CHAPTER II

THEORIES AND MECHANISM
2. Basic Theories

This chapter describes different theoretical details associated with the phenomenon of photoconductivity directly or indirectly. First some simple models are described and in the latter part mechanism of this phenomenon is described.

2.1 Some simple models

2.1.1 Energy band models

The photoconductivity phenomenon which involves the movement of electrons and holes through the systems can be explained by Energy band model. The energy states of an isolated atom derived by Schrödinger wave equation, are found to consist of discrete levels separated by regions of forbidden energies. These discrete levels separated by forbidden region are broadened into bands due to interaction with crystal lattice (Bloch 1928, Mott and Gurney 1940 and Seitz 1939). The highest occupied energy band filled with electrons is known as valence band and the lowest unoccupied energy band is known as conduction band. However, non-periodicity due to presence of impurities or lattice irregularities in crystal lattice gives rise to localized levels in the forbidden band.
As a result of absorption of energy equal to or greater than the band gap energy, electrons are raised into conduction band leaving behind a positive vacancy known as hole. However, when the hole migrates to a centre where an electron can recombine with it, this process may give rise to luminescent emission (radiative transition) or heat (non-radiative transition).

Fig. 2.1 shows different kinds of possible transitions. Transition A is direct band to band transition with the wavelength approximately corresponding to band gap energy. The impurity centre may absorb radiations of energy less than the band gap energy which results in a transition either to the excited state of the centre C or to the conduction band B giving rise to a band on the longer wavelength side of the fundamental absorption band. The absorption of energy may also result in a transition in which the hole migrates to the luminescent centre and captures its ground state electron, the loss of which is compensated by capturing an electron from the conduction band. Such recombination may be radiative.
FIG. 21 ENERGY BAND MODEL
Based on energy band scheme the following models were proposed by different workers.

(i) Schön-Klasens Model

Schön (1942), Klasens (1946) and Klasens et al (1948) proposed a hole migration theory. The model is shown in fig 2.2. The absorption of light in the fundamental absorption band results in free electron and hole (1) which move in their respective bands leading to photoconductivity. The hole may then be diffused to impurity centre (2) where it gets captured with the electron located there (3). Since this centre can capture an electron, a free electron may migrate to it (4) and gets captured (5) giving off the excess energy as emission. In this way one cycle is completed and this process may be repeated.

According to this model the decay time of photoconductivity and luminescence would be expected to be alike contrary to the observed decay of photoconductivity which is many times less than that of luminescence (Bube 1951, Lambe and Klick 1955). However, presence of non-radiative centres having a small cross section for electron and large cross section for holes may be considered as a solution of this contradiction.
(ii) Lambe-Klick model

This model is shown in fig 2.3. Lambe and Klick (1955, 1956) proposed this model to account for the difference between the decay times of luminescence and photoconductivity. The free carrier which plays the essential role is 'hole'. In this model luminescent level is considered closer to the conduction band and is filled when the cycle begins. Due to absorption of light electron-hole pairs are created (1) which gives rise to photoconductivity due to movement in their respective band (2 and 4). The hole then diffuses to impurity centre where it captures the electron from the centre (3) and gives rise to emission. Finally the electron wandering in the conduction band is captured (5) by the centre with a release of small amount of energy as infrared radiation or vibrational quanta. Since the luminescent transitions and the capture of free electrons occur in different part of the cycle, a difference in time constants of decay of luminescence and photoconductivity is expected.

(iii) Donor-acceptor model

According to Prener and Williams (1958) and coworkers (Apple and Williams 1959, Williams 1980)
simultaneous incorporation of activator and co activator in the host lattice results in discrete levels of acceptors (level I in fig 2.4) situated just above the valence band and those of donors (level II) situated just below the conduction band. Luminescent transition takes place from the excited state of the donor to the ground state of the acceptor. The transition probability will be sensitive to the amount of overlap between level I and II and is essentially determined by covalent characteristic of the bindings.

This model has been supported experimentally by a number of workers (Hopfield et al 1963, Thomas et al 1964, 1965, Hoogenstraaten 1958, Schaffer and Wiliams 1984, Era et al 1968, Shionoya 1970). According to this model the photon energy of a donor-acceptor pair emission ($h\nu$) separated by intrapair distance $r$ is given by

$$h\nu(r) = E_g - (E_d + E_a) + \frac{e^2}{\epsilon r}$$ (2.1)

where $E_g$ is the energy of the band gap, $E_d$ and $E_a$ are the binding energies of the isolated donor and acceptor respectively, $e$ is the electronic charge and $\epsilon$ is the dielectric constant.
FIG. 2.2 THE SCHÖN-KLASENS MODEL

FIG. 2.3 THE LAMBE-KLICK MODEL

FIG. 2.4 THE DONOR-ACCEPTOR MODEL
Radiative cross section $\sigma(r)$ for a pair of electron and hole was estimated as (Thomas et al 1965, Dean and Partrick 1970)

$$\sigma(r) = A' r^2$$

(2.2)

where $A'$ is a constant. The transition probability of a pair emission is given by (Thomas et al 1965).

$$W(r) = W_0 \exp(-2r/r_B)$$

(2.3)

where $W_0$ is a constant and $r_B$ is the Bohr radius of the shallower hydrogenic level. Since the possible intra-pair distance is discrete in the crystal lattice, the characteristic line structure is expected in the emission spectrum as a feature of a donor-acceptor pair emission and has actually been observed in GaP (Hopfield et al 1963, Thomas et al 1964, 1965 and Dean et al 1968), ZnSe (Dean and Merz 1969) and CdS (Shionoya et al 1974, 1975).

From the equation 2.1 the apparent peak of an emission band consisting of unresolved lines resulting from various pairs should shift towards lower
energy during decay (t-shift) and towards higher energies with increasing excitation intensities under continuous excitation (j-shift). On the basis of such shift Shionoya (1966) applied this model to emission bands of ZnS and Bhushan et al (1979) to those of rare earth doped ZnO. In their latter studies on photoconductivity of rare earth doped ZnO (Bhushan and Diwan 1986) they proposed that release of valence electrons from rare earths was responsible for sensitization effect due to such impurities.

2.1.2 Configuration co-ordinate model:

This model has been found to be very suitable for the luminescence of systems in which both absorption and emission takes place in the same centre. It also explains the non-radiative process of multiphonon emission. In the description of lattice in the harmonic approximation, the potential energy can be described as a function of the coordinates of the lattice particles by the equation (Haug 1972).

\[ W = \frac{1}{2} \sum_{\nu\lambda} C_{\nu\lambda} (X_\nu - A_\nu)(X_\lambda - A_\lambda) \]  

\[ \text{-------------------(2.4)} \]
In normal coordinates, $W$ is the sum of oscillator potentials:

$$W - 1/2 \sum_{\alpha} M \omega_{\alpha}^{2} Q_{\alpha}^{2}$$

(2.5)

In the first case $C_{\nu\alpha}$ represents coupling parameters and $A_{\nu}$ the equilibrium positions. In the other equation, $\omega_{\alpha}$ represents the normal frequencies and $Q_{\alpha}$ the normal coordinates. In both cases, $W$ is a parabola if we keep all other coordinates fixed except dependence on a single coordinate $X$ or $Q$.

The total energy of the crystal, which is considered as the sum of potential energy $W$ and the electron energy, when plotted as a function of coordinates describing the total configuration of the lattice ($X$ or $Q$) gives parabolic shape which may be different for two different electron states (fig 2.5). The difference of two electron energies is given by the energy difference of the vertices of the two parabolae. At the intersection of the two parabolae their relation to the two states must be changed so that lower state remains below the higher. The absorption and emission of light is explained with the help of fig 2.5. 'A' represents the equilibrium position of the ground state ie the energetically lowest state. If the centre absorbs light
Excited State (ES)

Ground State (GS)

TOTAL ENERGY

CONFIGURATION COORDINATE

E_Q

FIG. 25 CONFIGURATION COORDINATE MODEL
it is raised to excited states 'B'. Since B is not an equilibrium value then the electron will adjust a new equilibrium and will move into the state C. From here it returns to the ground state at D with the emission of light. The difference between B and C is given off as lattice vibrations. The centre then relaxes from non equilibrium value 'D' to equilibrium value 'A' and gives up energy to the lattice vibrations. It is clear that the energy of absorbed photon is greater than that of emitted photon, the shift is known as Stoke's shift.

According to Mott and Gurney (1940) if sufficient thermal energy is given to a centre in the excited state at C the centre might reach to E and make a transition to the ground state there. Thus the usual photon would not be emitted and thermal quenching of luminescent emission would be observed. The probability of such transition \((P_T)\) is given by-

\[
P_T = S \exp\left(-\frac{E_Q}{kT}\right) \tag{2.8}
\]

where \(E_Q\) is the energy of intersection point above the minimum of the excited state. Thus at the intersection of ground and exited state configurations the electron
can escape the excited state and return to its equilibrium position by generation of several phonons. Such process is called multiphonon emission.

To describe radiationless transition resulting from an excited state to the ground state the different models proposed are shown in fig 2.6 and 2.7. The first one is called Seitz model (1939) and the other one is known as Dexter model. In the first model the system after excitation relaxes to such an extent that its minimum A lies outside the ground state curve and this increases the probability of non-radiative transitions. According to the other model, let us consider that the transition is to a point B on the excited state curve which is higher in energy than the point of close approach of the curves at C. Immediately after the absorption acts and before reaching at new equilibrium the centre may find itself near C sufficiently long that radiationless transitions to the ground state can occur.

The configuration coordinate model has been found to be suitable for F centre in KCl (Russell and Klick 1956), ZnS phosphor (Shionoya 1966) and for the green band of ZnO (Bhushan and Chukichev 1988).
FIG. 26 CONFIGURATION COORDINATE MODEL
FIG. 2.7 CONFIGURATION COORDINATE MODEL
There are certain models which explain the systems, which absorb exciting energy from the host solid or in a centre called sensitizer and emit or dissipate energy without movement of charge carriers in a centre called activator, which is different from the one responsible for absorption, such models are discussed in following lines:

(i) Cascade mechanism

In this mechanism, radiative transfer of energy takes place through the emission of photon by one centre and the reabsorption of the emitted photon by the second centre. An essential condition for the mechanism to hold is that the spectral distribution of sensitizer must overlap the absorption spectrum of the activator.

(ii) Resonance transfer mechanism

In this process non radiative transfer of energy takes place between sensitizer and emitter (Klick and Schulman 1957) due to the near field interaction (Teegarden 1966). The resonance transfer to be efficient a fairly strong overlap in energy should exist between the states of relaxed sensitizer and those of
activators. The energy transferred by resonance transfer process to a 'Killer' or 'Poison' centre is degraded without emission and thus gives rise to concentration quenching phenomenon (Dexter and Schulman 1954).

(iii) Exciton migration mechanism

According to this mechanism exciton created due to absorption of exciting energy at the sensitizer is virtually migrated to the activator by return of an electron at sensitizer from excited state to ground state. Thus electron is excited at activator. The efficiency of this process depends on the probability that an activator ion will reside within a critical volume surrounding the sensitizer and hence the concentration of the activator (Windischmann 1970).

2.2 Mechanism of photoconductivity

2.2.1 Electronic transitions

The different processes involved in the phenomenon of photoconductivity are: (i) absorption and excitation (ii) trapping and capture (iii) recombination. There are three possible types of absorption transitions resulting in photoconductivity.
In Fig 2.8 transition 1 corresponds to absorption by the atoms of the crystal itself producing a free electron and free hole for each photon absorbed. The transition 2 corresponds to absorption at localized imperfections in the crystal producing a free electron and hole bound in the neighbourhood of the imperfection. Transition 3 corresponds to absorption raising an electron from the valence band to an unoccupied imperfection level producing a free hole and an electron bound in the neighbourhood of imperfection. Processes like (i) formation of exciton, (ii) transition between ground and excited state of imperfection and (iii) within allowed bands, resulting due to absorption are unimportant because they do not produce free carriers.

To understand direct and indirect transitions, let us consider the electron momentum in one dimensional case as $p_e = -\hbar k$

and the momentum associated with the absorbed photon in the crystal as

$$p_{pt} = 2\pi \hbar v_n/c$$

where $k$ is the propagation or wavevector, $v$ is the frequency of the light, $\hbar$ is the velocity of light and $n$ is
FIG. 28 ELECTRONIC TRANSITIONS
(absorption and excitation)
the index of refraction. For conservation of momentum,

\[ k = k' - k = \frac{2\pi \nu \eta}{c} \quad \text{-------------------------(2.8)} \]

In terms of representations given in fig 2.8, one can compare \( k \) with the \( k_{\text{max}} = \frac{\pi}{a} \) to determine how large a departure from a vertical transition is allowed. For this we assume that energy is conserved approximately for both transitions and the energy difference involved is given by \( \Delta E = h\nu \). Then

\[ \Delta k/k_{\text{max}} = 2\nu na/c = 2na \Delta E/\hbar c \quad \text{-------------------------(2.9)} \]

Now when \( k=0 \), one gets a vertical transition in fig 2.9 and such transitions are also called direct transitions. Such transitions are important when both conduction and valence band extrema are located at the same value of \( k \). If the conduction band minimum occurs for different \( k \) values from the valence band maximum then there is not only the possibility of direct transition (\( \Delta k = 0 \)) but also the possibility of indirect transition (\( \Delta k \neq 0 \)). Indirect transitions involve either the absorption of both a photon and a phonon or the absorption of a photon and emission of phonon.
FIG. 2.9 DIRECT AND INDIRECT TRANSITIONS BETWEEN VALENCE AND CONDUCTION BANDS
The momentum and energy conservation relations for indirect transitions are given by

\[ k_{pn} = k_f - k_i \]  \hspace{1cm} (2.10) \]

and

\[ E_{pt} + E_{pn} = E_G \]  \hspace{1cm} (2.11) \]

where \( k_{pn} \) is the \( k \) vector for the phonon, and \( k_f \) and \( k_i \) are the \( k \) vectors for the final and initial states of the transition, \( E_{pt} \) is the photon energy, \( E_{pn} \) is the phonon energy and \( E_G \) is the width of the forbidden gap.

In terms of absorption coefficient the conditions for different transitions are expressed as follows:

\[ \alpha \propto (E_v - E_i)^{1/2} \] for allowed transitions and \[ \alpha \propto \begin{cases} (E_v - E_f)^{3/2} & \text{for forbidden transitions} \\ \alpha \propto (E_{pt} - E_G)^2 & \text{if allowed direct transitions at } k=0 \\ \alpha \propto (E_{pt} - E_G)^3 & \text{if forbidden direct transitions at } k=0 \end{cases} \] for indirect transition
Here $E_v$ represents the energy of the top of the valence band and $E_i$ is the energy of the initial state from which transition is made.

(ii) Trapping and capture

The carriers made free due to absorption of photon may be captured either by (i) trapping centre or by (ii) recombination centres. If the captured carrier has a greater probability of being thermally re-excited to the free state than of recombining with a carrier of opposite sign at the imperfection, the corresponding centres are called trapping centres. However, if the captured carrier has a greater probability of recombining with a carrier of opposite sign at the imperfection than of being re-excited to the free state then the centres involved are called recombination centres. Transitions 5 and 5' in fig 2.10 show the trapping and thermal release of electrons in electron traps. Similarly transitions 4 and 4' in this figure represent thermal release of holes in hole traps. Transitions 6 and 7 show capture of a hole and that of an electron respectively. The distinction between traps and recombination centres may be normally done on the basis of the relative probability of thermal ejection versus recombination.
FIG 210 ELECTRONIC TRANSITIONS
(trapping and capture)
However, a centre with an energy level lying near one of the band edges will be more likely to act as a trap than as a recombination centre and vice versa for centres with levels lying near the middle of the forbidden gap. A recombination centre at one condition of light level and temperature may act as a trap at some other condition of light level and temperature.

(iii) Recombination mechanisms

Transitions in which excited carrier gives up its energy in order to recombine with a carrier of opposite type are considered in terms of radiative (emission of photons) and non-radiative (emission of phonons). Some of the transitions showing radiative process are shown in fig. 2.11. Transition 8 corresponds to recombination between free electrons in the conduction band and free holes in the valence band. In this transition, the lost energy is emitted as photons with approximately the energy of the band gap. Such emission is also called edge emission. In the case of radiative recombination occurring between free electrons in conduction band and free holes in valence band the capture coefficient for radiative recombination is given as

\[ C_r = \frac{r^2 \hbar^3}{8 \pi^2 c^2 d(XT)^2 \langle m_e^* \cdot m_h^* \rangle^{3/2}} E_G^{1/2} \]
FIG. 2.11 ELECTRONIC TRANSITIONS (recombination)
where $r$ is the index of refraction, $d$ represents the thickness in which photons are observed.

The other radiative processes are represented by transitions 9 and 10 which corresponds to an electron being captured by an excited centre containing a hole and hole being captured by an excited centre containing an electron respectively. Other radiative processes are transitions at localized centres, transition at isoelectronic centres and donor-acceptor transitions (described earlier).

If the energy of the recombining carrier is dissipated by the emission of phonons then the process is called non-radiative. Such processes may occur in terms of (i) multiphonon emission (described earlier), (ii) Auger effect and (iii) non-radiative defects.

Capture in a large excited orbit with subsequent successive decreases in energy among the excited states of Coulomb attractive centre has been used to explain the large capture cross sections. The maximum cross section of a Coulomb attractive centre by knowing the radius at which a free electron diffuses
into the centre. Using this concept the cross section for non-radiative processes is given as

\[ \sigma = \pi r_c^d = 9 \pi e^2/16 \varepsilon^2 (kT)^2 \quad (2.13) \]

Auger recombination is a three-carrier process, two of which take part in recombination process and the third of which takes up the excess energy. This recombination process might make use of an exciton, one member of exciton carrying off the excess energy to be dissipated in the capture of the other member. This process is shown in fig 2.12 (a and b).

The lifetime in Auger recombination involving an imperfection level is given by

\[ \frac{1}{T_A} = a n p + b n^2 \quad (2.14) \]

in an n-type material. The first term expresses Auger excitation of a minority carrier, the second term expresses Auger excitation of a majority carrier. The constant \( b \) is the Auger recombination coefficient. In most extrinsic materials the second term dominates.
2.12 AUGER RECOMBINATION PROCESSES
Non-radiative defects such as surface recombination, crystal defects providing regions where a localized continuum of states can bridge the energy gap and cluster of vacancies (or a precipitate) of impurities can form non-radiative centres (Bhushan 1985).

2.2.2 Photoconductivity processes

(i) General Concept

If \( n \) and \( p \) represent the densities of free electrons and holes respectively and \( \mu_e, \mu_h \) are the electron and hole mobilities, then the conductivity of an insulator or semiconductor is given by

\[
\sigma = e(n \mu_e + p \mu_h)
\]

(2.15)

If photoexcited holes are captured by imperfections much more rapidly than the electrons and conductivity is dominated by electrons in both light and dark, the dark conductivity is expressed as

\[
\sigma_0 = n_0 e \mu_0
\]

(2.16)

and the conductivity under illumination is

\[
\sigma = n e \mu
\]

(2.17)
By substituting these values in equ. (2.17) we obtain

\[ \Delta \sigma = \sigma - \sigma_0 \geq \mu_0 \Delta n + \Delta \mu \]  

Thus photoexcitation produces changes in both carrier density \( \Delta n \) and carrier mobility \( \Delta \mu \).

(ii) Lifetime

If \( f \) represents electron-hole pairs per second per unit volume due to photoexcitation of the photoconductor then

\[ \Delta n = \frac{f}{\tau_n} \]  

\[ \Delta p = \frac{f}{\tau_p} \]  

where \( \tau_n \) and \( \tau_p \) represent the free lifetime of an electron and a hole respectively.
The equ. (2.19) shows that the change in carrier density can be either by a change in excitation rate $f$ or in lifetime $\tau_n$ i.e.

$$\delta (\Delta n) = \tau_n \delta f \delta \tau_n$$

(2.21)

Normal photoconductivity concerns with change in $\Delta n$ with a change in $f$. A change in $\tau_n$ with a change in $f$ may also occur. Three ranges may be distinguished

$$\Delta \alpha \propto f; \tau_n \text{ constant, independent of } f$$

(2.22)

$$\Delta \alpha \propto f^a; \tau_n \propto f^{-b}, 0 < a < 1$$

(2.23)

$$\Delta \alpha \propto f^b; \tau_n \propto f^{\alpha}, a > 1$$

(2.24)

The behaviour shown by equ. (2.22) is called a linear variation of $n$. Further, equ. (2.23) and equ. (2.24) show a sublinear and a superlinear variation respectively.

(iii) Photoexcitation dependence of mobility

The following three processes express mobility as a function of photoexcitation:

\[\Delta \alpha \propto f^\alpha; \tau_n \propto f^{-\beta}, 0 < \alpha < 1\]

\[\Delta \alpha \propto f^\beta; \tau_n \propto f^{\gamma}, \alpha > 1\]
(i) Photoexcitation to remove the charge on charged impurity centres dominating the scattering of free carriers, (2) excitation of carriers from a low mobility band to a high mobility band, thus producing photoconductivity even though \( \Delta \approx 0 \) exactly and (3) change in mobility due to photoexcitation reduction of barrier heights to free carrier flow in an inhomogeneous material. If \( \mu_b \) represents the mobility of carriers moving through the material with barrier height \( E_b \), then it is represented as

\[
n e \mu_b = (n e)^{E_b/KT} e \mu \quad \text{-------------------------(2.25)}
\]

where \( n \) and \( \mu \) are the values in the nonbarrier regions of the material, then the mobility

\[
\mu_b = \mu e^{-E_b/KT} \quad \text{-------------------------(2.26)}
\]

Since \( E_b \) may be reduced by photoexcitation that produces trapping of charged carriers in or near the barriers, the mobility defined in this way becomes a strong function of excitation intensity as well as temperature.
(iv) Photosensitivity

Photosensitivity means photoconductivity per unit excitation intensity i.e., the change in conductivity caused by excitation, divided by the excitation intensity. Normally there are three different ways to describe photosensitivity: (i) In terms of the product $\mu$ : it is comparable to considering it as change in conductivity per photon absorbed, (ii) Named as detectivity: Which relates photosensitivity to the ratio of the photoconductivity and the dark conductivity and (iii) In terms of gain: The gain of a photoconductor is defined as the number of charge carriers passing between the electrodes per photon absorbed and expressed by the equ.

$$G = \frac{\Delta i}{eF} \quad \text{------------------------(2.27)}$$

where $\Delta i/e$ is the number of electrons passing per second, and $F$ is the total number of photons absorbed per second producing electron-hole pairs. The gain may also be expressed as the ratio of the carrier lifetime to transit time between electrodes.

$$G = \frac{T}{t_n} \quad \text{------------------------(2.28)}$$
Since the transit time is given by
\[ t_n = \frac{1}{\mu_v} \] for an electrode spacing of \( l \), \( G \) is given by

\[ G = T_n \frac{\mu_v}{1^2} \quad \text{(2.23)} \]

The gain depends on the applied voltage, the electrode spacing and the product \( T\mu \) and is a function of materials and device properties.

(v) Quasi or steady state Fermi level

If \( E_{fn} = E_0 - E_F \) and \( E_{fp} = E_F - E_V \), then the carrier densities in a semiconductor are expressed as

\[ n = N_c e^{-E_{fn}/kT} \quad \text{(2.30)} \]

\[ p = N_v e^{-E_{fp}/kT} \quad \text{(2.31)} \]

From the product these two expressions one can get

\[ E_{fn} + E_{fp} = kT \ln \left( \frac{N_c N_v}{n p} \right) \quad \text{(2.32)} \]

Since \( E_G = kT \ln \left( \frac{N_c N_v}{n_1^2} \right) \quad \text{(2.33)} \)
The Fermi levels describe the density of free electrons and holes in steady state. The case of occupation of all imperfection levels which are still essentially in thermal equilibrium under photoexcitation can also be described by them. Thus the occupation of levels in effective thermal equilibrium with the conduction band and valence band may be given by $E_{fn}^*$ and $E_{fp}^*$ respectively. For the steady state Fermi level situation equs. (2.34) and (2.36) show that the two steady state Fermi levels are separated by an energy equal to $\Delta E = \Delta E_{fn} - \Delta E_{fp} = K T \ln (n_p/n_i^2)$. The situation is shown in fig 2.13.

For the difference between $E_{fn}^*$ and $E_{fp}^*$ we have

$$E_{fn}^* - E_{fp}^* = K T \ln \left( \frac{m_e^*}{m_h^*} \right)^{3/2} \frac{2}{p/n}$$  \hspace{1cm} (2.37)
FIG. 2.13 STEADY-STATE ELECTRON AND HOLE FERMI LEVELS
which is valid for thermal equilibrium as well as for steady state conditions.

(vi) Demarcation level

The occupancy of levels in effective thermal equilibrium with one of the band is given in terms of the corresponding steady-state Fermi level. The demarcation level defines the boundary between occupancy determined by effective thermal equilibrium with the nearest band, and occupancy determined by recombination kinetics. The location of demarcation level depends upon the specific values of the capture coefficients \( C_n \) and \( C_p \) for a particular type of imperfection. Thus, there is one set of demarcation levels (electron and hole) for each kind of imperfection as defined by a particular set of capture coefficients.

To describe the correlation between Fermi levels and demarcation levels, let us consider the situation described in the fig 2.14 and equate the probability of thermal excitation of electrons out of electron-occupied levels to the conduction band, to the probability of capture of free holes by these electron-occupied levels. If \( n_L \) is the density
FIG. 2.14 COMPETING RATES FOR STEADY-STATE FERMI LEVELS AND DEMARCATION LEVELS
electron-occupied levels lying $E_I$ below the conduction band,

$$n_IN_c e^{-Edn/KT} = n_I + C_p$$ \hspace{1cm} (2.38)

(as $E_I = Edn$)

where $Edn$ is the positive energy difference between the conduction band edge and the electron demarcation level for the centre with capture coefficients $C_n$ and $C_p$.

Setting

$$N_c = n e^{Ef_n/KT}$$ in equ. (2.38) then

$$Edn = Ef_n - KT ln \left( \frac{C_p}{C_n} \cdot \frac{P}{n} \right)$$ \hspace{1cm} (2.39)

and by setting $P = n e^{Ef_p/KT}$

$$Edn = Ef_p + KT ln \left( \frac{C_n}{C_p} \cdot \left( \frac{m_e}{m_h} \right)^{3/2} \right)$$ \hspace{1cm} (2.40)

Similarly by considering competition between thermal excitation of holes to the valence band and electron capture by these holes at imperfections we get.

$$Edp = Ef_p - KT ln \left( \frac{C_n}{C_p} \cdot \frac{n}{p} \right)$$ \hspace{1cm} (2.41)
The typical sets of Fermi levels and demarcation levels in insulator and semiconductors are shown in fig 2.15. It is also true that

$$E_{dp} = E_{fn} + kT \ln \left( \frac{C_D}{C_n} \cdot \left( \frac{m^*}{m_e^*} \right)^{3/2} \right) \quad \text{--- (2.42)}$$

(vii) Simple kinetics

The kinetics of photoconductivity in intrinsic semiconductor with thermal and optical excitations can be considered in terms of fig 2.16. If the optical and thermal excitation rates are \( f \) and \( g \) respectively, then the rate of change of free electrons and holes are given by

$$\frac{dn}{dt} = \frac{dp}{dt} = f + g - npC_i \quad \text{--- (2.44)}$$

where \( C_i \) is the capture coefficient. In thermal equilibrium

$$g = n_0 p_0 C_i = n_i^2 C_i \quad \text{--- (2.45)}$$

the addition of photoexcitation \( f \) gives
FIG. 2.15 TYPICAL LOCATION OF STEADY-STATE FERMI LEVELS AND DEMARCATION LEVELS FOR A PARTICULAR IMPERFECTION
FIG. 2.16 TRANSITIONS FOR A SIMPLE INTRINSIC MODEL
\[ f+g=(n_0 + \Delta n)^2 \mathrm{C}_i \]  
\[ \text{since } (n_0 + \Delta n) = (P_0 + \Delta P) \]

these two eqns. give

\[ f = \Delta n (2n_0 + \Delta n) \mathrm{C}_i \]  
\[ \text{---------------------------(2.47)} \]

Now if \( \Delta n \ll n_0 \) we get, characteristic behaviour of semiconductor-type.

\[ \tau_n = \tau_p = \frac{\Delta n}{f} = \frac{1}{2n_0 \mathrm{C}_i} \]  
\[ \text{---------------------------(2.48)} \]

In this case the lifetime is constant and depends on the dark conductivity of the material. The photoconductivity varies linearly with \( f \). And when \( \Delta n \gg n_0 \), we get the characteristic behaviour of insulator-type.

\[ \tau_n = \tau_p = \frac{\Delta n}{f} = \frac{1}{\mathrm{C}_i^2} \Delta n = (\frac{1}{\mathrm{C}_i^2} f)^{1/2} \]  
\[ \text{---------------------------(2.49)} \]

In this case the lifetime varies inversely as the square root of the excitation intensity and depends on the change in carrier density. The
photoconductivity varies as the square root of $f$. The existence of imperfection levels in non-intrinsic-high resistivity semiconductor or insulator may cause the lifetime to depart from the relation (2.49), and thus the electron and hole lifetimes become unequal. However, when the excitation intensity is high enough such that the recombination of free electrons and holes dominate the behaviour of eq. (2.49) is found.

(viii) Growth and decay curves

To consider growth and decay of photoconductivity following four factors are important:

(1) The very slow growth of photoconductivity observed under suitable circumstances.

(2) The increase in the decay rate found when thermal freeing of holes from sensitizing centres competes with thermal freeing of electrons from traps.

(3) Growth and decay transients involving overshoots and undershoots of the equilibrium value.

(4) The effect of high electric fields for short periods.

Due to trapping a very slow growth of
photocurrent following the beginning of a low level excitation can follow directly. The majority carriers initially excited will be immediately trapped by empty traps, and considerable time may be required before the steady state Fermi level has been raised sufficiently as a result of excitation to support an appreciable free carrier density.

Decay curve may be expressed by the following expression

$$\Delta i = \Delta i_0 / (1 + at)^b$$ \hspace{1cm} (2.50)

where $a$ and $b$ are constants which may vary with temperature, light intensity and the time during decay. The probability of an electron (hole) escaping from a trap with depth $E$ and electron (hole) capture cross section $S_t$ at a temperature $T$ is given by

$$P = N_{eff} V S_t \exp(-E/KT)$$ \hspace{1cm} (2.51)

where $N_{eff}$ is the effective density of states in the conduction (valence) band. The rate of change of trapped electrons during decay is given by

$$\frac{dn_t}{dt} = -n_{tp}$$ \hspace{1cm} (2.52)

Neglecting the probability of re-
trapping of freed electrons by empty traps, the solution of equ. (2.52) is

\[ n_t = n_0 \exp (-\Gamma t) \]  \hspace{1cm} (2.53)

where the lifetime \( \Gamma \) is given by

\[ \Gamma = \frac{1}{(V_S N_A)^{-1}} \]  \hspace{1cm} (2.54)

and can usually be considered as a constant. Here \( S_r \) represents capture cross section of recombination centre for holes and \( N_r \) the density of holes in the recombination centre. The decay equation is given by

\[ \Delta n = n_t \cdot \Gamma e^{-\Gamma t} \]  \hspace{1cm} (2.55)

If there are many different kinds of traps, with different \( E \) values, the resulting decay curve can be considered as the sum of many exponentials of the form of (2.55).

If retrapping is included, the rate of trap emptying must be multiplied by the ratio of the capture probability for recombination centres and empty
traps in equ.(2.53). Usually uniform distribution of traps is considered. The form of distribution can be obtained from measurements of decay by using the equation.

\[ \frac{T_0}{T} = (n_T) K T / n \]  \hspace{1cm} (2.56)

Here \( T_0 \) is the measured decay time and \( (n_T) K T \) is the density of traps in a width \( K T \) of the forbidden gap below the location of the Fermi level during steady excitation.

(ix) Electrode effects

For photoconductivity studies one of the pre requisites is use of proper electrodes. The ideal electrodes should have no resistance and should not be affected by illumination, temperature or applied electric field. A number of factors control the behaviour of semiconductor or insulator-metal contacts. The important factors which control the behaviour are (a) improper matching of work functions between the metal and the semiconductor (b) presence of surface states on
the semiconductor, producing an intrinsic surface barrier and (c) presence of a thin layer of third material which in turn causes barrier for reasons a and b. Considering work function as a dominant factor following kinds of contacts can be considered.

(A) Nonohmic contacts

Considering a contact between a metal and an n-type semiconductor having the work function of the metal greater than that of the semiconductor, transfer of electrons from semiconductor to metal occurs as shown in fig. 2.17. In this case a depletion layer results in semiconductor from which all free electrons have been removed. If it is considered that the total charge in this region comes from ionized donors, then the potential distribution in the depletion layer, is given by

\[ \frac{d^2V}{dx^2} = -4\pi N^+e/\varepsilon \]  

in this equ. \( N^+ \) represents the ionized donor density. The solution of this equ. is

\[ V = -2\pi N^+e/\varepsilon \cdot x^2 \]  

\]  

\]  

\]  

\]
FIG. 2.17 POTENTIAL BARRIER OF A NONOHMIC CONTACT
The thickness of the depletion layer \( d \) is given by

\[
d = \left( \frac{e V_0}{2 \pi \epsilon N^+} \right)^{1/2}
\]

where \( e V_0 \) represents the barrier height.

Using the relation for capacitance associated with such a barrier layer and depletion layer

\[
C = \frac{\varepsilon A}{4 \pi d}
\]

we get,

\[
\frac{1}{C^2} = 8 \pi V_0 / \varepsilon A^2 e N^+ \]

with a positive bias \( V \) volts this relation changes to

\[
\frac{1}{C^2} = 8 \pi (V_0 - V) / \varepsilon A^2 e N^+ \]

From this relation it is clear that a plot between \( 1/C^2 \) and applied voltage a straight line is obtained with slope related to \( N^+ \) and intercept related to \( V_0 \). If these are acceptor levels in the material then \( N^+ = N_D - N_A \). In this case photoexcitation will result in
capture of photoexcited holes by these acceptors resulting in an increase of the charge in the depletion layer. Photoconductors having nonohmic electrodes can never give gain greater than unity.

(B) Ohmic contacts

In this case a junction is made between a metal and n-type semiconductor having the work function of the metal smaller than that of the semiconductor. Thus, transfer of electrons from metal to semiconductor will occur as shown in fig 2.18. The result is an accumulation layer of excess charge in the semiconductor. The current voltage characteristic of such a contact is ohmic over a range of voltages. At sufficiently high voltage the injected charge becomes comparable to the charge already present in the semiconductor itself after that a space charge limited current flows. The potential variation with distance is described by the equ. (2.57).

\[ \frac{\partial^2 V}{\partial x^2} = -4\pi e^2 n(x)/\varepsilon = -4\pi n_0 e^2 e^{-V(x)/kT}/\varepsilon \]  \((2.83)\)
FIG. 2.18 OHMIC CONTACT BETWEEN METAL AND SEMICONDUCTOR
The solution of this equ. is

\[ V(x) = 2kT \ln \left[ \frac{x}{x_0} \right] \]  \hspace{1cm} (2.64)

where,

\[ x_0 = \left( \frac{e kT}{2 \pi n_0 e^2} \right)^{1/2} \]  \hspace{1cm} (2.65)

so that,

\[ n(x) = n_0 \left( \frac{x_0}{x + x_0} \right)^2 \]  \hspace{1cm} (2.66)

Under the application of an electric field, the potential distribution shown in fig 2.18 is found. The accumulation layer behaves like a virtual cathode to supply charge to the semiconductor to maintain charge neutrality.

(C) Injection

When charges move into a crystal from an ohmic contact under the effect of an applied electric field to produce a condition of non-charge-neutrality resulting in the space-charge-limited current, the phenomenon is known as single injection if only one type
of carriers are injected. The injected current should be such that the dielectric relaxation time of the material may be equal to the transit time of the injected carrier, and thus

$$V = 4\pi \sigma L^2 / \epsilon \mu$$

(2.67)

If ohmic contacts for both types of carriers are present on a crystal, application of voltage leads to injection of both electrons from cathode and holes from the anode. Such phenomenon is called double injection. The current density is given in terms of the total injected charge

$$j = j_0 + \int_{\text{H}} \epsilon V^3 / 4\pi L^5$$

(2.68)

Mayer et al (1965) have found $V^3$ variation in a p-i-n silicon junction device.
2.2.3 Models for photoconductivity

The following models have been considered for the phenomenon of photoconductivity:

(i) Junction models

In a p-n junction during formation of the junction, electrons flow from n-side to the p-side and holes from p-side to n-side until a counter balancing barrier is formed. When this type of p-n junction is reverse biased (n-side positive), there is a high dark resistance for the junction, since the p-region cannot supply free holes to the n-region. Due to photoexcitation an electron-hole pair can be formed within a diffusion length of the junction and such pairs can traverse the junction. The photoconductive process would come to an end when the excited electron-hole pairs cross the junction. The maximum gain in this case is greater than unity.

A p-i-n junction consists of a high resistivity intrinsic region introduced between the p-type and n-type regions. In this case the collection of photoexcited carriers can be controlled by drift due to
an applied electric field, rather than by the slower process of diffusion across the junction as in the simple p-n junction case.

In the case of an n-p-n junction the forward biased p-n junction plays the role of an electrode that replenishes electrons and hence it is possible to have gains greater than unity. The gain $G$ (ratio of time required for holes to diffuse out of the p-region to the time required for electrons to diffuse across the p-region) is expressed by

$$G = \frac{L_{pn} n_1 \mu_e / W p \mu_h}{L_{pn} n_1 \mu_e / W p \mu_h} \quad (2.69)$$

In this relation $L_{pn}$ represents the diffusion length of the holes in the first n-region and $W$ the width of the p-region and $n_1$ refers to the first n-region. The gain in such junctions may be as high as several hundred.

A variety of reasons may be thought for the potential barriers in such structures. In thin films or layers of photoconducting materials, there may be intergrain barriers in a polycrystalline layer. The photoexcitation reduces the height of the barriers
through the production of a localized trapped space charge. The barriers affect the transport of charges which limits the flow of majority carrier through a material (fig 2.19). The conductivity in presence of thin barrier is given by

\[ \sigma = ne^2 \bar{v}_b e^{-E_b/\kappa T} \]  \hspace{1cm} (2.70)

here \( \bar{v} \) represents average velocity and \( l_b \) is the average distance between barriers. Using the relation

\[ \bar{v} = ne \mu_b \]  \hspace{1cm} (2.71)

we get,

\[ \mu_b = e \bar{v} l_b e^{-E_b/\kappa T} / \kappa T \]  \hspace{1cm} (2.72)

Thus, due to change in \( E_b \) which presumably results from the trapping of minority carriers in the immediate vicinity of the barrier, \( \mu_b \) is also affected and is given by (Bube 1974)

\[ \Delta \mu_b = -e \bar{v} l_b \Delta E_b e^{-E_b/\kappa T} / (\kappa T)^2 \]  \hspace{1cm} (2.73)
As lifetime of majority carriers determines $\Delta n$, the trapped time of minority carriers captured before recombination determines $\Delta \mu_b$ due to photoexcitation. Therefore, one is concerned with majority carrier lifetime in $\Delta n$ modulation and that with trapped time in $\Delta \mu_b$ modulation. However, quite different behaviour have been found for PbS films (large $\Delta p$ and small $\Delta \mu$) and CdS-CdSe films (large $\Delta \mu$ and small $\Delta n$).

(ii) Homogeneous materials

Five simple models for homogeneous photoconducting systems are shown in fig 2.20. The variation between systems is considered in terms of (1) the nature of the contact and (2) the freedom of a carrier to move through the crystal.

In first case (fig 2.20a) electrodes are ohmic for both electrons and holes. Thus, both electrons and holes are free to move through the crystal. However, only direct recombination between electrons and holes terminates the additional conducting resulting from photoexcitation. In this case the gain is given by the expression.

$$G = \left( T_n \mu_e + T_p \mu_h \right) V/1^2 \quad \text{(2.74)}$$
The second case (fig 2.20b) describes the situation where the cathode is ohmic for electron flow, but the anode is blocking for hole flow. In this case also, both electrons and holes are free to move through the crystal. The hole lifetime is terminated when the hole passes out of the crystal at the cathode thus the hole lifetime is equal to the hole transit time. When the hole leaves the crystal the replenishment of electrons stops, then the lifetime of electron is also equal to the hole transit time. Thus, we get following formula for gain:

\[ G = \left( \frac{t_p}{t_n} \right) + 1 = \left( \frac{\mu_e}{\mu_h} \right) \frac{\mu_h}{\mu_h} \] \hspace{1cm} (2.75)

Here the gain exceeds unity, but not as large as in the first case.

The third case fig (2.20c) concerns with the situation where none of the electrodes is ohmic for electrons or holes. This is the case of homogeneous material with two blocking contacts, which is analogous to the case of the p-n junction. In the present case the maximum gain is unity.

In the fourth case (fig 2.20d) the cathode is ohmic for electron flow, but the anode is not
ohmic for hole flow. In addition, only electrons are free to move through the crystal because photoexcited holes are captured at imperfections. The gain is contributed solely by electrons and is given by eqn. (2.29)\[ T_n \left( e^{T_n} - 1 \right) \]. The electron lifetime depends on the capture cross section of the imperfections. Large values of \( T_n \) and \( G \) result if this cross section is sufficiently small. This system is homogeneous analogue of the n-p-n-junction case.

In the fifth case (fig 2.20e) the contacts are blocking and only electrons are free to move through the crystal. In this case since a positive space charge builds up in the crystal to counter balance the applied electric field no steady state photoconductivity is possible.

2.2.4 Recombination kinetics

The models concerned with one or two types of recombination centres have been mainly used to describe the variation of the free carrier lifetime with excitation intensity, temperature and thermal equilibrium Fermi level position.
FIG. 2.19 A BARRIER OF HEIGHT $E_b$ TO MAJORITY-CARRIER ELECTRON FLOW

FIG. 2.20 MODELS FOR PHOTOCONDUCTIVITY IN A HOMOGENEOUS MATERIAL
(i) One centre models

(A) Without traps

Suppose \( N_I \) recombination centres are located sufficiently close to the Fermi level in such a way that they are partly occupied, \( n_I \) being occupied by electrons and thus \( (N_I - n_I) \) being not occupied by electrons or occupied by holes.

If the density of free carriers is assumed to be much smaller than \( n_I \) and \( (N_I - n_I) \), then no appreciable change occurs in \( n_I \) or \( (N_I - n_I) \) under photoexcitation, then the corresponding lifetimes for electrons and holes are given by

\[
\tau_n = \frac{1}{C_n (N_I - n_I)} \quad \text{(2.76)}
\]

\[
\tau_p = \frac{1}{C_p n_I} \quad \text{(2.77)}
\]

These two times are independent and unequal.
Next, the density of free carriers can be considered much greater than \( n^1 \) or \((N^1 - n^1)\), a condition which can be achieved under high excitation intensities. For charge neutrality \( n = p \) and therefore \( T_n = T_p \).

If \( n^1 \) represents the density of electron occupied imperfections under the high excitation conditions, and \((N^1 - n^1)^*\) represents the density of empty centres under excitation, by equating equ.(2.76) and (2.77) the following equ. is obtained,

\[
\frac{1}{C_n (N^1 - n^1)^*} = \frac{1}{C_p n^1} \tag{2.78}
\]

which reduces to

\[
\frac{n^1}{N^1} = C_n \left( C_n + C_p \right) \tag{2.79}
\]

Then the lifetime

\[
T_n = T_p = \frac{1}{N^1 \left[ C_p C_n / (C_p + C_n) \right]} \tag{2.80}
\]

If \( C_p \ll C_n \), it reduces to \( 1/N^1 C_p \) and

If \( C_n \ll C_p \), it reduces to \( 1/N^1 C_n \). Thus the rate of recombination is determined by the smaller of the two capture coefficients.
(B) With traps

Models involving one type of recombination centre and traps for the majority carriers have been developed to explain experimental observations of high resistivity semiconductors. In most of the photoconducting materials, traps with different depths are found, simplifying form of a quasi-continuous trap distribution with depth is used. The particle conservation relation is

$$
\Delta n + \Delta n_t = \Delta (N^I - n^I) \quad \text{----------------------(2.81)}
$$

i.e. for each photoexcited electron, there is a trapped photoexcited hole in a recombination centre. The principle properties are as follows-

(a) When $\Delta n \gg n_t$, the recombination is bimolecular and $\Delta n \propto f^{1/2}$. The response time in this case is equal to the electron lifetime.

(b) When $\Delta n \ll \Delta n_t$, the recombination is monomolecular and $\Delta n \propto f$, provided the distribution of trap is reasonably uniform with depth. However, when $\Delta n \ll \Delta n_t$ and also the distribution of trap density with depth is sufficiently nonuniform, $\Delta n \propto f^m$ where $0.5 \leq m \leq 1$. The
response time in this case is determined by the time required for the recombination of all free carriers. Since $\Delta n/T$ is the rate at which free electrons leave the conduction band, the time required to remove $\Delta n_t$ carriers is $\Delta n_t/(\Delta n/T)$, which leads to the following relation between the response time $T_0$ and the lifetime $\tau$

$$T_0 = \tau (1 + \Delta n_t/\Delta n) \quad \text{(2.82)}$$

where $\Delta n_t$ is the density of traps that must empty in order for the Fermi level to drop by $kT$ from its steady-state position under photoexcitation.

(ii) Two centre models

Such models are used to explain phenomena like (1) an increase in photosensitivity resulting from the incorporation of additional recombination centres (imperfection sensitization) (2) a variation of photoconductivity with a power of light intensity greater than unity (super linearity) (3) a rapid decrease in photosensitivity above a certain temperature (thermal quenching) and (4) a decrease in photoconductivity excited by a primary light when a secondary light of longer wavelength is simultaneously shined on the sample.
(optical quenching). Such phenomena can not be explained in terms of the previous models. To describe such models let us consider processes shown in fig 2.21. It is assumed that initially the material consists of certain recombination centres with relatively large capture coefficients for both electrons and holes to which imperfection centres with considerably different set of capture coefficients are then added. In n-type sensitization, the added sensitizing centres have a very small capture coefficients \( C_n \) for electrons and a much large coefficient \( C_p \) for holes.

Considering the situation shown in fig 2.21 b in which hole demarcation level of the sensitizing centres lies above them, their occupancy is determined by effective thermal equilibrium with the valence band, they do not affect the lifetime of free electrons, and the situation is substantially unchanged from that with the sensitizing centres absent. However, the demarcation level lies below the level of the sensitizing centres under suitably high excitation intensities or low temperatures. When this occurs in a material with \( \Delta n \ll N_i \) the density of imperfections, the sensitizing centres with small \( C_n \) become largely occupied by holes,
FIG. 2.21 FEATURES OF THE TWO-CENTRE RECOMBINATION MODELS
and at the same time the density of holes in the previous recombination centres with large Cn is reduced. The net effect is an increase in the electron lifetime.

When the hole demarcation level is lowered through the level of the sensitizing centres by increasing light intensity at fixed temperature the photosensitivity increases due to increase in electron lifetime resulting in superlinearity of photoconductivity. Further, when the hole demarcation level is raised through the level of the sensitizing centres by increasing the temperature at fixed excitation intensity, the photosensitivity decreases as the electron lifetime decreases resulting in thermal quenching of photosensitivity. Finally, when the hole demarcation level is below the level of the sensitizing centres, a second light source can excite electrons optically from the valence band to the hole-occupied sensitizing centres, releasing these holes to be captured by the recombination centres giving rise to what is called optical quenching.