Chapter 1

Introduction

1.1 Introduction to semiconductor optical and electrical properties

After the invention of bipolar transistor there was a significant development in the material characterization as well as device fabrication, based on the optical and electrical properties of semi conducting materials. With the advent of the characterization techniques a number of materials reached the advanced state of development, when their properties are in demand to provide specific functions (1). First and foremost of these materials is silicon. Other examples are GaAs, AlAs, GaP and InP.

Optical and electrical properties of semiconductors are determined by:

1. The chemical composition of the pure perfect crystal – This determines intrinsic properties such as the fundamental energy gap and effective masses of the carriers.

2. Lattice defects such as vacant and interstitial sites and complexes there of, which introduce electron states within the band gap of the material – Such defects occur as a consequence of the way in which the crystal is grown, its thermal history and as a by product of doping by ion implantation.

3. Chemical impurities, which introduce electron states within the band gap. (These states may be near one of the band edges.)
4. Dimensions of the structure – When the dimensions become similar to or less than de Broglie wavelength of electron, the energy levels of the structures are changed by quantum size effect.

Optoelectronic properties of semiconductors can be described in terms of electron activities in semiconductors. These include (a) optical absorption by which free carriers are created, (b) electronic transport by which free carriers contribute to electrical conductivity of the material and (c) capture of free carriers, leading either to recombination or trapping (2). Major transitions in a homogeneous semiconductor are shown in Fig. 1.1.

![Fig. 1.1 Major transitions in homogeneous semiconductors. (a) intrinsic absorption. (b) and (c) extrinsic absorption. (d) and (e) capture and recombination, (f) trapping and detrapping.](image)

1.1.1 Optical process

Optical process includes intrinsic optical absorption corresponding to raising of an electron from the valence band to the conduction band (a) and extrinsic optical absorption corresponding to the raising of an electron from an imperfection to the conduction band (b) or the raising of an electron from the valence band to an imperfection (c). Optical absorption is described quantitatively through the absorption constant \( \alpha \). If intensity of light incident on a material of thickness ‘d’ with absorption constant \( \alpha \) is \( I_o \), intensity of the transmitted light \( I \) is approximately (neglecting reflection and interference effects).

\[
I = I_o \exp (-\alpha d) \quad (1.1)
\]
(1) Intrinsic optical absorption

Intrinsic optical absorption corresponds to photo excitation of an electron from valence band to conduction band (Fig. 1.1(a)). It may be classified into two as direct and indirect optical transitions. If minimum of the conduction band is at the same point in ‘k’ space as maximum of the valence band, a transition occurs involving only absorption of a photon. Such a transition is called “direct optical transition”. Minimum photon energy for absorption

\[ h\nu = E_{\text{Gd}} \]

where \( E_{\text{Gd}} \) is the direct band gap of the material and change in momentum on transition, \( \Delta k = 0 \). If minimum of the conduction band is at a different point in ‘k’ space from maximum of the valence band, an optical transition from top of the valence band to bottom of the conduction band must involve absorption of a photon and a simultaneous absorption or emission of a phonon. In this case, \( E_{\text{Gi}} = h\nu = E_{\text{Gd}} \pm E_{\text{phonon}} \), where \( E_{\text{Gi}} \) is the indirect band gap of the material and \( E_{\text{phonon}} \) is the energy of the phonon involved in the process. Compound semiconducting materials like CdS, GaAs and CdTe have direct band gap, whereas GaP has indirect band gap and Ge and Si have both direct and indirect band gap.

In a direct band gap material, optical absorption occurs near the surface of the material whereas for a material having indirect band gap, light penetrates much deeper into the material. Hence in the former case, the magnitude of the intrinsic photoconductivity (defined as increase in conductivity caused by intrinsic absorption) depends critically on the surface lifetime. In indirect band gap materials, the surface lifetime is much less important. If a direct band gap material is used in a p-n junction type device (where junction collection of photo excited carriers is important), a shorter diffusion length ‘L’ is required for carrier collection by the junction, whereas in an indirect material a large L is necessary, if the entire photo excited carriers are to be collected.

Direct band gap materials have higher intrinsic luminescence efficiency, associated with recombination of electrons and holes resulting in the emission of photons, because of shorter value of radiative recombination lifetime. But indirect materials have a lower intrinsic luminescence efficiency since the longer lifetime for radiative recombination allows competing processes for non-radiative recombination to become important.
Extrinsic optical absorption

Absorption involving imperfections is called extrinsic optical absorption. Here absorption coefficient is proportional to the density of absorbing centers ($N_a$).

$$\alpha = S_o N_a \quad (1.2)$$

Here $S_o$ is the proportionality constant called the “optical cross section” for the absorption process. If $E_i$ is the depth of an impurity level below the conduction band and if energy of the incident radiation $h\nu > E_i$, continuous absorption will be caused due to excitation of electrons from the center to the conduction band (Fig 1.1(b)). If $E_i$ is small (shallow impurities) its effect will be observed only at low temperatures when a considerable fraction of the impurity centers are not-ionized (Fig. 1.1(f)). Similarly, electrons may be excited into unionized acceptor centers near the valence band (Fig 1.1(c)). Impurity centers may be excited like group III and group V impurities in Si and Ge. Excitation from the ground state to the excited states of an impurity center would lead to a line absorption spectrum.

1.1.2 Carrier transport

Carrier transport phenomena arise from motion of electrons and holes in semiconductors under the influence of electric and magnetic fields. In a polycrystalline semiconductor thin film, factors like film defects, surface scattering and grain boundaries complicate identification of electrical properties. Grain boundaries in compound semiconductor films are different from those in elemental semiconductors. Boundaries for larger crystallite films differ from those for small-grained ones. The physical, structural, electrical and optical characteristics of grain boundary regions are drastically altered by exposure to impurities, diffusion and field effects (3). So care may be taken in applying a proper model for interpreting the analysis of electrical properties. Important parameters related to electrical properties are resistivity, carrier density, carrier mobility and surface recombination velocity.

1. Resistivity - In Petritz model (4) for measurement of resistivity, single grain and single boundary are considered initially. Then it is averaged over many grains. The total resistivity

$$\rho_g = \rho_1 + \rho_2 \quad (1.3)$$
where the subscript (1) signifies the grain or crystallite and (2) signifies the boundary. Most of the semiconductors have resistivities in the range $10^3$ to $10^6$ $\Omega$cm at room temperature. The most important property of semiconducting material is the negative temperature coefficient of resistance. Addition of suitable impurities with low ionization energy can lead to variation of resistivity of the material. Commonly used measurement techniques are Four point probe and Van der Pauw method.

2. Carrier density – In intrinsic semiconductors charge carriers are thermally generated electron-hole pairs. Energy distribution of charge carriers can be obtained using Fermi-Dirac statistics.

When $E_c - E_f > kT$

$$n = N_c \exp \left(- \frac{(E_c - E_f)}{kT} \right) \quad (1.4)$$

and

$$p = N_v \exp \left(- \frac{(E_f - E_v)}{kT} \right) \quad (1.5)$$

Where $N_c$ and $N_v$ are “effective density of states” in the conduction band and valance band respectively.

For intrinsic material, at absolute zero

$$n.p = N_c N_v \exp \left(- \frac{E_g}{kT} \right) \quad (1.6)$$

Intrinsic carrier concentration varies with temperature and band gap. For semiconductors with large band gap there is practically negligible number of mobile charge carriers. In order to increase conductivity, impurities are added to the material, resulting in the formation of localized discrete energy levels within the forbidden band. Techniques to measure carrier density are Hall effect, Capacitance-voltage and Optical absorption measurement.

3. Mobility – Mobility is the velocity per unit field acquired by a charge carrier as a result of the application of an electric field. Mobility is intimately connected
with the nature of the energy band. In a non-ionic binding \( \mu \) is proportional to \( m^*^{-3/2} \). Mobility is therefore characteristic of the material and the magnitude can be altered considerably by variations in temperature and purity of the material. In a material having increased ionic character, mobility is expected to decrease because of greater electrostatic interaction between the free charge carriers and the charged ions of the crystal. But a large increase in electron mobility is found as one goes from the period 5, group – IV element to III – V compound in the same period. Mobility maximum is associated with small effective masses found in the III – V compounds.

Mobility of charge carriers in materials with predominantly covalent bonding will usually be higher than that in materials with predominantly ionic bonding (5). In the case of compound semiconductors, the covalent nature decreases and ionic conductivity increases in the order IV-IV, III-V, II-VI and I-VII. Hence mobility decreases in the compound semiconductors in the same order.

Crystal vibrations and imperfections in the form of impurities, defects and dislocations interrupt motion of charge carriers in a crystal. Since effects of crystal vibrations can be expected to increase with increase of temperature, mobility should decrease with increasing temperature. At the imperfection, scattering changes the mobility of charge carriers. Scattering can be in two ways. In one type of scattering, Coulomb force is directly involved because of the attraction or repulsion between the charge carriers and charged ions of the crystal. The other type is the one in which scattering is the result of a deviation in the local potential experienced by a charge carrier. Hence the mobility of charge carriers will be greater for a given material, when it is pure and structurally perfect.

In a photoconducting material, contribution of photoexcited carriers to conductivity depends on free lifetime and mobility. Flow of current through polycrystalline material is limited by the presence of grain boundaries. Light absorbed in this region reduces resistance of the barrier and the current flow through the whole material will be much greater than it would be without radiation. The
effect of this barrier is described in terms of an effective mobility $\mu_g$. According to Petritz model $\rho _1 << \rho _2$, the carrier concentration is not reduced but all carriers take part in the conduction process with reduced mobility (4).

$$\mu_g = \mu \exp(-\phi_g/kT) \quad (1.7)$$

If $\mu$ is the mobility of charge carriers inside the grain and free carrier density $n$, then to consider this material as a homogeneous one, $\mu$ is replaced by $\mu_g$

$$\Delta \sigma = e(n\mu_{g1} + \Delta \mu_{g2}) \quad (1.8)$$

Hence mobility variation with intensity can also change conductivity of the material. Svein Espevik et al. (6) reported the effect of oxygen on mobility and hence photoconductivity in chemically deposited Lead sulfide thin film. C. Julien et al. (7) reported variation of mobility with temperature and the grain boundary effects. The effect of grain size on mobility and barrier height in In$_2$Se$_3$ was reported by G. Micocci et al. (8). Chen-ho Wu et al. (9) reported that photoconductivity of sprayed CdS thin film is caused primarily by an increase in electron mobility. Mobility variation with illumination intensity is also reported in this study.

4. Surface recombination velocity - One of the electrical properties due to minority carrier is surface recombination velocity. Electrons and holes recombine at the surface much greater than the body recombination rate. The net rate of holes ($S_a$) absorbed by the surface of an n-type material is

$$S_a = s \Delta p \quad (1.9)$$

where 's' has the dimension of a velocity and is called the 'surface recombination velocity'. Surface recombination velocities in germanium is found to vary from $10^6$ to $10^3$ cm/S at 300 K. Large surface recombination velocities are found in ground or sand-blasted surfaces and low values for surfaces polished in a suitable etching solution. For many technological applications, special precautions are taken to ensure that surface recombination velocity is not high. If the surface recombination rate near a point contact is very high, it may adversely affect the
properties of the contact. In thin film photo conducting material, if surface recombination velocity is very high, decay process dominates and bulk lifetime will be reduced. If $s \tau << d$ (thickness of the film), surface recombination has little effect on the magnitude of the photocurrent. On the other hand, $s \tau >> d$ magnitude of the photocurrent is independent of $\tau$ and depends only on surface conditions.

### 1.1.3 Recombination and trapping

A free electron may be captured at an imperfection as in Fig. 1.1(d) or a free hole may be captured at an imperfection as in Fig. 1.1(e). Capture process is described through capture coefficient ($\beta$) such that the rate of capture ($R$) of a species with density '$n$' by a species with density '$N$' is given by

$$R = \beta nN$$  \hspace{1cm} (1.10)

$\beta$ is often expressed as product of capture cross section ($S$) and average thermal velocity ($v$) of the free carrier.

$$\beta = \langle S(E)v(E) \rangle = Sv$$  \hspace{1cm} (1.11)

The averages are over electron energy. Lifetime of a free carrier ($\tau$) is given by

$$\tau = 1/\beta N$$  \hspace{1cm} (1.12)

Comparing the above equation with Eq. (1.10) shows that rate of capture or rate of recombination is equal to $n/\tau$. At steady state, rate of recombination is equal to rate of excitation $G$, we get

$$n = G\tau$$  \hspace{1cm} (1.13)

The above equation states that the average density of a species present at any time is given by the product of rate at which the species is being generated and the average lifetime of a member of the species. If more than one type of recombination process is present, the individual recombination rates are added to get total density of species.
A captured carrier at an imperfection may also be thermally reexcited to the nearest energy band before recombination occurs. In this case, the imperfection is referred to as a "trap", and the capture and release processes are called "trapping" and "detrapping" (Fig. 1.1(f)). If \( R_c \) is the capture rate of free carriers with density \( \beta \) by imperfections with density \( N \), such that \( R_c = \beta n N \), and if \( R_d \) is the thermal detrapping rate given by \( n_1 \nu \exp(-\Delta E/kT) \), where \( n_1 \) is the density of trapped carriers, \( \nu \) is a characteristic "attempt to escape frequency", and \( \Delta E \) is the activation energy for detrapping, then the imperfection acts like a recombination center if \( R_c > R_d \) but like a trap if \( R_c < R_d \). Physical situation of electrical current flow under illumination involves the effect of the contacts and nature of the transport of free carriers. Electrical contacts must be ohmic, which is the ability to replenish carriers, to maintain charge neutrality in the material.

Presence of defects introduces more additional energy levels in the forbidden gap. Unlike the bands themselves, which extend throughout the crystal, the additional levels are localized at the crystal defect. General effects of defects on electronic properties are the following.

1. Due to donor or acceptor – A donor is a defect that is neutral when electron occupied or positive when unoccupied and an acceptor is a defect that is negative when electron occupied or neutral when unoccupied. This means that a donor defect has an extra electron that it can contribute to conduction band or an acceptor defect has a deficiency of an electron that can be filled from valence band in which it produces a hole. Presence of such defects affects the density of free carriers and hence electrical conductivity of the material. Important parameters of these defects are their density and ionization energy.

2. Due to trap – A defect can capture an electron or a hole with such a small release of energy that the trapped carrier is in general released to the nearest band before capture of a carrier of opposite type can occur. Presence of these defects can lead to carriers in localized states near the band edge. A typical effect of such trapping is to make photoconductivity decay time longer than the lifetime of free carriers (10). Important parameters of traps are their density and ionization energy for the trapped carrier.
3. Due to recombination center – A defect can capture an electron or a hole with large thermal ionization energy that the captured carrier has a high probability of recombining with a carrier of the opposite type before being thermally re-excited to the band. The presence of recombination centers usually reduces the lifetime of free carriers. Important parameters of recombination centers are their density and capture cross-sections for electrons and holes.

When capture or recombination occurs, excess energy of the captured/recombining carrier must be released. This occurs either by creation of a photon (radiative process-luminescence), or by the excitation of free carriers. Recombination centers can be classified according to their effects.

a. Sensitizing center – This center has large capture cross-section for minority carriers but much smaller capture cross-section for majority carriers so that lifetime of majority carriers and hence the magnitude of the photoconductivity is greatly increased (11).

b. Killer center – Killer centers have a large capture cross-section for majority carriers so that the number of free carriers and hence the magnitude of the photoconductivity are drastically decreased (12).

c. Poison centers – The centers have a large nonradiative capture cross-section for carriers, so that they compete with other defects with a radiative capture cross-section and reduce the luminescence efficiency.

d. Optical absorption center – An electron associated with a defect can be photo excited from the defect to conduction band, from the valence band to the defect, or between the ground state and excited states of the defect. In this way the defect makes a contribution to the extrinsic optical absorption of the semiconductor. Important parameters are the optical cross-section and the density of defects available for photo excitation.

e. Scattering center - These centers behave as scattering centers in determining the mobility of free carriers. Important parameters are the scattering
cross-section and the defect density. If the defects are charged they have large coulombic cross-section for scattering and make a major impact on the mobility. If the defects are neutral, their effect on the mobility is much smaller and important only at low temperature and for high density of neutral defects.

The same defect can play the role of donor, electron trap, recombination center for holes, optical absorption center or scattering center. It is also possible for the same defect to act as a trap under one set of temperature and photo excitation conditions and then as a recombination center under another set of conditions. Depending upon the nature of the defect in the material, relaxation process can be radiative or nonradiative. Imperfections incorporated in photoconductors can have three basic effects on photoconductivity. They may change photosensitivity, speed of response, and can extend spectral response of photoconductivity to long wavelength side of the absorption edge. Optoelectronic properties arising due to extrinsic optical absorption are luminescence, photoconductivity, negative or persistent photoconductivity, optical quenching etc:

(1) **Luminescence**

In a transition, if the captured carrier has greater probability of recombining with carrier of opposite sign, the relaxation of electronic energy will be lost as photons and luminescence emission is observed. The possible transitions are depicted in Fig. 1.2

![Fig. 1.2 Major radiative transitions in semiconductors](image-url)
Free electron may recombine directly with free hole. But the probability of this transition is minimum. The lost energy in this case is emitted as photons with (approximately) the energy of the band gap (Fig. 1.2(a)). Such emission is called "edge emission". Another possible transition is either an electron being captured by an excited center containing a hole (Fig. 1.2(c)) or a hole being captured by an excited center containing an electron (Fig. 1.2(b)). Radiative transition is also possible when an electron is captured by an excited center containing a hole (Fig. 1.2(d)), or a hole being captured by an excited center containing an electron (Fig. 1.2(e)). The edge emission has its maximum at the absorption edge. But the band at the longer wavelength and lying near the edge is associated with recombination at an imperfection.

M. Balkanski et al. (13) reported two photoluminescence bands in α-In$_2$Se$_3$ semiconductor: one at 1.523 eV and the other at 1.326 eV. R. K. Ahrenkiel et al. (14) reported a strong band gap transition of CdTe that peaks at 1.47 eV. K. Topper et al. (15) studied the effects of post-deposition treatment on the PL spectra of CuInSe$_2$ absorber layers. It is reported that the intensity on the PL peak at 1.445 eV was drastically influenced by post-deposition treatments. G. A. Medvedkin et al. (16) identified the point defects in CuInSe$_2$ single crystals grown with the deviation from valence stoichiometry using photoluminescence and photoresponse studies.

(2) Photoconductivity

The basic principle involved in photoconductivity is that when photons of energy greater than that of the band gap of the semiconductors are incident on the material, electrons and holes are created resulting in the enhancement of electrical conductivity. This phenomenon is called intrinsic photoconductivity. It is also possible to observe photoconductivity when the energy of the incident photon is less than that of the band gap. When the energy of the photon matches the ionization energy of the impurity atoms, they are ionized, creating extra carriers and hence an increase in conductivity is observed. This phenomenon is called extrinsic photoconductivity.
In a homogeneous material, conductivity is expressed as
\[ \sigma = e \left( n \mu_n + p \mu_p \right) \]  
(1.14)

where \( n \) and \( p \) are the densities of free electrons and holes, and \( \mu_n/\mu_p \) are the electron/hole mobilities. In homogeneous material under equilibrium condition \( n \) and \( p \) are uniform throughout the material. Photoconductivity occurs when the values of \( n \) and \( p \) are enhanced due to photon absorption.

\[ \Delta \sigma = e \left( \Delta n \mu_n + \Delta p \mu_p \right) \]  
(1.15)

In insulators, values of \( \Delta n \) and \( \Delta p \) may be much larger than the corresponding free carrier densities in the dark. In semiconductors the effect of radiation can be considered as a small perturbation on large dark carrier density. Consider the case of one carrier transport in a non-homogeneous material. Then on illumination

\[ \sigma + \Delta \sigma = (n + \Delta n) \left( \mu + \Delta \mu \right) \]  
(1.16)

\[ \Delta \sigma = e \mu \Delta n + (n + \Delta n) e \Delta \mu \]  
(1.17)

But

\[ \Delta n = G \tau_n \]  
(1.18)

Where \( G \) is the photo excitation rate and \( \tau_n \) is the electron lifetime

\[ \Delta \sigma = e \mu G \tau_n + n e \Delta \mu \]  
(1.19)

But in the above process \( \tau_n \) may itself be a function of excitation rate \( \tau_n(G) \). Therefore three types of effects may occur (17).

1. Increase in carrier density with constant lifetime \( \tau_n \), so that \( \Delta \sigma = e \mu G \tau_n(G) \). The photoconductivity is proportional to \( G \) so that a log-log plot of \( \Delta \sigma \) vs \( G \) has a slope of unity.

2. Increase in carrier density with lifetime \( \tau_n \) as a function of photo excitation intensity so that \( \Delta \sigma = e \mu G \tau_n(G) \). If \( \tau_n \) varies as \( G^{(\gamma-1)} \), then \( \Delta \sigma \) varies as \( G^\gamma \). If \( \gamma < 1 \), the lifetime decreases with increasing excitation rate, the behavior is said to be "sublinear". If \( \gamma > 1 \) the lifetime increases with increasing excitation rate, the behavior is said to be "supralinear".
3. Increase in carrier mobility, so that $\Delta \sigma = n e \Delta \mu$. The possible mechanisms arise due to the change in mobility are

a. Scattering by charged impurities may change under photo excitation either through a change in density of such charged impurities or through a change in the scattering cross section of such impurities.

b. If the material is polycrystalline and contains intergrain potential barriers, photo excitation can reduce the height of these barriers as well as the depletion width, giving rise to an increase in carrier mobility.

c. Photo absorption may result in the excitation of carrier from a band characterized by a mobility to another band having a different mobility.

In the case of insulators at high photo excitation rates $\Delta n \gg n$, $\Delta p \gg p$ and

$$\Delta \sigma = Ge \left( \tau_n \mu_n + \tau_p \mu_p \right)$$

Thus the lifetime – mobility product is a measure of the photoconductor’s sensitivity to photo excitation.

Photoconductivity phenomenon is described on the basis of three quantities – photosensitivity, the spectral response and the speed of response.

1. Photosensitivity – It may be described as $\Delta \sigma$ or $\Delta \sigma/\sigma$. These two definitions may be complementary in some cases. In an optical process $\Delta \sigma$ and $\sigma$ increases. If $\sigma$ increases more rapidly than $\Delta \sigma$, then photosensitivity defined as $\Delta \sigma$ increases but the photosensitivity defined as $\Delta \sigma/\sigma$ decreases. So specific sensitivity is a measure of the materials’ actual sensitivity in terms of $\tau \mu$ product. It is the photoconductance per unit excitation intensity, measured in units of $m^2/\Omega$ watt. Another measure of photosensitivity is the photoconductivity gain. It is the number of charges collected in the external circuit for each photon absorbed. Imperfections, which act as efficient recombination centers decrease photosensitivity by decreasing free carrier lifetime. On the other hand imperfection, which has large capture cross-section for one type of charge and small cross-section for another type may increase photosensitivity.
If an atom of group II or VI of a II-VI compound is substituted by an atom of group III or VII, respectively, then there will be an extra electron at the cation or at the anion site, i.e., the impurity atom of these elements will act as a donor. Similarly, if they are replaced by atoms of group I and V, then there is a lack of electron and an acceptor state is created. The vacancies at anion sites are equivalent to donors since the electrons from cations are not used in the binding but they are free. Another method for increasing the sensitivity of a given material is by irradiating the sample with fast electrons (18). T. Yoshida et al. (19) reported the photoenhancement by irradiation in CdS. The mechanism of photoconductivity in polycrystalline cadmium sulphide layers, and the effect of doping on response time and mobility are discussed by J. W. Orton (20). Svein Espevik (6) reported the photoconductivity in chemically deposited lead sulfide thin film and the effect of oxygen on mobility and lifetime in this material. It is also reported that chemisorbed oxygen introduced donor-type imperfections in the PbS, which act as sensitizing centers for p-type photoconductivity in the material.

2. Spectral response of photoconductivity – There is a close correlation between the optical absorption spectrum and the photoconductivity spectral response. The general shape of absorption spectrum and spectral response of photoconductivity is pictured in Fig. 1.3

In the high absorption region (I), photoconductivity is controlled by the surface lifetime. In the intermediate range of region (II), there is strong absorption and the photoconductivity is controlled by the bulk lifetime, with a maximum occurring when absorption constant is approximately equal to reciprocal of the sample thickness. In the low absorption region (III), the photoconductivity is also controlled by the bulk lifetime but decreases with increasing wavelength as the absorption decreases. Imperfections may extend the spectral response of photoconductivity to long-wavelength side of the absorption edge. It is also observed that the response goes down on the shorter-wavelength side also, even though the absorption coefficient is high in this spectral region. This is because the photons of these energies are absorbed at or near the surface of the semiconductor, where recombination velocity is higher than that in the bulk. The extension of spectral response to the high-energy side by
selecting a proper valence band structure of the photoconducting material is discussed by J. L. Shay et al. (21) and N. V. Joshi et al. (22). Again E. Bertran et al. (23) reported the shift of absorption edge in CdS due to doping of Indium and the influence of Indium concentration on the refractive index.

3. Speed of response – It is inversely proportional to the time constant associated with the increase of photoconductivity to its steady state value after turning on the photo excitation (the rise time), and the time constant associated with the decrease of photoconductivity to its dark value after turning off the photo excitation (the decay time). In the absence of traps in the material, free carrier lifetime determines the value of these time constants.

The simplest rate equation is

\[
\frac{dn}{dt} = G - n/\tau \quad \text{assuming } \Delta n = n \quad (1.21)
\]

At steady state

\[
n = G\tau \quad (1.22)
\]
The rise curve is described by

\[ n(t) = G\tau [1 - \exp(-t/\tau)] \]  

(1.23)

and for the decay curve

\[ n(t) = G\tau \exp(-t/\tau) \]  

(1.24)

In the presence of traps, additional time-dependent processes are involved with "trap filling" during the rise and "trap emptying" during the decay. Therefore the measured response time \( \tau_o \) (usually taken to be the time required for the photoconductivity to decay to \( 1/e \) of \( G\tau \) or steady state Fermi energy to drop by \( KT \)) will be larger than the free carrier lifetime \( \tau \).

(2a) Lifetime

Lifetime of photo-excited carriers is the key parameter in photoconductivity. The following are the different types of lifetimes involved in the study of photoconductivity.

1. Free lifetime – This is the time during which the charge carrier is free to contribute to conductivity. Or in other words it is the time that an excited electron spends in the conduction band or an excited hole spends in the valence band. Free lifetime of a charge carrier can be terminated by recombination. Again it can be interrupted if the carrier is trapped and is resumed when the carrier is freed from the trap. It is undisturbed if the carrier is extracted from the crystal by the field, at the same time an identical carrier is injected into the crystal from opposite electrode.

2. Excited lifetime - It is the total time the carrier is excited between the act of excitation and the act of recombination, or extraction without replenishment. The excited lifetime includes any time that the carrier may spend in traps, it is therefore usually longer than the free lifetime.

3. Pair lifetime - This is the free lifetime of an electron-hole pair. If either electron or hole is captured, or is excited without replenishment, the pair lifetime is terminated.
4. Minority-carrier lifetime - This is the free lifetime of the minority carrier—electrons in p-type materials and holes in n-type materials. Usually the pair lifetime is equal to the minority carrier lifetime.

5. Majority carrier lifetime - Majority carrier lifetime is the free lifetime of the majority carrier—electrons in n-type materials and holes in p-type materials. If the density of free carriers in a material is very much greater than the density of recombination centers, as in semiconductors, the majority carrier lifetime will be equal to the minority carrier lifetime. If the density of free carriers is much less than the density of recombination centers—as in insulators, the majority carrier lifetime can be much larger than the minority carrier lifetime. Photosensitivity is frequently obtained by incorporating centers, which capture minority carriers rapidly and have a much smaller probability of capturing majority carriers to bring about recombination (24).

J. W. Orton et al. (20) reported the mechanism of photoconductivity in polycrystalline cadmium sulphide layers, and the effect of doping on response time and mobility. W. P. Lee et al. (25) reported the effect of ultra violet irradiation on the effective minority carrier recombination lifetime of silicon wafers. T. L. Chu et al. reported increase in lifetime of charge carriers in solution grown cadmium sulfide films due to doping of Boron (26).

(3) Negative photoconductivity

Negative photoconductivity occurs in a material when absorption of radiation causes decrease of conductivity lower than the dark conductivity of a material. This phenomenon is different from optical quenching of photoconductivity, in which the photoconductivity excited by a primary radiation is decreased by the absorption of a suitable secondary radiation.

If minority carriers are optically freed from centers, a negative photoconductivity will result because of the rapid recombination of these minority carriers with majority carriers. One of the models for negative photoconductivity is formulated by Stockmann (27). The two level model is outlined in the figure below (Fig.1.4).
According to this model, occurrence of negative photoconductivity requires the following conditions:

1. Thermal ejection of electrons from level $E_1$ must be slower than the recombination of electron and hole at region I.

2. Holes must not recombine directly with electrons in level $E_2$.

3. Level $E_1$ must lie above the Fermi level.

4. Cross-section of centers $E_1$ for majority carriers must be much less than that of centers $E_2$.

5. Density of centers $E_2$ and their cross-section of minority carriers must not be too small.

In short, the function of these types of centers in the presence of radiation, is to create holes by accepting electrons from the valence band but at the same time not to increase the number of free electrons. The second type of centers have a high cross-section for electrons and holes and consequently they capture electrons from the conduction band and holes from the valence band, and recombine them. Thus the net number of mobile charge carriers is reduced due to incident radiation giving rise to negative photoconductivity. Its dependence on temperature, intensity of illumination and bias voltage have been studied in the ternary compound TIGaSe$_2$ by S. G. Abdullaev et al. (28) using this model.
Another model to explain the negative photoconductivity in p-type semiconductors has been reported by N. V. Joshi et al. (29). It is proposed that electrons ejected from the inner level can recombine with holes at the top of the valence band and bring about negative photoconductivity. This phenomenon has been demonstrated in Cd$_{1-x}$Fe$_x$Se, in the above reported study.

Fig. 1.5 shows the photoconductivity spectrum of Cd$_{1-x}$Fe$_x$Se at 300 K. At 1.7 eV the reduction in the current was large in the presence of radiation, where the absorption continues to increase. In this model negative photoconductivity is explained on the basis of energy level scheme of iron in Cd$_{1-x}$Fe$_x$Se (29). According to this model radiation of energy 1.72 eV excites electrons from the inner level of iron to the top of the valence band, where they recombine with the holes and the photoconductance attains a value lower than dark conductance. The two main features of this model are (1) it explains the reduction of current due to monochromatic radiation and (2) this model is applicable to low band gap materials where two or more types of localized levels are generally not observed. R. A. Hopfel (30) reported high negative photoconductivity in a p-type GaAs-AlGaAs quantum well structure at low temperature. In this material photoresponse is negative over the entire spectral range. In the

![Fig. 1.5 Photoconductivity and optical absorption spectrum of Cd$_{1-x}$Fe$_x$Se](image)
earlier mentioned model reported by N. V. Joshi et al. (29), negative photoconductivity is observed only for a particular wavelength. This suggests that negative photoconductivity in quantum well structures has different types of origins and for the entire region of the spectrum it cannot be due to a single mechanism.

(4) Persistent Photoconductivity (PPC)

Photoconductivity that persists for a long time - minutes, hours or days after the cessation of the optical excitation is called persistent photoconductivity. The peculiar properties of semiconductors having persistent photoconductivity are:

1. Microscopic or macroscopic potential barriers separate charge carriers in real space and reduce the probability of recombination between them.

2. An energy state in the forbidden gap stores the charge carriers for a considerable amount of time before ejecting them to the conduction or to the valence band.

3. Photochemical reactions may create new trapping and recombination centers along with easily ionisable shallow donor levels.

4. The energy of the incident radiation is enough to deform the photosensitive material and perturb the localized energy states near the deformation sites.

Duration of time for which persistent photoconductivity is observed depends upon details of the origin of the potential barrier or types of traps or defect centers, their capture cross-section for electrons and holes and the probability of ejection of charge carriers to the conduction or valence band.

J. W. Farmer et al. (31) reported persistent photoconductivity in n-type GaAs epitaxial film on chromium doped semi-insulating GaAs substrate. A potential barrier similar to n-p junction is created due to relative difference between the Fermi-levels. Radiation reduces the height of the barrier and forward current cancels the reverse current originating from charge separation. When radiation is turned off, current will continue to flow until the barrier becomes sufficiently high to stop the flow. The time required for this, depends upon many
factors such as densities of charge carriers on both sides of the junction, width of the depletion layer and dielectric constant of the medium. D. V. Lang et al. (32) presented a model suitable for the CdS and CdTe type of materials based on the deformation of the lattice. According to this report, transition through the energy state caused by deformation of the defect can give rise to the observed persistent photoconductivity.

1.2 Lifetime measurements - different techniques

Techniques for lifetime determination are divided into two broad types, viz. those employing steady state measurements and those involving dynamic measurements. The measurement involves injection of carriers into the sample, together with some technique for monitoring the photocurrent or the time of decay. The appropriate technique is chosen depending upon the high or low injection levels, or carrier recombination via recombination center or deep trapping center.

1.2.1 Steady state methods

Steady state measurements include two methods: one depends on photoconductive (PC) and the other on photo electromagnetic effects (PEM). The same technique may be used to measure either lifetime or diffusion length. Both techniques do not measure time or length directly. Instead, lifetime or diffusion length is derived using a theoretical model to the measured photocurrent or photo voltage. Photoconductive methods are suitable only for measuring highly resistive material.

(a) Photoconductive measurements (PC)

A uniform semiconductor material is illuminated over its upper surface as shown in Fig. 1.6. Current flows between two ohmic contacts, c₁ and c₂ at each end. For PEM effect a magnetic induction B is applied normal to the direction of current flow and in the plane of the illuminated surface.
The effect of photoconductivity is measured by applying an electric field $E$ along the $z$ direction. In the case of a thick sample and when the incident radiation is strongly absorbed ($h\nu > E_g$)

$$I_{pc} = E \hbar (1-R_o) \Phi_o (\mu_n + \mu_p) \tau / (1+s)$$  \hspace{1cm} (1.25)

Where $R_o$ is the reflection coefficient of the surface, $\Phi_o$ is the number of photons incident on each square centimeter of the surface per second and ‘$s$’ is the normalized surface recombination velocity. The above equation is derived on the assumption that the influence of deep states is negligible ($\Delta n = \Delta p$) and therefore $\tau_n = \tau_p = \tau$. Measurement of photocurrent under steady state conditions yields a value for $\tau$ provided the other parameters are known. Incident photon flux and carrier mobilities must be measured together with the recombination velocity on the illuminated surface. This experiment requires careful attention to get all other parameters to obtain reliable value for $\tau$.

(b) Photo electromagnetic effect (PEM)

To study photo electromagnetic effect, a magnetic field is applied parallel to the $y$ axis as shown in Fig. 1.6. It is assumed that incident radiation is absorbed close to the top surface. Both electrons and holes diffuse downwards into the bulk of the material. In the presence of
the magnetic field, the diffusing electrons and holes are deflected in opposite directions along the z axis, giving rise to a current $I_{\text{PEM}}$. The current is measured under short-circuit conditions by a low impedance meter connected across the end contacts. PEM effect is the Hall effect, measured on diffusing carriers rather than on carriers drifting in an applied electric field.

$$I_{\text{PEM}} = e\Phi_0 (1-R_0) Bh (\mu_n + \mu_p) L_n/(1+s)$$

(1.26)

This equation is valid when the thickness of the sample is greater than diffusion length. Steady state PEM effect may be used to measure the minority carrier diffusion length $L_n$ provided $\mu_n$ and $\mu_p$ are known and both $\Phi_0$ and $s$ can be measured. It is always better to have ‘s’ very small and independent of $L_n$ and $\tau$. Similarity between $I_{\text{PC}}$ and $I_{\text{PEM}}$ suggests an alternative approach to measuring $\tau$ known as the ratio method.

$$I_{\text{PEM}}/I_{\text{PC}} = (B/E)(L_n/\tau) = (B/E)(D_n/\tau)^{1/2}$$

(1.27)

$$L_n = (\tau D_n)^{1/2}$$

(1.28)

$$\tau = (I_{\text{PC}}/I_{\text{PEM}})^2 (B/E)^2 D_n$$

(1.29)

Though equation (1.29) is independent of both light intensity and surface recombination velocity, it is still necessary to know the minority carrier mobility in order to determine diffusion coefficient $D_n$. If the sample has high conductivity it may be impossible to measure $I_{\text{PEM}}$ under short circuit conditions because the measuring instrument has very high impedance. Under such conditions open circuit voltage $V_{\text{PEM}}$ is measured instead of $I_{\text{PEM}}$.

1.2.2 Transient methods of measuring lifetime

Variation of photoconductance as a function of time over a certain period for the photoresponse to reach its maximum or minimum value is called transient photoconductivity. Transient method of lifetime determination involves monitoring the decay of excess carrier density following an injecting pulse. The variety of these methods arises from the range of possible injection processes and means for sensing $\Delta n$ or $\Delta p$. 
Carriers may be generated by optical injection, electron beam injection, injection at a p-n junction or metal contact, or by impact ionization under the influence of an electric field (33). Detection may involve a measurement of conductivity, luminescence, transmission of an infrared beam, absorption of microwave power or the current collected by a local probe or p-n junction (34). Complications due to surface recombination can be minimized by suitable surface treatment to make $s \ll 1$ and by making sample dimensions very much greater than a diffusion length.

(a) Conventional experimental set up and its analysis

The simplest and most conventional experimental set up for photoconductance measurement is shown in Fig. 1.7

![Fig. 1.7 A conventional experimental set up for photoconductance measurements](image)

A constant DC source and a high resistance $R_L$ are connected in series with the sample. Let $R_d$ and $R_{ii}$ be the resistance of the sample in the dark and under uniform illumination conditions. When there is no illumination photovoltage across the load resistance, $R_L$ is
Similarly, the voltage developed across illuminated sample is

\[ V_{ill} = \frac{R_L V}{R_L + R_{ill}} \]  \hspace{1cm} (1.31)

where \( V \) is the applied voltage. The difference between them is the signal response, which is given by

\[ S(V) = R_L V \left[ \frac{1}{(R_L + R_{ill})} - \frac{1}{(R_d + R_L)} \right] \]  \hspace{1cm} (1.32)

\[ = R_L V \left[ \Delta R / (R_L + R_{ill})(R_d + R_{ill}) \right] \]  \hspace{1cm} (1.33)

\[ \Delta R = R_D - R_{ill} \]  \hspace{1cm} (1.34)

The difference in conductance caused by the radiation is

\[ \Delta G = 1/R_{ill} - 1/R_d \]  \hspace{1cm} (1.35)

\[ \Delta R = (\Delta G) R_d R_{ill} \]  \hspace{1cm} (1.36)

Signal response \( S(V) = \frac{V R_L R_d \Delta G}{(R_L + R_d)(R_L + R_{ill})^2} \)  \hspace{1cm} (1.37)

Two limiting cases which may be encountered in the laboratory are:

1. Variation in the resistance of the sample with and without radiation is very small compared to the dark resistance \( R_d \), that is \( R_d = R_{ill} \).

   \[ S(V) = \frac{VR_L R_d \Delta G}{(R_L + R_d)^2} \]  \hspace{1cm} (1.38)

   All the parameters in the above equation are characteristic of a given photoconductor except load resistance \( R_L \). It is the only parameter that can be controlled to obtain the maximum photoresponse. The maximum response can be obtained by using \( \frac{dS}{dR_L} = 0 \). It is obtained when \( R_L = R_d \). This is the reason for using load resistance equal to dark resistance of the sample when the photo signal is weak.

2. In the case of highly resistive material, dark current is low which makes it very easy to measure photo current or voltage without any need to optimize the load resistance.
(b) Contact configuration

Experimental set up, contact configuration, preparation of the sample, and sample thickness play crucial roles in the output and analysis of the results of photoconductivity measurements. Commonly used contact configurations are shown in the figure below.

In Fig. 1.8 (a) the contacts are on the lateral side of the sample and in Fig. 1.8 (b) they are on the extreme ends. Here only a part of the sample is illuminated. In Fig. 1.8(c) the contacts are on the front and rear of the sample. Radiation passes through the transparent contact and is uniformly absorbed in the material. The amount of the absorbed radiation varies exponentially with the depth. Front surface recombination plays an important role in the first two cases, whereas the back surface recombination is also important for the last case.

![Figure 1.8](image)

Fig. 1.8 Different types of contact configuration that affect the analysis of the results.

In photoconductivity measurements, the response depends not only on the number of photo-generated carriers but also on their transport to the electrodes. While the contacts are made between metals and semiconductors, depending upon the work function, there is a flow of carriers from the higher to the lower Fermi level to equalize the Fermi level at the contact. In this process, electrons transfer from the semiconductor to the metal resulting in a depletion region in the semiconductor. This gives rise to perturbation of the band at the metal-semiconductor interface. The flow of carriers is influenced by the length of the depletion region and the amount of perturbation at the interface. When the regions near the contacts are illuminated, quasi-Fermi levels for electrons and holes move relative to the Fermi level of the metal. If the illumination is intense, the movement of the Fermi level may be large enough to change its overall properties. Therefore a substantial change in the photoconducting properties is possible if the contact region is illuminated.
Methods of measurement

Photoconducting properties of a given semiconductor depend on electrical and optical parameters. The semiconductor can have high or low resistance and the magnitude of variation in the resistance on illumination can be high or negligible. The response time can vary from pico seconds to a few minutes. The experimental technique must be different for each case.

Case 1. High resistivity and good photoresponse

These types of materials obviously have low dark current $I_d$, and photocurrent is much higher than $I_d$. In order to study photoconductivity response curves, photoresponse as a function of the wavelength is studied. Radiation source should be continuous in wavelength and the output is measured using a voltmeter as shown in the Fig. 1.7. If the relaxation curves are to be analysed, then the voltmeter should be replaced with an appropriate oscilloscope or digital multimeter. The most important aspect is that RC time constant of the measuring circuit should not be a limiting factor for the rise or decay curve. RC constant can vary from $10^{-6}$ to $10^{-1}$ sec. and this value sometimes coincides with the actual value of the response time. In a wide-band-gap semiconductor particularly group II-VI compounds, the response is slow and the above-mentioned situation may happen.

Case 2. Low resistivity and good photoresponse

This is common in narrow-band-gap materials ($E_g \leq 1\text{eV}$). Dark current is of the order of microamperes or even higher. In this case, modulation technique should be employed. The incident beam is chopped with a certain frequency by a mechanical or electro-optical chopper as shown in Fig. 1.9. This makes the photocurrent periodic with frequency equal to that of the chopper. The output is an ac photosignal on dc dark current. The ac signal, eventhough is very weak, can be separated by a lock in amplifier. This method has the additional advantage that it helps reduce the noise. N. V. Joshi et al. had used this technique in recording the photoconductivity spectrum of the ternary compound AgInS$_2$ (22).
Case 3. Low resistance and slow response

For such samples the value of the dark current is quite high and the chopping technique is not useful because of the slow response. In this case, dark current can be balanced by a wheatstone's bridge and then an operational amplifier amplifies the potential difference originating from the variance of the resistance of the sample. This technique has been used to detect weak signal in the ternary compound CuInTe$_2$ by N. V. Joshi et al. (35)
Case 4. High resistivity, slow response and very weak photosignal

This property is observed in organic semiconductors and also in some inorganic semiconductors. Examples are chromium-doped semi insulating GaAs or iron doped InP. Resistivity of such samples is high and response is slow. This is because impurity atom creates defect states, which may act as recombination centers. The recombination process reduces the lifetime of the carriers in conduction or valence band and therefore intensity of the response is reduced. In addition, traps retain electrons for a considerable time and hence the response becomes slow. In this case, measurement is taken for every wavelength giving sufficient time for each measurement for the photocurrent to reach its saturation value. Such a measurement is done in chromium doped GaAs for the study of structural details by P. Lenczewski and E. Fortin (36).

1.2.2 (a) Modulation method

Measurement difficulties increase when lifetime decreases. Distortion free recording of a decay curve with a time constant of $10^{-4}$ sec. requires a receiver band width of 100 MHz and such band widths are not only difficult to achieve, but also carry much increased receiver noise. It is also difficult to provide the necessary short injection pulses. Signal voltages are usually small for low injection levels. A solution to this problem is to use ac modulation of the injection source and to measure the relative phase and amplitude of the resulting modulation in conductivity, photovoltage or luminescence (37). A large phase shift develops when $\omega t$ approaches unity, where $\omega$ is the angular modulation frequency $= 2\pi f$.

Consider a spatially uniform generation rate of minority carriers through out the sample volume

$$G = G_0 + G_t e^{i\omega t}$$  \hspace{1cm} (1.39)

Then component of conductivity at frequency $\omega$ is measured. As electrical conductivity, $\sigma \propto n$, the expression for $\Delta n(t)$, the excess electron density, as a function of time can be obtained by solving the continuity equation.

$$\frac{d\Delta n}{dt} = G - \Delta n/\tau_{\text{n}} \text{ (surface effects are neglected)}$$  \hspace{1cm} (1.40)
But the generation function may be nonuniform and the surface recombination rate will generally differ from that in the bulk. Diffusion equation describing spatial distribution of minority carriers within the sample having length and breadth much greater than thickness, in the direction of light propagation is

$$D_n \frac{d^2(\Delta n)/dx^2}{dx} + G e^{-\Delta x} - \Delta n/\tau_n = d(\Delta n)/dt \quad (1.41)$$

$$G = G_o + G_i e^{i\omega t} = \alpha \phi = \alpha(\phi_o + \phi_i e^{i\omega t}) \quad (1.42)$$

where $\phi = $ photon flux, $\phi_o = $ incident photon flux, $\phi_i = $ amplitude of modulation in photon flux, $\phi = \phi_o + \phi_i e^{i\omega t}, \alpha$ being the absorption coefficient for the incident light, then

$$\Delta n = \Delta n_o + \Delta n_i e^{i\omega t} \quad (1.43)$$

Steady state component of $\Delta n$ satisfies the relation

$$D_n \frac{d^2\Delta n_o}{dx^2} + G_o e^{-\Delta x} - \Delta n_o/\tau_n = 0 \quad (1.45)$$

Then equation for $\Delta n_i$ is

$$D_n \frac{d^2\Delta n_i}{dx^2} + G_i e^{-\Delta x} - \Delta n_i/\tau_n - i\omega \Delta n_i = 0 \quad (1.46)$$

Here electron lifetime $\tau_n$ is to be replaced by an effective recombination lifetime $\tau_n'$

$$\tau_n' = \tau_n/(1 + i\omega \tau_n) \quad (1.47)$$

(a) Experimental set up

Kerr cell modulates an appropriate filtered light source and the beam is split to provide a reference signal from a photo multiplier. Modulated illumination produces a sinusoidal variation in sample conductance, which is converted to an ac voltage by passing a constant dc current through it. The amplitude and phase of this signal voltage may then be measured, as a function of modulation frequency, using the vector voltmeter. An oscilloscope can also be...
used as a detector, applying reference and signal voltages to the X and Y inputs, respectively, and resistance-capacitance time constant is adjusted until the two voltages are in phase. Then the photoconductive response time is given by $\tau_{\text{eff}} = RC$. Choo et al. could measure lifetime in the order of sub-nanosecond using modulation frequencies from 1KHz to 40 MHz applied to GaAs light emitting diode (38).

Two complications may arise in interpretation, due to trapping and surface barrier effects. Effect of traps can be made inactive by shining an additional unmodulated white light source onto the sample to saturate the traps. Surface band bending occurs in most semiconductors and the incident light will modulate the amplitude of band bending. Carriers generated near the surface will exchange with those in surface states. This charge transfer represents a capacitive component of photocurrent, which is larger in heavily doped material. Its occurrence may be tested by observing whether $\tan \phi$ decreases with increasing light intensity.

1.2.2 (b) Stored charge method

In a forward biased p-n junction, the diode current is carried almost entirely by minority carriers on the low-doped side. Under steady state conditions, these holes are distributed over a region extending a few diffusion lengths into the n-type material, where they recom-
bine with majority electrons at a rate, which exactly balances the injection rate. If the forward bias is suddenly removed, the injected minority carrier distribution decays due to this recombination process and a measurement of the decay rate yields a value of the minority carrier lifetime $\tau_p$ (39).

There are two methods to measure $\tau$. Both are initiated by forward biasing the diode and then switching it abruptly to either an open-circuit or reverse-biased condition. In the first case, the junction voltage is measured as a function of time and $\tau$ is derived from its decay rate. This method is known as open circuit voltage decay (OCVD). In the second case reverse current is monitored and $\tau$ obtained from its time dependence. In this case, the difference is that minority carriers are removed not only by recombination but also by being swept back across the junction by the reverse bias field. This reverse bias step-recovery method is referred to as the "stored-charge" method. In the case of asymmetric junction, one obtains a value of $\tau$ for the lightly doped (base) material. The most important aspect of this technique is that the material property (base) can be studied by making measurements on completed device.

In a forward biased abrupt $p^+$-n diode, current flows largely by injection of holes into the n-type base. Smaller density of minority electrons in $p^+$ side is neglected. The experimental arrangement is shown in the Fig. 1.12.

![Fig. 1.12 Experimental arrangement for measuring current in the stored charge method.](image)
Initially the switch is in position f. Then the diode is forward biased and a forward current $I_f$ flows. A steady state distribution of the injected holes is established in the base as indicated by curve-1 in Fig. 1.13. At time $t = 0$, the circuit is switched rapidly to position r, reverse biasing the diode with the voltage $V_r$ in series with a current limiting resistor $R$. Initially because of the high density of holes in the junction region, the junction resistance remains low and the reverse current is given by $I_r = V_r/R$. This current represents the reverse flow of holes back into p+ region and can be controlled by the choice of $V_r$ and $R$.

Hole density on the n side of the junction decreases as shown by curve-2 and after a time $t_1$, known as the storage time takes the form of curve-3. The time $t_1$ is defined as the time at which the hole density at the junction plane $p_n(0)$ has decayed to zero. For times $t > t_1$ the junction resistance is no longer negligible, the junction voltage rises and the reverse current falls to the steady state saturation value $I_s$ appropriate to the reverse bias $V_r$. The hole distribution now appears as in curve-4 and the junction resistance is very much larger than $R$, therefore $I_s << I_r$ ($I_r = V_r/R$).

![Diagram](image-url)

Fig. 1.13 The shape of the minority hole distribution on the n side of a p+ - n diode during the recovery period.
Time dependence of the diode current is represented in Fig. 1.14. Storage time $t_1$ is characterized by the constant reverse current $I_s$ after which the current decays to $I_r$. Recovery time ($t_2$) is usually defined as the time taken for the current to fall to a value of $I/10$. Recombination lifetime ($\tau_p$) of the injected holes may be determined from this recovery behavior through any of the following three analyses (1) measurement of $t_1$ (2) measurement of $t_2$ (3) measurement of the integral under the reverse-current curve, which represents the total charge extracted from the n-side of the junction.

![Fig. 1.14. The form of the reverse-current recovery curve for a p+n diode. The times $t_1$ and $t_2$ represent the charge-storage and charge-recovery periods. $I_s$ is the steady-state reverse saturation current and $I_r = V/I/R$.](image)

1.3 Effects of dopants and temperature on lifetime

Photoconductive decay curve deviates from simple exponential nature due to the presence of defect states and their distribution. Hence transient photo conductivity becomes one of the powerful techniques for studying optically active traps as the transient curves contain a wealth of information about kinetics of the charge carriers. But the parameters responsible for kinetics of the charge carriers vary from sample to sample and are very sensitive to the factors like temperature, level of radiation, effects of contacts and surface conditions.
1.3.1 Effect of dopants on carrier lifetime

A major effect of trapping is to make the experimentally observed decay time of the photocurrent, after the excitation has ceased, longer than the carrier lifetime. If no trapping centers are present, then observed photocurrent will decay in the same way as the density of free carriers do and the observed decay time will be equal to the carrier lifetime. If trapping centers are present, but the free carrier density is much greater than the density of trapped carriers, again the observed decay time of the photocurrent will be equal to the carrier lifetime. But if the density of free carriers is comparable to or less than the density of trapped carriers, then the trapping of carriers during the course of decay can prolong the decay so that the observed decay time is longer than the actual lifetime of a free carrier. If the density of trapped carriers is much greater than the density of free carriers, the entire decay of photocurrent is effectively dominated by the rate of trap emptying rather than by the rate of recombination.

In the absence of traps in the material, free carrier lifetime determines the value of the time constant. In the case of uniform generation of excess carriers throughout the sample and neglecting surface recombination, excess hole concentration in n-type material may be derived from the equation

\[ \frac{d(\Delta p)}{dt} = G - \Delta p/\tau_p \]  

(1.48)

where \( G \) is the generation rate of electron hole pairs. After reaching a steady state condition, illumination is suddenly switched off. For values of \( \Delta p \) sufficiently small

\[ \Delta p = \Delta p_0 \left( \exp\left(-t/\tau_p\right) \right) \]  

(1.49)

and the corresponding photocurrent is

\[ i_p = i_{p0} \left( \exp\left(-t/\tau_p\right) \right) \]  

(1.50)

so that photoconductivity decays exponentially with time constant \( \tau_p \). When the illumination is switched on at \( t = 0 \), held constant from \( t = 0 \) to \( t = t_0 \) and switched off at \( t = t_0 \)

Then

\[ i_p = i_{p0} \left( 1 - \exp\left(-t/\tau_p\right) \right) \quad 0 \leq t \leq t_0 \]  

(1.51)

\[ = i_{p0} \left( 1 - \exp\left(-t_0/\tau_p\right) \exp\left(-\left(t-t_0\right)/\tau_p\right) \right) \quad t \geq t_0 \]  

(1.52)

The variation of \( I_p \) with time is shown in Fig. 1.15
If only recombination centers are present the analysis will be unchanged. But if high density of traps ($\Delta n \neq \Delta p$) are present, transient decay will not correspond to an exponential with time constant $\tau_p$. Consider a material having traps which can capture electrons but unlikely to capture holes. Such traps are called 'safe traps'. Let $\tau_p$ be the minority carrier lifetime of holes in n-type material and $\tau_1$ the average lifetime of hole before it is caught in a safe trap (10). Let $\tau_2$ represent the mean time a hole spends in a safe trap before being re-excited to the valence band. The equation satisfied by $\Delta p$ is

$$\frac{d(\Delta p)}{dt} = G - \Delta p/\tau_p - \Delta p/\tau_1 + \Delta N_s/\tau_2$$  \hspace{1cm} (1.53)$$

$G$ – rate of generation of electron hole pairs and $\Delta N_s$ is the excess hole concentration in the safe traps

$$\frac{d(\Delta N_s)}{dt} = \Delta p/\tau_1 - \Delta N_s/\tau_2$$  \hspace{1cm} (1.54)

so that in equilibrium

$$\Delta N_{so} = (\tau_2/\tau_1)\Delta p_o$$  \hspace{1cm} (1.55)

$$\Delta p_o = G\tau_p$$  \hspace{1cm} (1.56)

Presence of the safe traps does not therefore affect the number of minority carriers. From the condition of space charge neutrality
\[ \Delta n = \Delta p + \Delta N_s \] 

(1.57)

In equilibrium

\[ \Delta n_o = \Delta p_o + \Delta N_{so} = \Delta p_o (1 + \tau_2/\tau_1) \] 

(1.58)

Total charge generation due to illumination is

\[ e\mu_p \Delta p_o + e\mu_n \Delta n_o = e\mu_p \Delta p_o + e\mu_n \Delta p_o (1 + \tau_2/\tau_1) \] 

(1.59)

\[ e\Delta p_o (\mu_p + \mu_n + \mu_n \tau_2/\tau_1) \] 

(1.60)

But \( \Delta p_o = G\tau_p \). Steady state conductivity due to illumination is

\[ \Delta\sigma_o = eG\tau_p (\mu_p + \mu_n + \mu_n \tau_2/\tau_1) \] 

(1.61)

and steady state photocurrent is

\[ i_{p0} = eG\tau_p Ed (\mu_p + \mu_n + \mu_n \tau_2/\tau_1) \] 

(1.62)

where ‘d’ is the thickness of the material and \( E \) is the applied potential between the electrodes. From the above equation, it is clear that if \( \tau_2 \gg \tau_1 \) the traps will cause a considerable increase in photocurrent and when this condition holds, excess hole spends considerably longer time in a safe trap than in the conduction band.

Consider the case if \( \tau_2 \gg \tau_1 \) and \( \tau_p \). If the illumination is suddenly cut off after the steady state has been established, the minority carrier concentration will drop rapidly with time constant \( \tau_p \) since initially \( \Delta p/\tau_1 = \Delta N_s/\tau_2 \). After this initial drop

\[ \frac{d(\Delta N_s)}{dt} = - \frac{\Delta N_s}{\tau_2} \] 

(1.63)

so that \( \Delta N_s \) decreases with time constant \( \tau_2 \). The number of excess carriers (electrons) is now nearly equal to \( \Delta N_s \), so

\[ \Delta n \equiv \Delta N_s \] 

(1.64)

\[ i_{p0} = eG\tau_p Ed\mu_n (\tau_2/\tau_1) \exp (-t/\tau_2) \] 

(1.65)

The trapped holes are slowly released and while they are trapped, they cause an excess of majority carriers equal to the number of trapped minority carriers. The form of variation of photocurrent is shown in Fig.1.16
Initial fractional drop in the photocurrent is small if $\tau_2 \gg \tau_1$. The distribution of trapping centers in semiconductors is frequently much more complex than the above mentioned model. There may be several kinds of traps present, and each of them may not even correspond to a single energy level, but have a distribution of levels.

### 1.3.2 Effect of temperature on carrier lifetime

Recombination and capture processes are characterized by time constants that reflect capture cross-section and density of the imperfections involved. Thermally activated imperfection emptying or filling has a rate of change that depends upon the capture cross-section and ionization energy. These processes are functions of temperature also. At fixed temperature the rise or decay of photoconductivity, luminescence or photo capacitance is controlled by the value of the parameters like capture cross-section, density of imperfections involved and activation energy at that temperature. In thermally stimulated decay, the variables can be measured as a function of time but under conditions in which the temperature itself is varying with time (2).
Chapter 1

The simplest decay process is one in which there is exponential decay.

\[ i(t) = i_0 \exp(-t/\tau) \]  \hspace{1cm} (1.66)

It is assumed that \( \tau \) is independent of time. If the process involved is one in which trapped electrons are being thermally freed from traps to the conduction band, then

\[ 1/\tau = N_c \beta_n \exp(\Delta E/kT) \]  \hspace{1cm} (1.67)

where \( N_c \) is the effective density of states in the conduction band, \( \beta_n \) is the capture coefficient of the traps for electrons and \( \Delta E \) is the trap depth or ionization energy. If \( i(t) \) is measured at different temperatures, then a plot of \( \ln i(t) \) vs \( t \) at each temperature is a straight line characterized by a time constant of \( \tau(T) \). Then the plot of \( \ln \tau(T) \) vs \( 1/T \) (an Arrhenius plot) is a straight line with a slope equal to \(-\Delta E/k\) and intercept depending on \( \beta_n \).

1.3.3 Rate window technique

A decay sampling technique, particularly suited to computerized analysis, is known as the “rate window approach”. Two times are chosen during the decay process, \( t_1 \) and \( t_2 \) (\( t_2 > t_1 \)) and the signal \( i(t) \) is measured at each of these times. Then \( i(t_1) - i(t_2) \) is plotted as a function of temperature. The result is a curve exhibiting a maximum at a particular temperature, which can be suitably interpreted to obtain the trap parameters. Fig. 1.17 shows the rate window approach to measurement of DLTS. In the present study, decay time is calculated from the photoconductive decay (PCD) curve at different temperatures during a particular interval of time and plotted as a function of temperature. It is found that the decay time varies with trap parameters.
1.4 Importance of lifetime measurements

The lifetime of charge carriers is one of the important parameters to characterize a material because it plays a critical role in determining the semiconductor device parameters. Room temperature minority carrier lifetime is expected to have a significant influence on the
conversion efficiency of solar cell since it is a direct measure of the efficiency of the various radiative and non radiative loss channels of the photoexcited carriers. B. Ohnesorge et al. reported the correlation between the carrier lifetime of the absorber layer at room temperature and short circuit current density ($J_{sc}$), the open circuit voltage ($V_{oc}$) and solar cell efficiency ($\eta$) in Cu(In,Ga)Se$_2$ solar cells (40). It is shown that a cell made of absorbing material with longer lifetime has a high open circuit voltage and hence high efficiency. However there was negligible increase in the short circuit current.

Lifetime measurement can be used to study the radiation effect on materials. W. P. Lee et al. reported the variation in lifetime due to ultraviolet irradiation on thermally oxidized silicon wafers (25). In this study, it has been established that UV photons modify the density of two interface traps and oxide charge density. These modifications directly affect the lifetime of charge carriers. K. L. Narayan reported the prolonging of photoconductive decay in ion implanted CBD CdS thin films (41).

The presence of traps and trap parameters can be studied from lifetime measurements. R. K. Arenkiel et al. reported the dominant transport and recombination mechanism in polycrystalline silicon and CdS thin films using temperature dependent lifetime measurements (14). R. H. Bube et al. used lifetime measurement as one of the techniques to determine trap parameters in CdS crystals (42). S. Mora et al. reported the measurement of minority carrier lifetime in CuInS$_2$ (43). They made an attempt to improve the efficiency of the homojunction CuInS$_2$ solar cells by improving the material property. M. Ichimura et al. reported the fast and slow decay components of the excess carrier concentration and measured the corresponding lifetimes. The origin of slow decay is discussed on the basis of the numerical simulation of the recombination process and the presence of traps with a very small electron capture cross-section (44).
References


15. K. Topper, J. Kranser, J. Bruns, R. Scheer, A. Weidinger, D. Brauning, Solar Energy
Materials and Solar Cells, 49 (1997) 383


27. Stockmann, Z. Physik, 143 (1955) 348


34. ibid 71
42. R. H. Bube, Gustavo A. Dussel, Ching-Tao Ho and Lewis D. Miller, JAP, 37 (1) (1966) 21
43. S. Mora, N. Romeo and L. Tarricone, Solid State Communications, 29 (1979) 155