($\tau$), fall time ($t_f$), gain and mobility from TOF technique for In$_2$Se$_3$, InSe, Ga$_2$Se$_3$, GaSe, Sb$_2$Se$_3$ and SbSe thin films

<table>
<thead>
<tr>
<th>Thin films</th>
<th>Rise time ($t_r$) µsec</th>
<th>Transit time ($T_t$) µsec</th>
<th>Life time ($\tau$) µsec</th>
<th>Fall time ($t_f$) µsec</th>
<th>Gain $\tau/ T_t$</th>
<th>Mobility $\text{cm}^2/\text{V} \cdot \text{sec}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$Se$_3$</td>
<td>14</td>
<td>56</td>
<td>230</td>
<td>740</td>
<td>4.1</td>
<td>5.89x10$^{-5}$</td>
</tr>
<tr>
<td>InSe</td>
<td>21</td>
<td>170</td>
<td>1550</td>
<td>3760</td>
<td>9.1</td>
<td>1.94x10$^{-4}$</td>
</tr>
<tr>
<td>Ga$_2$Se$_3$</td>
<td>13</td>
<td>24</td>
<td>143</td>
<td>435</td>
<td>5.9</td>
<td>1.37x10$^{-4}$</td>
</tr>
<tr>
<td>GaSe</td>
<td>16</td>
<td>36</td>
<td>188</td>
<td>465</td>
<td>5.2</td>
<td>9.16x10$^{-5}$</td>
</tr>
<tr>
<td>Sb$_2$Se$_3$</td>
<td>15</td>
<td>42</td>
<td>320</td>
<td>740</td>
<td>7.6</td>
<td>7.85x10$^{-5}$</td>
</tr>
<tr>
<td>SbSe</td>
<td>18</td>
<td>28</td>
<td>135</td>
<td>660</td>
<td>4.8</td>
<td>1.17x10$^{-4}$</td>
</tr>
</tbody>
</table>

**4.4 Application of diodes and solar cells**

**4.4.1 Solar cell**

The photovoltaic effect is the process of conversion of light energy into electricity. A solar cell is a device, which is made by partnering a p-type semiconductor and n-type semiconductor. The semiconductors are chosen such that one of the semiconductors absorbs a significant portion of the light spectrum. Absorption of light depends on the bandgap of the material. If the bandgap is greater than the energy of the photon, light just passes through. On the contrary, if the bandgap is less than the energy of the photon, the photon is absorbed. The absorbed photon gives rise to Electron-Hole pairs (EHP). These excess carriers are swept across the junction by the electric field and are collected at the contacts. This gives rise to photocurrent and can be made to deliver power to a load. Thus the important steps in solar energy conversion are:

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1- Absorption of radiation
2- Generation of carriers
3- Diffusion of minority carriers to the edge of the depletion width
4- Separation of minority carriers by the electric field.
5- Collection of carriers at the contact.

The absorption of light by a semiconductor can be described by the relation

\[ I = I_0 e^{-\alpha(\lambda)t} \]  \hspace{1cm} (4.33)

\( I_0 \) - Intensity of light incident on the semiconductor
\( \alpha \) - Absorption coefficient which is a function of wavelength
\( t \) - Depth of material from surface of incidence.

Fig. 4.21 shows the idealized relation between energy (vertical axis) and the spatial boundaries (horizontal axis). When the solar cell is exposed to sunlight, photons hit valence electrons, breaking the bonds and pumping them to the conduction band.

Sunlight is a spectrum of photons distributed over a range of energy as shown in Fig. 4.22. The PV cells can produce electricity without operating at high temperature and without mobile parts. These are the salient characteristics of photovoltaics that explain safe, simple, and reliable operation.

Silicon (Si), one of the most abundant materials in the Earth’s crust, is the semiconductor used in crystalline form (c-Si) for 90% of the PV applications today. Other materials which are used in the development of solar cells are called thin-film semiconductors, for example amorphous silicon (a-Si), copper indium gallium diselenide (Cu(InGa)Se\(_2\) or CIGS), and cadmium telluride (CdTe). Silicon and III-V semiconductors, made from compounds such as gallium arsenide (GaAs) and gallium indium phosphide (GaInP) are the materials used in concentrator technology that is still in its demonstration stage.

Figure 4.23 shows the trends in efficiency achieved over the past 20 years for all the major PV technologies. These results are for small area “champion cells”, the one-of-a-kind result that establishes the potential of a given material system and device technology. The highest efficiency is for the most expensive and complex devices, based on III–V technologies like GaAs and GaInP, consisting of multiple devices with different optical and electrical properties, grown on top of each other.
Figure 4.21 Schematic diagram of a solar cell.

Figure 4.22 The spectrum of sunlight
These multijunction (MJ) cells outperform other cell technologies for three reasons. These are made from very perfect and high-purity crystalline materials, and can capture either a wider range of the solar spectrum or the same range more efficiently than other devices. These are operated with high concentration factors, using lenses, which increase the efficiency.

Continuing down the efficiency axis we come to the three leading thin-film PV contenders, Cu(InGa)Se$_2$ (CIGS), CdTe and a-Si in that order. The main motivation for interest in thin-film photovoltaics has always been the possibility of lower cost, not higher performance. These cell performance has always been a factor of about 2 lower than Si-wafer technologies until ~2000, when Cu(InGa)Se$_2$ cells with efficiencies of 19% were reported, putting them in potentially close competition with multi-Si, although there are vast differences in the manufacturing experience base between Cu(InGa)Se$_2$ and multi-Si. Finally, we note that the category of “Si film” solar cells in Figure 4.23 is a special case of solar cells developed entirely by one company (Astropower in the USA), in which they are attempting to achieve the high performance of polycrystalline Si with the low-cost approach of thin films.

Figure 4.23 Efficiency for various cell technologies measured under standard laboratory test conditions
### 4.4.2 Diode and solar cell characteristics

When a p-type material and n-type material are joined then p-n junction is formed. The electrons from the n-type material move to the p-type material leaving behind ionized donors, on the other hand, holes from the p-type material would move to the n-type material leaving behind ionized acceptors. The region of ionized acceptors and ionized donors, put together, is referred to as the space charge region. The charges on both sides give rise to an electric field. This field will oppose the natural diffusion tendency of the majority carriers. The diffusion potential or built-in potential is given by Eq (4.34) and this difference in potential produces a bending of energy bands in the semiconductor,

$$V_{bi} = \frac{kT}{q} \ln \left( \frac{N_A N_D}{n_i^2} \right)$$

(4.34)

where:

- \(N_d\) is Donor carriers concentration on the n-side
- \(N_a\) is Acceptor carriers concentration on the p-side
- \(V_{bi}\) is built-in potential
- \(k\) is Boltzmann’s constant
- \(n_i\) is intrinsic carrier concentration

We have made many diodes of the samples \(M_xSe_{1-x}\) (\(x = 0.4, 0.5, 0.6, 0.7\) where \(M=In, Ga, Sb\)). These are characterized in the diode setup. The p-n junction diode allows the current conduction in the forward direction and blocks the current flow in the other (reverse) direction. The ideal diode I-V characteristic is given by the following equation Eq (4.35).

$$I = I_0 \left( e^{qV_d/kT} - 1 \right)$$

(4.35)

where, \(I_0\) is the reverse saturation current, \(V_d\) is the voltage applied across the diode terminals, \(q\) is the electron charge, \(k\) is Boltzmann’s constant, \(T\) is the ambient temperature in Kelvin, and \(n\) is an ideality factor. For the ideal p-n junction, \(n\) is close to 1. In practice, it can vary anywhere from 1.2 to 2 or more. The setup of a p-n junction with power supply (Keithley 6517A) connected with computer is shown in figure 4.24. In forward bias, once the applied voltage is greater than a few \((kT/q)\), we can neglect 1 in Eq (4.35). Logarithms on both sides of the equation, we get Eq (4.36)
\[
\ln(I) \equiv \ln(I_o) + \left[ \frac{qV_a}{nkT} \right]
\] (4.36)

Thus, the plot of \( \ln(I) \) vs. \( V_a \) is a straight line with a slope = \( \frac{q}{nkT} \). The y-intercept gives the reverse saturation current i.e. \( \ln(I_0) \). From slopes we can calculate the ideality factor and the reverse saturation current [37].

![Schematic diagram for Measuring the I-V characteristic of diode](image)

Figure 4.24 Schematic diagram for Measuring the I-V characteristic of diode

From the I-V characteristic of diode, at forward biasing, we can find forward resistance (\( R_f \)) and build-in voltage (\( V_{b0} \)) whereas at reverse biasing, we can find breakdown current (\( I_{b0} \)) and breakdown voltage (\( V_{b0} \)). In practice, the reverse current increases with applied reverse bias due to an increase in the generation of carriers in the depletion regions of diode. The voltage at which breakdown happens is known as the reverse-bias breakdown voltage \( V_{br} \) of the diode and can be measured from the reverse-bias I-V characteristics of the p-n junction device.

A solar cell is a large-area p-n junction designed in such a way so as to allow the incidence of light in the semiconductor regions of the device. In the figure 4.25 under dark or no-illumination conditions, the solar cell behaves exactly like a diode and can be characterized in the manner outlined in the previous section. Under illumination, the I-V characteristics of the solar cell shifts into the fourth. The important figures of merit for a solar cell are the following:
1. Open-circuit voltage ($V_{oc}$). This is the voltage appearing across the device when device is in open-circuit with no current flowing through the terminals.

2. Short-circuit current ($I_{sc}$). This is the current flowing through the device when the terminals are short-circuited, i.e. $V=0$.

3. Maximum Power ($P_{max}$). This is maximum of the product $I*V$ in the fourth quadrant. The voltage and current at which the power is maximum is $V_m$ and $I_m$. In assessments of solar cell performance, one often encounters,

$$FF = \frac{P_{max}}{I_{sc} \cdot V_{oc}} = \frac{I_m \cdot V_m}{I_{sc} \cdot V_{oc}}$$

(4.37)

where FF is known as the fill factor and is always less then unity.

![Figure 4.25 Setup of test solar cell.](image)

**4.4.4 Results and discussion of Diodes**

We have made many diodes and solar cells depending on the layers and type of conduction (p or n) carriers. The geometry of the sample includes beginning with the evaporation of thin film of aluminum (~200 nm thickness) on clean glass slide by thermal vacuum deposition then deposited (~1000 nm) p-type thin film and n-type material (~1000) nm over it to made p-n junction. It is followed by the deposition (~200 nm) of guard aluminum in the form of long strips over the n-type thin film. There should not be any contact between the two electrodes as shown in figure 4.26.
Figures 4.27, 4.28 and 4.29 represent current –voltage curve of p-n junction diodes, the plot of ln(I) vs. V_A is a straight line with a slope = q / n kT. The y-intercept gives the reverse saturation current (Iₒ) and we have calculated from slope the ideal factor (n) and listed in table 4.6. The values of I-V parameters of p-Sb₂Se₃ / n-InₓSeySe₃ pn junction diode as shown in figure 4.27 and 4.30, the built-in voltage (V₉n) is 1 volt, forward resistance (Rₒ) is 2331 Ω, ideal factor (n) is 13, saturation current (Iₒ) 4.11x10⁻⁵ Amp, breakdown current (I₉d) is 2.88x10⁻⁴ Amp and breakdown voltage (V₉d) is 3.5 volt. The values of I-V parameters of p-GaₓSeySe₃ / n-SbxSe1-x pn junction diode as shown in figure 4.28 and 4.31, the built-in voltage (V₉n) is 2.5 volt, forward resistance (Rₒ) is 751 Ω, ideal factor (n) is 23, saturation current (Iₒ) 2.78x10⁻⁶ Amp, breakdown current (I₉d) is 7.25x10⁻⁴ Amp and breakdown voltage (V₉d) is 4.2 volt.

We have plotted I-V curves of four p-n junction diodes consisting of same alloy as shown in figures 4.29 and 4.32, but the change in the concentration of Sb metal from 40% to 70% atomic weight percentage and listed in table 4.6. It is clear that the phase change have been occurred in x=0.6 for SbxSe1-x from p-type to n-type carrier. The value of built-in voltage (V₉n) is 2.6 volt for p-Sb₂Se₃ / n-SbxSe2 because the atomic weight percentage between 40<x<70. Whereas the value of V₉n is 1.0 volt for p-Sb₂Se₃ / n-SbxSe2 because the atomic weight percentage 40<x<60.
Figure 4.27 $\ln(I_0)$ vs. $V_A$ for $p$-$Sb_2Se_3$/$n$-$In_3Se_2$ pn junction diode

Figure 4.28 $\ln(I_0)$ vs. $V_A$ for $p$-$Ga_2Se_3$/$n$-$Sb_2Se_3$ pn junction of a diode
Figure 4.29 $\ln(I_o)$ vs. $V_a$ for $p$-Sb$_2$Se$_3$ / $n$-Sb$_3$Se$_2$, $p$-SbSe / $n$-Sb$_3$Se$_2$, $p$-Sb$_2$Se$_3$ / $n$-Sb$_7$Se$_3$, and $p$-SbSe / $n$-Sb$_7$Se$_3$ for pn junction of a diode.
Electronic, 15 No. 12 (2004) 787-792

[37] J. J. Liou and J.S.Yuan, Semiconductor Device Physics and Simulation