THE DETERMINATION SENSITIZING CENTERS AND BAND GAP OF THE PHOTOCONDUCTIVE MATERIALS

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ABSTRACT

THE DETERMINATION OF SENSITIZING CENTERS AND BAND GAP OF THE PHOTOCONDUCTIVE MATERIALS

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In this study, Selenium(Se) photoconductor was developed by mixing the powder Se with the powder of Chlorine (Cl) under the conditions of high vacuum and high temperature. The production of ZnS photoconductor was also accomplished from the mixture of ZnS and ZnCl powders under the same conditions. It was found that the developed Se and ZnS photoconductors were very sensitive to the light. The density of sensitizing centers in these photoconductors were determined by using Capacitance-Voltage (C-V) and Space-Charge-Limited methods. The energy value of band gap of Se and ZnS and the energy levels of sensitizing centers in the forbidden gap of Se and ZnS were evaluated by variation of photoconductivity excitation with wavelength method.

The density of sensitizing centers was found to change linearly with the light intensity; the energy value of band gap of Se and ZnS photoconductors were found to be in good agreement with theoretical values.

Keywords: Recombination Centers II, Sensitizing centers, Photosensitivity , Se, ZnS

ÖZET

FOTOİLETKEN MALZEMELERİN HASSASLAŞTIRMA MERKEZLERİNİN VE BAND ARALIKLARININ HESAPLANMASI

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Bu çalışmada, yüksek vakuum ve yüksek sıcaklık koşullarında Selenyum (Se) tozları Klör (Cl) tozları ile karıştırılıp Selenyum fotoiletkeni geliştirildi. Aynı şartlar altında Çinkosülfür (ZnS) ve Çinkoklörür (ZnCl) tozları karıştırılıp Çinkosülfür fotoiletkeni yapıldı. Geliştirilen fotoiletkenler ışığa karşı oldukça hassastırlar. Bu fotoiletkenlerdeki hassaslaştırma merkezlerinin yoğunluğu Kapasitör-Voltaj (C-V) ve sınırlandırılmış boşluk yükleri methodları kullanılarak bulundu. Se ve ZnS'nin yasak bölgesindeki hassaslaştırma merkezlerinin enerji seviyeleri dalgaboyu ile fotoiletkenlik uyarımının değişmesi methodu kullanılarak elde edildi.

Hassaslaştırma merkezlerinin yoğunluğu ışık yoğunluğu ile düzgün değiştiği görüldü; Se ve ZnS fotoiletkenlerinin band enerji değerlerinin teorik değerleri ile çok iyi uyum içinde olduğu bulundu.

Anahtar Kelimeler: Birleşme merkezleri II,
Hassaslaştırma merkezleri,
Fotohassaslık, Se, ZnS

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LIST OF SYMBOLS

A	Cross-section area
C	Capacitance
ΔI	Change in current
Δn	Density of optically excited free-electron per unit volume
Δp	Density of optically excited free-hole per unit volume
$\Delta\sigma$	Change in conductivity
e	Electronic charge
E_c	Conduction band energy level
E_{dn}	Electron demarcation energy level
E_{dp}	Hole demarcation energy level
E_{fn}	Electron fermi energy level
E_{fp}	Hole fermi energy level
Eg	Energy band gap
E_I	Centers energy level below the conduction band
E_{II}	Recombination center II energy level
E_t	Trap energy level
E_v	Valance band energy level
ϵ	Epsilon
F	Total number of excitations/sec
f	Number of excitations/cm^3-sec
G	Photoconductivity gain
I	Current
k	Boltzmann constant
L	Electrode spacing

L	Light intensity
m_e	Effective mass of electrons
m_h	Effective mass of holes
μ	Mobility
μ_n	Electron mobility
μ_p	Hole mobility
N	Recombination center per unit volume
n	Density of free-electron per unit volume
N_c	Effective density of states in the conduction band
n_I	Density of center occupied by an electron
N_n	Density of recombination center for hole
N_p	Density of recombination center for electron
N_r	Density of recombination centers containing holes
N_{r1}	Total recombination centers I
N_{r2}	Total recombination centers II
n_{r1}	Electron-occupied recombination center I per unit volume
n_{r2}	Electron-occupied recombination center II per unit volume
ν	Optical frequency-of-escape factor for thermal excitation
n_t	Density of recombination centers under applying of voltage
N_v	Effective density of states in the valance band
∂_n	Net charge in photoconductor
p	Density of free-hole per unit volume
p_I	Density of holes captured at the center
ρ_r	Hole-occupied total recombination center or sensitizing center in per unit volume

p_{r1} Hole-occupied recombination center I per unit volume

p_{r2} Hole-occupied recombination center II per unit volume

Q Total charge

r Diameter of atom

S Capture cross section of recombination center

S_{II} Capture cross section of II center

S_n Capture cross section of recombination center for free electrons

S_p Capture cross section of recombination center for free holes

s_{n1} Capture cross section of recombination center I for free electrons

s_{n2} Capture cross section of recombination center II for free electrons

s_{p1} Capture cross section of recombination center I for free holes

s_{p2} Capture cross section of recombination center II for free holes

S_t Capture cross section of traps

σ Conductivity

T Absolute temperature

τ Free-carrier lifetime

τ_n Free-electron lifetime

τ_p Free-hole lifetime

τ_0 Free-carrier response time to changes in light intensity

t Transit time between the electrodes

t_n Transit time of electron between the electrodes

t_p Transit time of hole between the electrodes

V Voltage between the electrodes

V_{max} Applied maximum voltage to crystal

v Thermal velocity of free-carrier

Introduction

The beginning of the modern era of photoconductivity can be dated at about the end of World War II. Willoughby Smith observed a real photoconductive effect in selenium in 1873[1], the selenium photoconductor which soon came into usage depended on photoconductivity in selenium, i.e., an increase in conductivity because of absorption of light and the generation of a voltage because of the absorption of light. The later years the selenium photoconductor is used as a photocell. The first such selenium photocell was produced by Adams and Day in 1876[2].

Investigation of the photoconductivity process by Gudden and Phol and their contemporaries began in 1920's, principally with zinc sulphide, diamond, and alkali halides. They showed that light absorption, the excitation of luminescence by light, and excitation of photoconductivity by light, all of which had a similar dependence on the wavelength of the light for a given material. They studied the effect of impurities on the response spectrum of photoconductivity in ZnS, discovering that in presence of impurities in sample had extended to the region of photosensitivity to longer wavelength. They found that the incorporation of some impurities, such as Fe in ZnS could reduce the photosensitivity of the material. They found the prime importance of the phenomenon that only one electronic charge passes between the electrodes for each light photon absorbed.

The new photoeffects were discovered in the early 1930s. In 1931, Dember [3] reported that a potential difference was developed between the electrodes in diamond and zinc sulphide in the direction of the light, for strongly absorbed light. Such a potential difference may be set up in nonhomogeneously excited materials because of the unequal coefficient of electrons and holes freed by light, as pointed out by Frenkel in 1935. This photoeffects emphasized the importance of taking into account both electrons and holes in considering the effects of light on photoconductors.

Early research in the field of photoconductivity was concentrated primarily on selenium. A complete bibliography of the early work on selenium between 1907 and 1927 was published by Piersel. The motion of electrons inside an insular was shown definitely for the first time in diamond by Gudden and Phol in 1920[4], and by 1927 it had been reasonably established that photoconductivity in selenium was due to the liberation of electrons inside the crystal.

In 1917, Case investigated some 162 mineral specimens and added to the photosensitive materials known at that date (selenium). The six new photosensitive materials added are bismuth sesquisulfide, molybdenum sulphide, silver sulphide, lead sulphide, silver iodide, and silver oxide.

The work of Gudden and Phol in the 1920s added zinc sulphide, cadmium sulphide, diamond, and the alkali halides to the list of photosensitive materials which were extensively investigated. In 1923, Gudden and Phol carried out an extensive examination of materials in an effect to find a correlation between the chemical nature of the material and the presence of photosensitivity. They examined the nitrates, sulphides, carbonates, fluorides, chlorides, bromides, iodides, oxides, and sulphides of a number of cations, which they separated into two categories, depending on whether or not the electronic structure of the cation had

a noble-gas configuration. Cations without such a configuration are Pb^{+2}, Tl^{+}, Hg^{+2}, Cd^{+2}, Ag^{+}, Zn^{+2}, and Cu^{+}. Compounds of these cations were found to possess photosensitivity. Of the compounds formed with cations with a noble-gas electronic configuration (Ba^{+2}, Sr^{+2}, Ca^{+2}, Mg^{+2}, K^{+}, Na^{+}). The most sensitive photoconductors today do have cations without a noble-gas electronic configuration.

Another extensive investigation of photosensitive materials was reported by Bergman and Hansler[5] in 1936. Using the Dember effect, they obtained the wavelength for maximum response, the relative sensitivity, and the conductivity type (whether current is carried primarily by electrons or holes) for more than 20 compounds.

A detail quantitative investigation of the mechanism of photoconductivity was difficult. The need for single crystals was clear, but the techniques required for the synthesis are to incorporate impurities (cations) into the crystals to increase the sensitivity of the photoconductors. The importance of crystal defects such as vacancies in determining the photoconductivity characteristics of a material has been increasingly evident in recent years. A perfect crystalline material has no energy states in its forbidden gap. But in real semiconductors or insulators there are always some imperfections associated with impurities or native crystallographic defects. In general, the exact nature of these centers are not well known and it is usual to classify them in terms of their observed behaviour, i.e., as donor or acceptor levels, sensitive centers, traps, etc.

In this study; we explained the determination of density of sensitizing centers in low-resistivity n-type Cl doped selenium crystal covered with Aluminium(Al) electrodes of both sides of crystal by using different methods such as C-V (Capacitance-Voltage) method and Space-charge-limited current method and the determination of density of

sensitizing centers in high-resistivity ZnCl doped ZnS crystal covered Aluminium(Al) electrodes of both sides of crystal by using C-V method. We also studied the determination of the band gap of photoconductors and the energy levels of sensitizing centers in the forbidden gap of n-type Se and ZnS photoconductors by using excitation of photoconductivity by light.

This study has been arranged as follows: Chapter 1 deals with electron processes in crystals, the band scheme, electric conductivity and electronic transitions between the bands. Chapter 2 includes theoretical consideration of photoconductivity, general mechanism of photoconductivity, lifetime of photoexcited carriers, means of photosensitivity, capture cross section of energy states in the forbidden gap, demarcation level, and effect of traps to the photoconductivity. The preparation of photoconductors (single crystals) will be explained in Chapter 3. Chapter 4 deals with electron doping to the crystals, the growth of photoconductivity by intensive light falling on photoconductors, by impurity incorporation, supralinearity, infrared and thermal quenching, space-charge-limited current with ohmic contacts, and determination of band gap of photoconductors, and the energy levels of sensitizing centers in the forbidden gap. Chapter 5 covers experimental section and the determination of sensitizing centers by using C-V and space-charge-limited methods. Finally, the experimental results will be discussed in Chapter 6.

CHAPTER 1

ELECTRON PROCESSES IN CRYSTAL

Photoconductivity processes involve the absorption of energy from light or from particles, the excitation of charge carriers from a nonconducting ground state to a higher energy state where they are free to contribute to the electrical conductivity, and return of charge carriers from the conducting state to their ground state. The discussion of these phenomena requires a background on the general nature of electron processes in crystals.

1.1 The Band Scheme and Electric Conductivity

A simple explanation for the differences in electric conductivity between different types of materials can be provided in terms of the energy-band scheme. There are three types of material which are metal, semiconductor and insulator. The difference between the valance band and the conduction band is called energy band gap.

$$E_g = E_c - E_v \qquad (1.1\text{-}1)$$

where E_g is the value of the energy band gap, E_c and E_v is the energy value of conduction and valance band respectively. In the metal, there is no energy band gap

(E_g=0). The value of energy band gap in semiconductor is usually changes between 0.2 eV and 2.0 eV. If the material has an energy band gap approximately greater than E_g>2.0 eV this material is insulator.

When an electron is excited from the valance band to the conduction band, it creates an electron deficiency in the valance band. This electron deficiency is named as a hole. Just as the electron in the conduction band is free to move under the action of an applied field, being attracted to the anode because of its negative charge, the hole in the valance band is also free to move under the action of a field. The hole, however, moves toward the cathode; it behaves, therefore, like a positive charge equal in magnitude to the negative charge of the electron. The hole itself does not move; it is electron moving toward the anode in the valance band which produce the relative motion of the hole toward the cathode. The conductivity σ is expressed as follows,

$$\sigma=e(n\mu_n+p\mu_p) \qquad (1.1\text{-}2)$$

where e is the electron charge, n and p are the density (number per unit volume) of free electrons and holes, respectively, μ_n and μ_p are the electron and hole mobilities, respectively. The mobility is the velocity per unit volume acquired by a charge carrier as a result of the application of an electric field. The mobility is intimately connected with the nature of the energy band in which the conductivity is occurring. The mobility is, therefore, characteristic of the material, although its magnitude can be altered considerably by variations in temperature and purity of the material.

1.2 Electronic Transitions

Some of the electronic transitions commonly found in photoconductors are shown schematically in the energy-band diagram of Figure (1.2-1). These transitions can

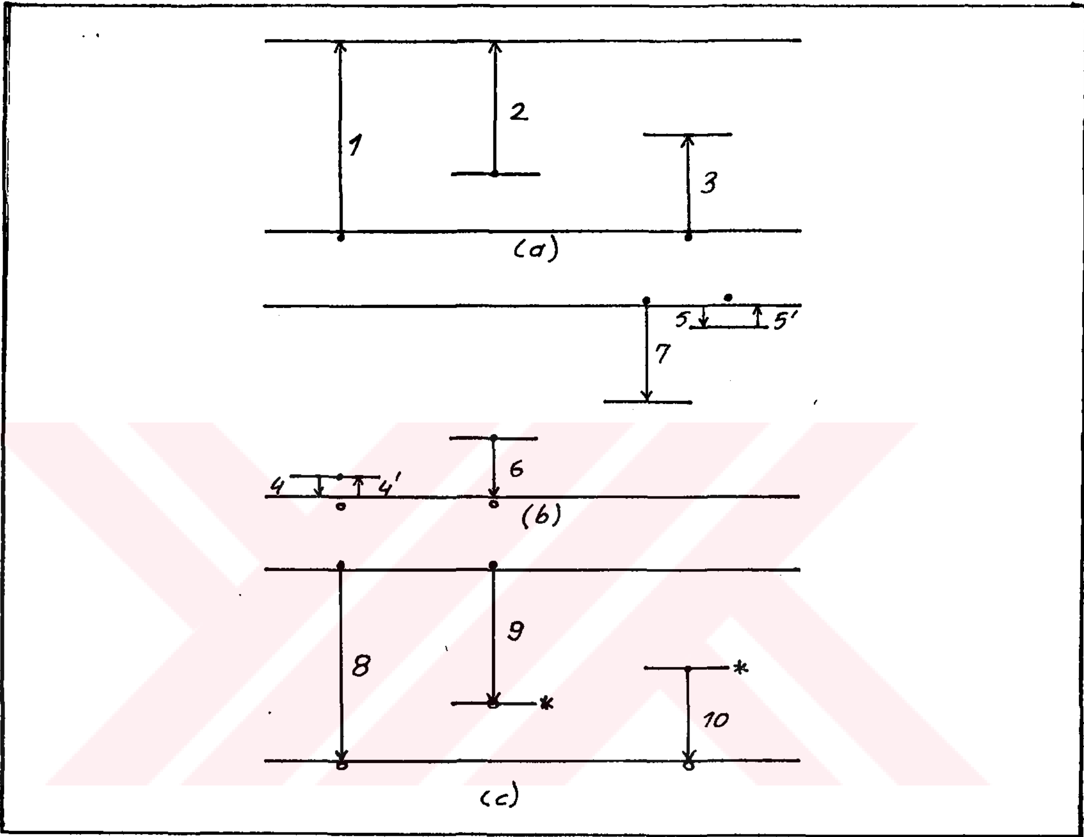

Figure 1.2-1 Common electronic transitions in photoconductors. (a) Absorption and excitation; (b) trapping and capture; (c) recombination.

conveniently be divided into three types: (1) absorption and excitation (Fig.1.2-1a); (2) trapping and capture (Fig.1.2-1b); and (3) recombination (Fig.1.2-1c).

1.2.1 Absorption and Excitation

There are three possible types of absorption transitions resulting in photoconductivity. Transition 1 corresponds to absorption by the atoms of the crystal itself, producing a free electron and a free hole for each photon absorbed. Transition 2 corresponds to absorption at localized imperfections in the crystal, producing a free electron and a hole bound in the neighbourhood of the imperfection for each photon absorbed. Transition 3 corresponds to absorption, raising an electron from the valance band to an unoccupied imperfection level, producing a free hole and an electron bound in the neighbourhood of the imperfection for each photon absorbed.

1.2.2 Trapping and Capture

Once electrons and holes have been freed by absorption of a photon of sufficient energy, they will remain free until they are captured at an imperfection (omitting for the moment the alternative possibilities that they may recombine directly or pass out of the crystal at the electrodes). We may classify these capturing centers in two groups: (1) trapping centers-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; (2) recombination centers- 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. Figure 1.2-1b displays trapping and thermal release of electrons in electron traps (transition 5 and 5'), and trapping and thermal release of holes in holes traps (electron transitions 4 and 4'); also capture of an electron (transition 7), and of a hole (electron transition 6) in recombination centers.

Although a center with an energy level lying near one of the band edges is more likely to act as a trap than as a recombination center (and vice versa for centers with levels lying near the middle of the forbidden gap), the distinction between traps and recombination centers is a distinction drawn on the basis of the relative probability of thermal ejection versus recombination. A recombination center occurs at one condition of light intensity and temperature and may act as a trap at another light intensity and temperature.

1.2.3 Recombination

Three simple types of recombination transition are shown in Figure 1.2-1c. The free electron may combine directly with the free hole, according to transition 8; the probability of this transition is usually rather small. Frequently transition of type 8 are radiative, i.e., the lost energy is emitted as photons whose energy is approximately equal to the energy of the band gap. Such emission is called edge emission.

Recombination may also occur, as is the more usual case, through recombination centers: either an electron being captured by an excited center containing a hole (transition 9), or a hole being captured by an excited center containing an electron (transition 10). Transition 9 and 10 may also be radiative.

CHAPTER 2

PHOTOCONDUCTIVITY PROCESSES

In this chapter; some photoconductive properties that are necessary for understanding of photoconductivity phenomena are introduced.

2.1 General Mechanisms

As mentioned in the previous chapter, the conductivity of an insulator or semiconductor was expressed as

$$\sigma=(n\mu_n+p\mu_p) \qquad (2.1\text{-}1)$$

where n and p were the densities of free electrons and holes, and μ_n and μ_p were the electron and hole mobilities respectively.

In a homogeneous material in which n and p are uniform throughout the material, after absorb the radiation, if the increases of n and p gives as Δn and Δp respectively photoconductivity changes as,

$$\Delta\sigma=e(\Delta n\mu_n+\Delta p\mu_p) \qquad (2.1\text{-}2)$$

In insulators the values of Δn and Δp may be much larger than the corresponding free-carrier densities in the dark, n_0 and p_0. In semiconductors the reverse is often true, and the effect of radiation can be considered as a small perturbation on a large dark carrier density. This is a reason for the fundamental difference between the treatment which must be given to photoconductivity in insulators and homogeneous semiconductors.

In a non-homogeneous material in which n and p are not uniform throughout the material, photoconductivity can result from a second mechanism involving the reduction by radiation of the resistance of barriers in the material. Consider, for example, a material with high-conductivity regions separated by narrow low-conductivity regions in the dark. The flow of current through the material is limited by the presence of the low-conductivity regions, which act as barriers to the flow of current between the high-conductivity regions. Light absorbed in the low-conductivity regions can reduce the resistance of these barriers such that the current flow through whole material is much greater than it would be without radiation.

In many discussions of photoconductivity it is possible to make two simplifying assumptions:

1- The conductivity is dominated by one of the carriers so that the contribution of the other can be effectively neglected.

2- The crystal stays neutral during the photoconductivity process without a build-up of appreciable space charge in the crystal,i.e.,$\Delta p=\Delta n$.

2.2 Lifetime

The lifetime of photoexcited carriers is the key parameter for an understanding of photoconductivity. The term "lifetime", however, has been used to describe a number

of different quantities, and it is, therefore, necessary to examine the concept in some detail.

If light falling on a photoconductor creates f electron- hole pairs per second per unit volume of the photoconductor, then

$$f\tau_n=\Delta n \quad (2.2\text{-}1a)$$

$$f\tau_p=\Delta p \quad (2.2\text{-}1b)$$

where τ_n is the free lifetime of an electron, τ_p is the free lifetime of a hole, and Δn and Δp are the additional free electron and hole densities respectively present as a result of absorption of light. Equation (2.1-2) for the photoconductivity can then be rewritten as

$$\Delta\sigma=fe(\mu_n\tau_n+\mu_p\tau_p) \quad (2.2\text{-}2)$$

The following types of "lifetime" must be distinguished:

(1) FREE LIFETIME

The free lifetime is the time that the charge carrier is free to contribute to the conductivity. It is the time that an electron spends in the conduction band, or the time that an excited hole spends in the valance band. The τ_n and τ_p of Eq.(2.2-2) are free lifetimes. The free lifetime of a charge carrier can be (a) terminated by recombination, or if the carrier is extracted from the crystal by the electric field without being replenished from the opposite electrode; (b) interrupted if the carrier is trapped, to be resumed when the carrier is freed from the trap; (c) undisturbed if the carrier is extracted from the crystal by the field at the same time as an identical carrier is injected into the crystal from the opposite electrode.

(2) EXCITED LIFETIME

The excited lifetime is the total time in which 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

The pair lifetime is the free lifetime of an electron-hole pair. If either electron or hole is captured, or is extracted without replenishment, the pair lifetime is terminated.

(4) MINORITY-CARRIER LIFETIME

The minority-carrier lifetime is the free lifetime of the minority carrier, i.e., the carrier which makes the minor contribution to the conductivity: 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

The majority-carrier lifetime is the free lifetime of the majority carrier, i.e., of electrons in *n*-type materials, and holes in *p*-type materials. If the density of free carriers in a material is much greater than the density of recombination centres, as is frequently true in semiconductors, the majority-carrier lifetime will be equal to the minority-carrier lifetime. But, if the density of free carriers is much less than the density of recombination centres, as is most often true for insulators, the majority-carrier lifetime can be much larger than the minority-carrier lifetime.

As we shall see later on, photosensitivity is frequently obtained by incorporating in a material centres which capture minority carriers rapidly, but then have a much smaller probability of capturing majority carriers to bring about recombination. In insensitive ZnS, for example, both the majority-carrier lifetime and the minority-carrier lifetime are of the order of 1 μsec. In sensitive ZnS, however, the majority-carrier lifetime may be increased to 1 msec while the minority-carrier lifetime has been decreased to 0.01 μsec or less.

2.3 Photosensitivity

When the term photosensitivity is used in this thesis, it means photoconductivity per unit excitation intensity, i.e., the change in conductivity caused by excitation, divided by the excitation intensity. A quantity called specific sensitivity is defined in units of square centimetres per ohm per watt. It is obtained by multiplying the photoconductance by the square of electrode spacing and dividing by the absorbed radiation power. The specific sensitivity is independent of applied voltage or light intensity if the photoconductivity varies linearly with voltage and light intensity. The specific sensitivity is an intrinsic property of the material, being proportional to the product of free-carrier lifetime and free-carrier mobility. This quantity has sometimes also been called photoresponse.

It is frequently convenient to think, as a third alternative, of the photosensitivity of a photoconductor in terms of the number of charge carriers which pass between the electrodes per second for each photon absorbed per second; the photoconductivity gain G is defined as

$$\frac{\Delta I}{e}=GF \qquad (2.3\text{-}1)$$

where ΔI is the photocurrent, and F is the total number of electron-hole pairs being created in the photoconductor per second by the absorption of light, i.e., F=*f*(volume).

The gain may also be expressed as the ratio of the free lifetime of a charge carrier to the time required for the carrier to move between the electrodes, called the transit time,

$$G=\frac{\tau_n}{t_n}+\frac{\tau_p}{t_p} \quad (2.3\text{-}2)$$

where t_n and t_p are respectively the transit times for electrons and holes. If the charge carriers move in a field which corresponds to the application of a voltage V across a distance L, the transit time is given by

$$t=\frac{L^2}{\mu V} \quad (2.3\text{-}3)$$

The expression for the gain is, therefore,

$$G=(\tau_n\mu_n+\tau_p\mu_p)\,\frac{V}{L^2} \quad (2.3\text{-}4)$$

2.4 Capture Cross Section

We restrict our attention at the moment to the recombination process by which the free lifetime of a charge carrier can be terminated. If there are N recombination centers per unit volume which can capture a free carrier, the lifetime may be expressed as

$$\tau=\frac{1}{vSN} \quad (2.4\text{-}1)$$

Where ν is the thermal velocity of the carrier $\{(2kT/m)^{1/2}\}$, and S is the capture cross section of the recombination centers for that type of charge carrier.

The capture cross section of a center is determined by the potential variation in the neighbourhood of the center. The largest capture cross sections occur for charged centers which exert a coulomb attraction on free carriers. Under the assumption that a free carrier will be captured if it approaches sufficiently close to a center so that the binding energy due to coulomb attraction is equal to or greater than kT. A simple estimate of the corresponding value of S can be made,

$$\frac{e^2}{r\epsilon}=kT \qquad (2.4-2)$$

or, at room temperature,

$$\pi r^2=S=\frac{10^{-10}}{\epsilon^2} \qquad (2.4-3)$$

For a dielectric constant ϵ of about 10, a maximum value of S of about 10^{-12} cm^2 is indicated. The normal value of S for an uncharged center is about the order of atomic dimensions, or 10^{-15} cm^2. It is possible, however, for a center actually to exert a coulomb repulsion for free carriers; such a center will have a very small capture cross section. The smallest values of S indicated by experiments to date are about 10^{-22} cm^2.

A wide range of values for the density of recombination centers N is also possible, from about 10^{12} cm^{-3} in some of the purest and most perfect crystals, to as high as 10^{19} cm^{-3} in crystals with high imperfection. Inserting these representative values of S and N into Eq(2.4-1) shows that the free lifetime can vary from 10^{-14} to 10^{3} sec. In many materials, average values of $S=10^{-15}$ cm^2 and $N=10^{15}$ cm^{-3} prevail

which, together with $v=(2kT/m)^{1/2}=10^7$ cm/sec at room temperature, lead to $\tau=10^{-7}$ sec. Experimental values of τ extend from 10^{-10} sec or less to as high as 10^{-2} sec.

2.5 Demarcation between Trapping Levels and Recombination Levels

Before we consider the effect of the presence of trapping on photoconductivity, we shall set forth in a little more detail the criterion for distinguishing between a trapping center and a recombination center. Whether a center is to be considered as a trapping center or as a recombination center depends on the relative magnitudes of (1) the probability of thermal freeing of the trapped carrier, and (2) the probability of recombination with the carrier of opposite sign occurring at the center, before thermal freeing of the carrier trapped first. To put this into mathematical terms, consider centers with levels lying at an energy E_I below the conduction band. These centers will act as electron trapping centers if

$$n_I p v S_p \ll n_I S_n v N_c \exp\left(-\frac{E_I}{kT}\right) \qquad (2.5\text{-}1a)$$

or as recombination center if

$$n_I p v S_p \gg n_I v S_n N_c \exp\left(-\frac{E_I}{kT}\right) \qquad (2.5\text{-}1b)$$

where n_I is the density of centers occupied by an electron, p is the density of free holes, S_n is the capture cross section for a free electron by a center occupied by a hole, S_p is the capture cross section for a free hole by a center occupied by an electron, and N_c is the effective density of states in the conduction band.

It is convenient to define the location of a demarcation level, separating trapping and recombination levels in the following way: When an electron (hole) is located at the electron (hole) demarcation level, it has equal probability of recombining with a free hole (electron) and of being thermally ejected to the conduction (valance) band. The occupation of a level lying above the electron demarcation level is determined by the conditions of thermal equilibrium between the levels and the conduction band. Similarly, the occupation of a level lying below the hole demarcation level is determined by the conditions of thermal equilibrium between the levels and the valance band. The occupation of levels lying between the electron demarcation level and the hole demarcation level is determined by the recombination kinetics of the material. Figure 2.5-1 shows schematically the relationship between the demarcation levels and the steady-state Fermi levels for an insulator, for which the density of photo excited carriers is much larger than the density of thermally excited carriers.

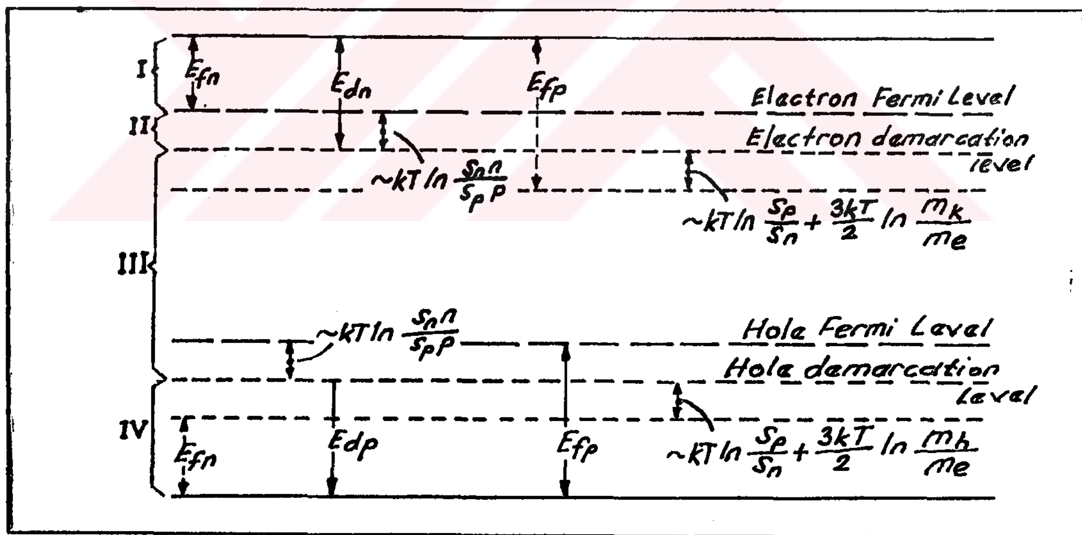

Figure 2.5-1 Fermi level and demarcation levels for an insulator.

The quantitative relationship between the demarcation levels and the steady-state Fermi levels may be derived in

the following way. First, let us consider the relationship between the electron Fermi level and the electron demarcation level for a certain type of centers. When the electron demarcation level is located at the level corresponding to these centers, by definition

$$n_I S_n N_c v \exp\left(-\frac{E_{dn}}{kT}\right) = n_I p v S_p \qquad \textbf{(2.5-2)}$$

which is the same form as Eq. (2.5-1) with E_I replaced by E_{dn}, the energy separation of the electron demarcation level from the bottom of the conduction band. Now using the following relation

$$n = N_c \exp\left(-\frac{E_{fn}}{kT}\right) \qquad \textbf{(2.5-3)}$$

we obtain

$$S_n n \exp\left(\frac{E_{fn}}{kT}\right) \exp\left(-\frac{E_{dn}}{kT}\right) = S_p p \qquad \textbf{(2.5-4)}$$

or

$$E_{fn} = E_{dn} + kT \ln\left(\frac{S_p p}{S_n n}\right) \qquad \textbf{(2.5-5)}$$

Since $nN_p v S_n = pN_n v S_p$, where N_p is the density of recombination centers for electrons, i.e., the density of recombination centers which have captured a hole, and N_n is the density of recombination centers for holes, we may rewrite Eq. (2.5-5) as

$$E_{fn}=E_{dn}+kT\ln(\frac{N_p}{N_n}) \qquad (2.5\text{-}6)$$

A similar relationship exists between the hole Fermi level and the hole demarcation level,

$$E_{fp}=E_{dp}-kT\ln(\frac{S_p p}{S_n n})=E_{dp}-kT\ln(\frac{N_p}{N_n}) \qquad (2.5\text{-}7)$$

where E_{dp} is the energy separation between the hole demarcation level and the top of the valance band.

Since a demarcation level is determined by the values of S_n and S_p of the centers involved, it is important to realize that each different type of center, as characterized by different values of S_n and S_p, has its own demarcation levels associated with it.

Both the electron Fermi level and the hole demarcation level depend on the density of free electrons. It is possible to derive a relationship, therefore, between E_{fn} and E_{dp}. Consider the hole demarcation level at the level corresponding to the centers under discussion. Then,

$$p_I n S_n v=p_I S_p N_v v\exp(-\frac{E_{dp}}{kT}) \qquad (2.5\text{-}8)$$

where p_I is the density of holes captured at the centers. Equation (2.5-3) can be used to substitute for n to obtain

$$N_c\exp(-\frac{E_{fn}}{kT})S_n=N_v S_p\exp(-\frac{E_{dp}}{kT}) \qquad (2.5\text{-}9)$$

or

$$E_{dp}=E_{fn}+kTln(\frac{S_p}{S_n})+\frac{3kT}{2}\ln(\frac{m_h}{m_e}) \qquad \textbf{(2.5-10)}$$

where m_h and m_e are the effective masses of holes and electrons, respectively. Similarly, a relation between the hole Fermi level and the electron demarcation level can be derived:

$$E_{dn}=E_{fp}-kTln(\frac{S_p}{S_n})-\frac{3kT}{2}\ln(\frac{m_h}{m_e}) \qquad \textbf{(2.5-11)}$$

As indicated in Fig.(2.5-1), levels are separated into four categories in an insulator by the Fermi levels and demarcation levels. Levels located in region I are electron traps and levels located in region IV are hole traps. Levels located in region III are recombination levels by definition of the demarcation levels. Levels located in region II are above the electron demarcation level, but below the electron Fermi level. Although these levels are still to be considered in thermal equilibrium with the conduction band, the density of occupied levels is high, and they will take part in the recombination process with free holes. In

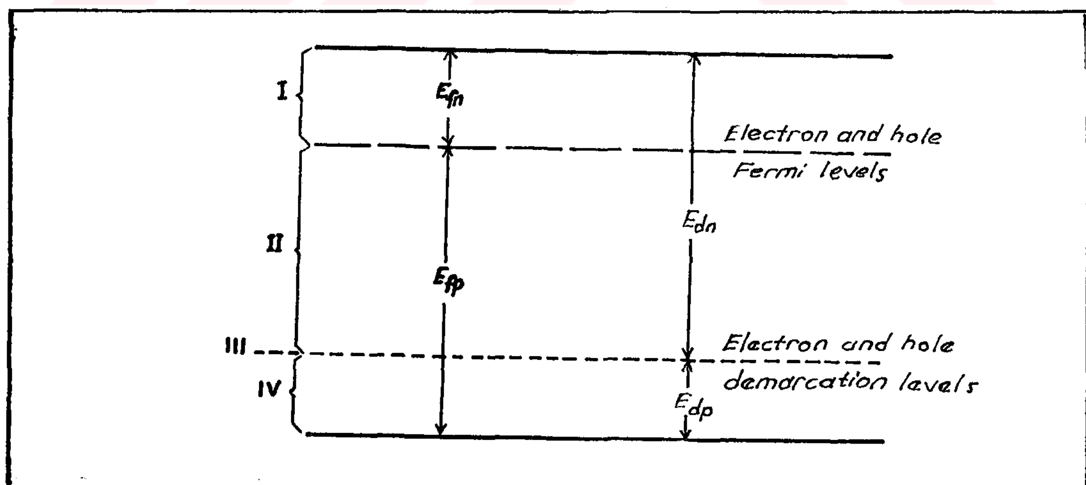

Figure 2.5-2 Fermi levels and demarcation levels for a semiconductor.

general, it is sufficient to consider effective recombination levels as all those that lie in either region II or region III.

The corresponding case for a semiconductor is shown in Fig. 2.5-2. The thermally excited density of free carriers is greater than the optically excited density. By definition, all levels are in thermal equilibrium with the bands, and there is only one Fermi level and one demarcation level. Regions I and IV have the same characteristics as for an insulator, but region II now extends from the Fermi level to the demarcation level, and region III having collapsed to a line at the demarcation level.

2.6 Effects of Trapping

If a material existed with no levels in the forbidden gap, then it would be strictly true that every excited carrier in the crystal would also be a free carrier. If a material existed with only recombination centers of the common type such that the majority-carrier lifetime is much greater than the minority-carrier lifetime, then it would still be true that every excited majority carrier would be a free carrier. If, however, as is the case in almost all real materials, there are also trapping centers as well as recombination centers, the number of free carriers may be less than the number of excited carriers.

A major effect of trapping is to make the experimentally observed decay time of the photocurrent, after excitation has ceased, longer than the carrier lifetime. If no trapping centers are present, then the observed photocurrent will decay in the same way as the density of free carriers, 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, the thermal freeing of trapped carriers during the course of the decay can prolong the decay so that the observed decay time is longer than the actual recombination determined lifetime of free carrier. In the extreme case that 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 addition to making the observed decay time longer than the lifetime of a free carrier, the presence of traps may also decrease the sensitivity of a photoconductor. Consider a material with n-type photoconductivity associated primarily with the majority carrier, the minority carrier being captured essentially immediately. We shall also consider the dark conductivity to be negligible. The condition for steady state is

$$f=vS_n nN_r \qquad (2.6\text{-}1)$$

where N_r is the density of recombination centers containing holes, and S_n is the capture cross section of these centers for a free electron. This equation is to be compared with the corresponding equation without trapping: $f=vS_n n^2$. Now, since $N_r=n+n_t$, a desensitizing effect is introduced when n_t is comparable to or greater than n. The lifetime of a free electron is reduced from $\tau=(vS_n n)^{-1}$ to

$$\tau=\frac{1}{vS_n N_r} \qquad (2.6\text{-}2)$$

It is necessary to consider this matter in somewhat greater detail in order to make sure that our definitions

of trapping centers and recombination centers remain consistent. Figure 2.6-1 presents four possible simple cases of recombination and trapping centers in terms of the location of the quasi-electron Fermi level in the dark and in the presence of illumination. Figure 2.6-1a shows levels

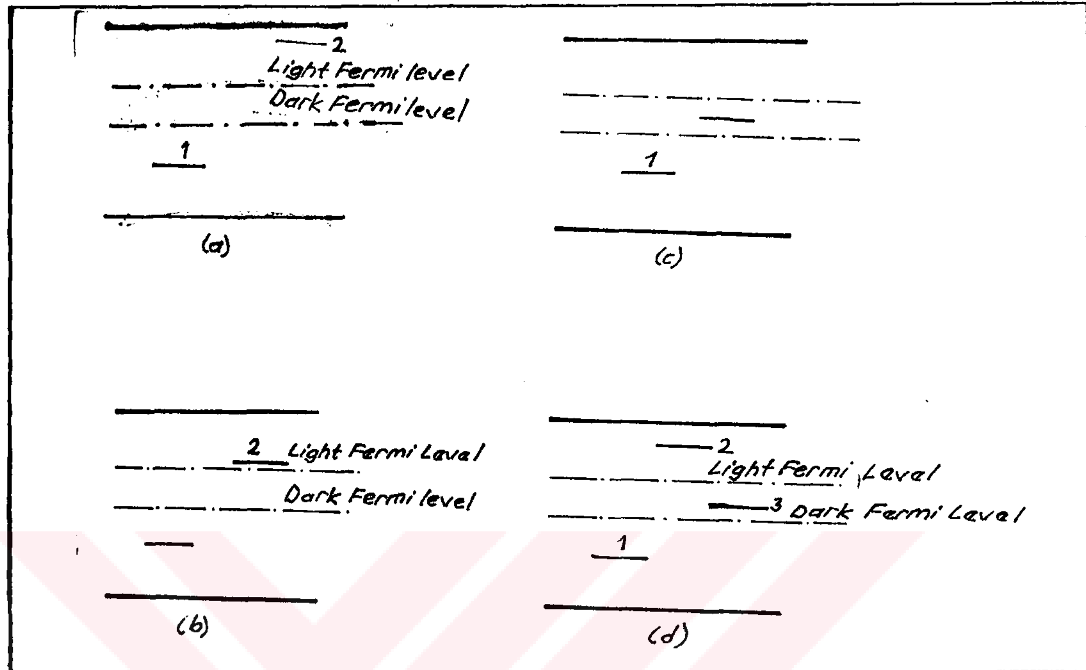

Figure 2.6-1 Relations between the location of trapping and recombination centers, and of the Fermi level, in the dark and under illumination.

for recombination centers 1 and trapping centers 2. When the Fermi level is raised in the presence of illumination, the occupation of trapping centers by electrons is increased, and some degree of desensitization results. If, however, the trapping levels lie considerably above the Fermi level in the light, their occupation even under illumination, and hence their desensitizing effect may be completely negligible. If, however, as in Fig.2.6-1b, the trapping levels lie near the Fermi level in the light, considerable desensitization may result. In both these cases, levels 2 are trapping levels, i.e., they lie above the Fermi level in both dark and light. It is possible, however, as

illustrated in Fig.2.6-1c that levels 3 may lie above the dark Fermi level but below the light Fermi level. The presence of levels 3 can cause a large desensitization, but it is no longer proper to refer to them as trapping centers under illumination. If trapping levels 2 are added to the picture of Fig. 2.6-1c to obtain Fig. 2.6-1d, it is probable that no desensitization due to the addition of the levels 2 will occur. Such desensitization will occur only if the density of trapped electrons in centers 2 is comparable to the additional recombination centers 3 formed by illumination.

The dependence of n and τ_0 on f and T will be explained briefly:

The variation of n as $f^{1/2}$ expected for a trap-free material is changed to a linear variation of n with f for a material with a uniform distribution of traps. A variation of n as $f^{1/2}$ can be found even with trapping. If the density of photoexcited electrons trapped above the electron Fermi level is greater than the density of photoexcited electrons trapped below the Fermi level. The experimental observation of a variation of n with a power of f between 1/2 and 1 can be described by assuming an exponential distribution of traps, the density of traps of energy E decreasing exponentially with the distance E from the bottom of the conduction band. Thus, in the range of light intensities for which the density of free carriers is less than the density of trapped carriers, this simple model provides a description for n varying with power of f between 0.5 and 1.0. For high light intensities, such that the density of free carriers is greater than the density of trapped carriers, bimolecular recombination will predominate, and n will vary as $f^{1/2}$.

The variation of n versus T in many photoconductors, the photocurrent is essentially independent of temperature, at least over large variation of temperature. Such an

independence is to be expected from the model involving a uniform trap distribution. For an exponential trap distribution of the form, $n_E dE = A\exp(-E/kT)dE$, the expected variation of photocurrent with temperature is somewhat more rapid, the photocurrent increasing by an order of magnitude for each increase of 100^0. If T_1 is set equal to 1000^0K, or by a factor of three for each increase of 100^0, if T_1 is set equal to 2000^0K. T_1 may be related to the equilibrium temperature corresponding to the trap distribution, i.e., the temperature at which the trapping centers were "frozen in" during the cooling of the material after crystallization. Only for the special case of a greater density of carriers trapped above the Fermi level than below is a rapid variation of photocurrent with temperature expected. Then an exponential variation is predicted, the photocurrent increasing with increasing temperature.

In our discussion of temperature dependence, we have considered the capture cross section S to be independent of temperature. Analysis of experimental data indicates that this is probably true, but that there are also certain types of center for which S is temperature-dependent and may indeed dominate the temperature dependence of the photocurrent. The cross section for coulomb attraction, for example, would be expected to vary as T^{-2} (Eq.2.4-2). The cross section for coulomb repulsion, involving an activation energy, might also be expected to vary quite rapidly with temperature.

Except for the special case in which the electron Fermi level lies well above a uniform trap distribution, for which the observed decay time is equal to the true carrier lifetime and is independent of f or T, the observed decay time is inversely proportional to the photocurrent. This means that the observed decay time is inversely proportional to a power of f between 1/2 and 1.0, depending on the specific case. The smaller is the excitation intensity, the longer is the observed decay time.

The maximum performance of a photoconductor or of real crystals with trapping present can be achieved only for such high light intensities that the density of free carriers exceeds the density of trapped carriers. At low light intensities, the observed decay time may be many orders of magnitude longer than the carrier lifetime corresponding to the observed gain. The maximum performance of a photoconductor at a given voltage is the observed decay time which is equal to the carrier lifetime.

CHAPTER 3

PREPARATION OF PHOTOCONDUCTORS

To describe adequately the variety of methods useful in the preparation of photoconductors would require a discussion of almost every method of preparation devised for semiconductors in general. Such a lengthy treatment is not the purpose of this chapter, but rather a brief outline of the different techniques, which have been tested in our laboratory, will be given

The preparation of photoconductors may be separated into two broad categories: (1) techniques for making large-area layer photoconductors, and (2) techniques for making single-crystal photoconductors, generally with smaller area than the layers. For most practical applications, the layer photoconductors are preferable because of the relative ease with which large-area photocells can be fabricated. For most investigation of the basic nature of photoconductivity, single-crystal photoconductors are preferable because of the relative ease of defining the relevant variables.

In this section, we consider the some type of photoconductor layers, such as, sintered and powder microcrystalline. There are other photoconductor layers, but, in this study, only sintered and powder crystal growth techniques investigated. The other layers require more sophisticated industrial techniques for making crystal growth. Now we consider briefly the powder and sintered crystal growth techniques.

3.1 Powder (Microcrystalline) Layers

3.1.1 Powder-firing techniques

Before techniques for the fabrication of other types of layers or of single crystals had been developed, powder was the normal form in which photoconductors were measured. Photoconductor cells were made by making a sandwich of photoconductor powder between two electrically conducting surfaces under slight pressure, one of the conducting surfaces being partially transparent to permit illumination of the sample. Although absolute values of photocurrents had little meaning in such measurements, they were useful for the detection of the existence of photoconductivity and of the spectral response associated with such photoconductivity. Measurements of absorption could be compared with measurements of photoconductivity, to compare the variation with wavelength of the incident light.

Sufficient photosensitivity from a powder crystal for the detection of photoconductivity is sometimes difficult, however, sufficient photosensitivity from a powder crystal can be obtained by several techniques which enable the powder crystal to compete with single crystal of the same materials. After photosensitive single crystals of CdS were known, considerable interest still remained in preparing a photosensitive powder of CdS which could be used to cover large areas, much larger those in which single crystals could be grown. One of the first results of such attempts was the realization that surface properties were much more important for powders than for single crystals. In particular, the interparticle contacts of the powder material could have a greater influence on the macroscopic electrical properties of the powder than the bulk properties of the powder itself. Kolomiets attributed an early failure to obtain a photosensitive CdS powder to high resistance between the grains.

High-sensitivity photoconductor layers, equivalent in many properties to single crystals, were prepared by Thomsen and Bube from CdS and CdSe powder. The process involves three firings and produces a powder with small and uniform particle size without grinding the product at any stage of the preparation. During the first firing, there is present, in addition to the CdS and $CuCl_2$,10% of $CdCl_2$,which acts as a solvent flux. In the first firing, the small particles of the original precipiated CdS are recrystallized into larger microcrystallites with chloride and copper impurities incorporated. The product has only fair photosensitivity. A second firing is carried out after the powder has received an impregnation of superficial chloride. The product has high photosensitivity but too high a dark conductivity. A third firing in sulfur vapor drastically reduces the dark conductivity while leaving the photosensitivity relatively unaffected. One of the most important features of this preparation is the role of $CdCl_2$, acting as a solvent and recrystallizing agent for CdS and CdSe. Sensitive CdS powders have also been prepared, using Ga donors and Cu or Ag acceptors.

Photoconducting powders are in general characterized by a nonlinear dependence of photocurrent on applied voltage. In many instances, the photocurrents varies as a power of the voltage greater than unity (third or fourth power) for low voltages below a "threshold" voltage, above which the photocurrents varies linearly with the applied voltage. The "threshold" voltage can be considered as a measure of the total barrier height due to interparticle contacts. Some of the work on CdS, ZnS, and CdSe photoconducting powders suggests that these powders may consist essentially of high-conductivity particles separated by photosensitive low-conductivity contact regions. The action of the light is thus to reduce the resistance between particles and to permit the freer flow of current between the high-conductivity particles. When sufficiently high fields are applied to the powder, a pulse of light will

trigger the powder so that the apparent dark conductivity after the pulse of light may be many orders of magnitude greater than that before the illumination. The higher-conductivity state persists until the field is removed.

3.1.2 Hydrothermal synthesis

The technique of hydrothermal synthesis has been applied to the preparation of photoconducting powders with a particle size less than 5 microns. The small particle size results from the fact that the preparation temperature is only 350^0 C instead of the usual 500 to 600^0 C. CdS together with chloride and a copper salt in the proper concentrations, is sealed into a quartz vial half filled with water. The vial is then sealed in an autoclave half filled with water and heated at 350^0 C for 50 hours. The increased pressure and temperature increase the solubility of the powder in water. During a subsequent slow cooling, recrystallization occurs. Ratios of photocurrents to dark current as high as a million are reported for powders prepared in this way, when illuminated with a few foot-candles.

3.2 Sintered Layers

3.2.1 Powder in solvent

Sintered layers of photoconductor are polycrystalline in nature and usually show fewer barrier effects due to interparticles contacts than powder photoconductors do. The sintered layers can be prepared from the initial suspension of CdS, ZnS or CdSe, $CdCl_2$, and $CuCl_2$, used for the preparation of photoconductor powders. The suspension is sprayed onto a suitable substrate and fired at 600^0 C. As in the preparation of the CdS, ZnS or CdSe during the firing,

the product is a firmly adherent polycrystalline layer, about 5 to 25 microns thick.

3.2.2 Sintered Pellets

Bridging the gap between photoconductor powders and single crystals are photoconductor pellets made by sintering powder under pressure. The sintered pellets of CdS are made by press moulding followed by sintering at 450^0 C for about 10 hours. The same methods can be applied to the ZnS powders that are made by press moulding followed by sintering at 600^0 C for about 15 hours.

In addition to these crystal growth methods, there are other methods such as single-crystal growth from solution. If a solvent can be found for the material from which it is desired to grow single crystals, crystals can be grown by recrystallization from solution. For most insulators and semiconductors, a suitable solvent is hard to find. The solvent of CdS and ZnS powders are NaOH acids. If the CdS and ZnS powders are mixed with NaOH acid and the mixing is heated to the approximately 1000^0 C under the high-pressure,the single-crystal can be grown.

3.3 Evaporated Layers

Of all the methods of preparing thin layers of photoconductors, evaporation in vacuum has received the most general application. The method provides a way of producing uniform layers of fairly large area with relative ease. Evaporation methods are not difficult to develop using the normal vacuum techniques, and usually may be sufficiently controlled to yield reprodicible results. The layers produced by evaporation may have a structure ranging all the way from amorphous to polycrystalline, depending on the vacuum, the rate of deposition, and the temperature of the substrate.

A detailed study of the evaporation of photoconducting layers of Se was carried out by Keck. The structure of the layer was shown to be amorphous for a substrate temperature less than 50^{0}C and a coating rate greater than 1 micron per minute, but crystalline for a substrate temperature greater than 50^{0}C and a coating rateless than 1 micron per minute.

Evaporated ZnS layers have been prepared by Rood and Studer. The purpose behind Studer's work was the preparation of transparent layers of luminescent materials. The layers are deposited on a substrate in a reaction chamber, heated to 1000 to 1200^{0}C and chamber containing for pressure of $1x10^{-5}$ mm Hg or greater.

The many of the photoconducting materials can be growth easly by evaporation techniques such as these materials are Se, Si, Ge, ZnS, CdS, ZnSe, CdSe, etc,.

CHAPTER 4

Introduction

In this chapter, we shall concentrate on those phenomena which are useful in giving direct information about the density of traps centers or recombination centers, energy distribution of these centers, identity of these centers and the energy band gap determination of a given photoconductor by using the photoconductivity methods.

The density of traps centers or recombination centers can be found by using many different different. Two of these methods are C-V methods and space-charge limited current dependence on voltage methods. The energy distribution of traps and recombination centers in the band gap which this phenomena gives us these centers which of traps or recombination centers. Another way to determine the identity of traps is to distinguish between trapping centers whose occupancy is determined by thermal equilibrium process, and recombination centers whose occupancy is determined by recombination kinetics. On the other hand, many of the most interesting properties of photoconductors result from a change in the behaviour of a single type of center, from a trapping center to a recombination center, or vice versa, with appropriate change in light intensity or temperature.

The nature of energy bands in photoconductor, is associated with the excitation transitions.

In order to describe the excitation transitions in photoconductors, it is neccessary to know the nature of the

initial and final states. In the previous chapter (Chapter 1) we considered such transitions that occured either between an imperfection level and allowed band of the crystal. Now, we shall turn our attention to the nature of the transitions between two allowed bands, i.e., the type of transition which occurs for photoexcitation with photons of energy greater than the band gap, or for excitation by X- rays, high-energy nuclear particles.

The values of the band gaps of insulators or semiconductors (photoconductors) are commonly measured by one of the six simple methods. In here, we explain the photoconductivity excitation as a function of wavelength of absorbed photons.

4.1 Electron Doping

We discuss here a most versatile concept for the understanding of the behaviour of photoconductors "Electron Doping".

The recombination centers were shown to govern the lifetime of carriers, that is, the sensitivity of photoconductors. Trapping states on the other hand played only indirect role in determining the sensitivity but were responsible for response times far in excess of lifetimes. The recombination centers were located so far from the band edges that thermal excitation to the band edges could obviously be neglected in comparison with rates of kinetic capture of free electrons and holes. By contrast, the trapping states were located close enough to a band edge that thermal exchange of electrons or holes with the band edge far exceeded the rate of capture of carriers from the opposite band edge. These distinctions between trapping states and recombination centers were qualitative. An approximate quantitative distinction between trapping states and recombination centers can be made using the steady-state Fermi level as fiduciary marks.

For the present let it be assumed that states lying between the steady-state Fermi level for electrons and the conduction band are trapping states for electrons. The steady-state Fermi level for electrons, E_{fn}, is defined as that Fermi level consistent with the density of electrons in the conduction band. Its energetic distance from the conduction band is given by

$$n=N_c \exp\left[-\frac{|E_{fn}-E_c|}{kT}\right] \quad (4.1\text{-}1)$$

Similarly, the energetic distance from the valance band of the steady-state Fermi level for holes, E_{fp}, is given by

$$p=N_v \exp\left[-\frac{|E_{fp}-E_v|}{kT}\right] \quad (4.1\text{-}2)$$

Let the states lying between the steady-state Fermi level for holes and the valance band be trapping states for holes. And let the states lying between the two steady-state Fermi levels be recombination centers. Figure 4.1-1 shows the location of the steady-state Fermi levels at a low and an intermediate level of excitation. In Figure 4.1-1a the states labelled I are recombination centers and those labelled II are traps. In Figure 4.1-1b, at a higher level of excitation, both states I and II are embraced by the steady-state Fermi levels and hence both groups of states make up the complement of recombination centers.

What has happened is that an increase in the level of excitation has brought the II states into the category of recombination centers. In brief, the photoconductor has been "doped" electronically (i.e., by increase of the level of excitation) with the II states just as effectively as if one had gone through the process of physically or chemically incorporating them in the host crystal.

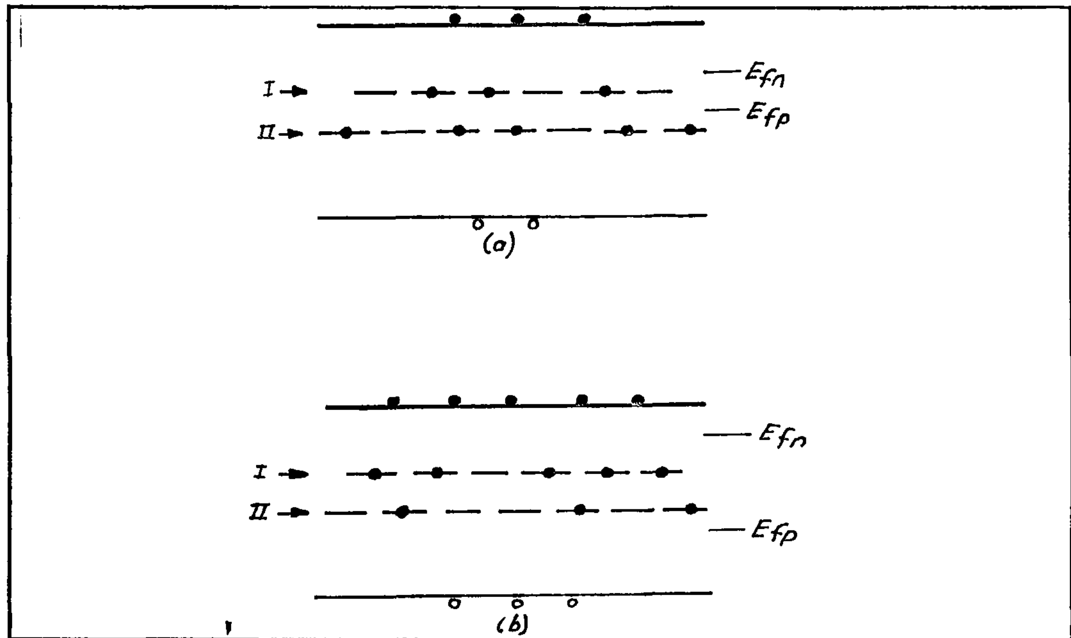

Figure 4.1.1 Electron doping (a) at a low level of excitation and (b) at an intermediate level of excitation.

"Electronic Doping" is a powerful concept because the II states may be chosen arbitrarily. Their capture cross sections for free carriers may be chosen to sensitize or desensitize the photoconductor when they are electronically added to the group of recombination centers. Hence, one has a simple and wide-ranging mechanism to account for the dependence of photocurrent (i.e., lifetime) on light intensity.

We will make use of this concept to account for current-light curves having an odd power dependence, for the surprising phenomenon of supralinearity, and for the less surprising phenomenon of sublinearity. This concept is interested in the demarcation between trapping states and recombination centers which are explained in the chapter 2.

4.2 Growth of Photoconductivity

There are some particular effects connected with the very slow growth of photoconductivity found under suitable circumstances. A very slow growth of photoconductivity following the beginning of a low intensity excitation can follow directly as the result of trapping. If there is a high density of empty trap centers for the majority carriers, almost every carrier initially excited will be almost immediately trapped and considerable time may be required before the steady-state Fermi level has been raised sufficiently as a result of the excitation, to support an appreciable free carrier density.

Slow growth of photoconductivity is especially prevalent in materials for which sensitization by the incorporation of impurities, as discussed in section 4.1, is a prominent characteristic of the photoconductivity. Although some of the features of the slow growth are consistent with the majority-carrier trapping, picture seem more in keeping with considering the sensitivity of the crystal to increase with time, as the hole demarcation level moves down and includes a portion of the sensitizing centers.

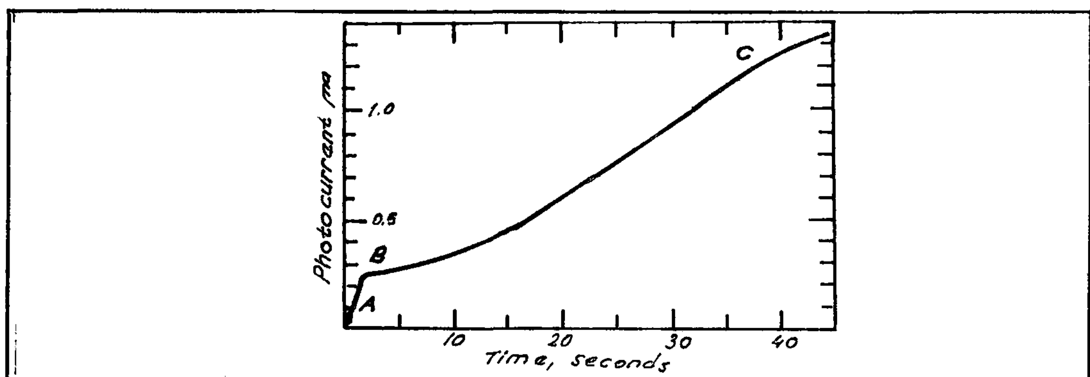

Figure 4.2-1 Rise of photoconductivity in a crystal.

Figure 4.2-1 shows a theoretical curve for a crystal at room temperature. Analysis of the data shows that the rapid rise between A and B occurs as the hole demarcation level moves down from considerably above the sensitizing levels in the crystal (photoconductors) to near these levels. From B to C occurs as more and more of the sensitizing-type centers are converted from trapping centers to recombination centers II. The slow growth, according to this viewpoint, corresponds to the time required for readjustment of empty and filled levels in the forbidden gap, holes becoming located at sensitizing centers with small recombination cross section, and electrons becoming located at centers with large recombination cross section up to fulling these centers. The increase in growth time caused by a long period in the dark before excitation, results, according to this view point,not from the thermal freeing of electrons from deep electron traps so much as from the thermal freeing of holes from deep hole traps, (the sensitizing centers).

4.3 Sensitization by Impurity Incorporation

In the previous section we have mentioned how increased photosensitivity in many materials is associated with the presence of compensated acceptors. These acceptors are negatively charged, so that they have a much larger cross section for the capture of free holes than they have subsequently for the capture of free electrons. We shall now consider this sensitization process in a little more detail. It is convenient to discuss the mechanism of sensitization prior to that of supralinearity, latter concept follows readily in terms of "electron doping."

Pure insulators (or semiconductors at low temperature) have in general a low sensitivity. The effect of incorporating donor and acceptor impurities in a material of II-VI type, for example, is shown in Figure 4.3-1. With

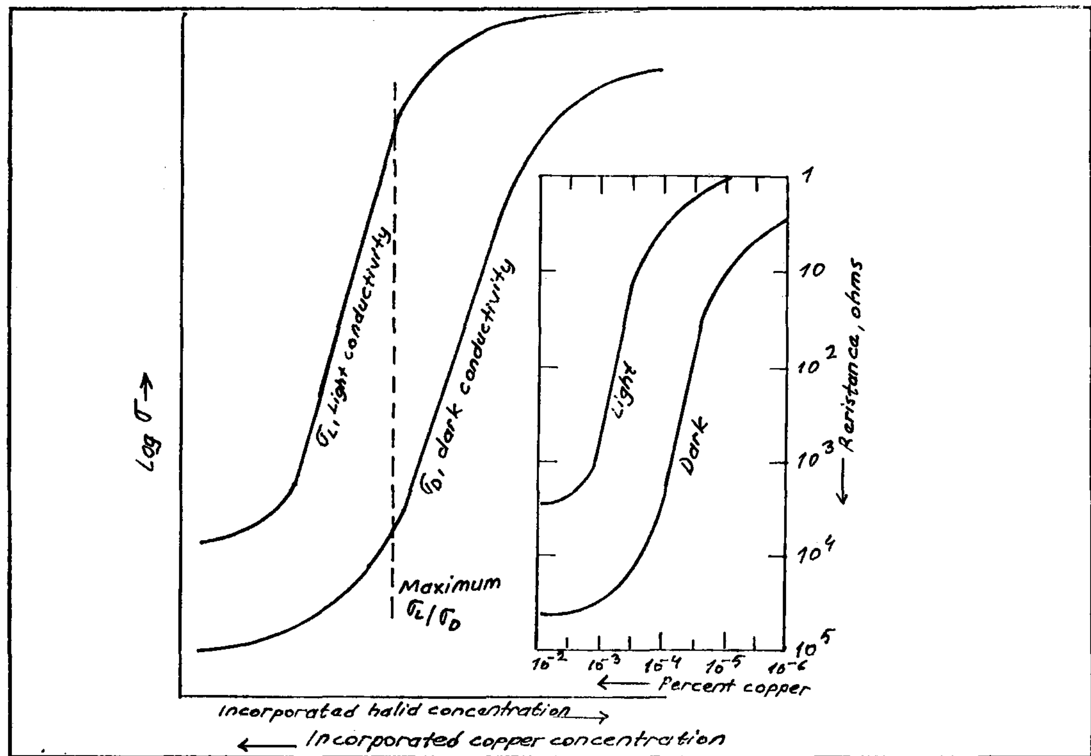

Figure 4.3-1 Light conductivity and dark conductivity as functions of impurity concentration.

increasing proportion of halide donor incorporated, both the dark conductivity and the light conductivity increase as shown. There is a certain proportion of incorporated donors for which the ratio of light conductivity to dark conductivity is a maximum. Incorporating copper acceptors reverses the effect of the donors and cause a decrease in light and dark conductivity along the same curves. In many preparation techniques it is most convenient to prepare highly conducting material first, with a high donor concentration, and then to compensate back to the optimum light/dark point by incorporating acceptors. The onset in Figure 4.3-1 shows actual data on the effect of incorporating copper acceptors in initially highly conducting evaporated layers of CdS. In this case the donors are not halide impurities, but rather excess cadmium (either interstitial cadmium atoms, or anion vacancies) naturally produced during the evaporation process. In order to

before the light conductivity starts to decrease.

Experimentally, a relatively pure crystal of CdS is found to have electron and hole lifetimes in the range of 10^{-6} to 10^{-8} sec. Such a crystal is regarded as an insensitive photoconductor. It can be converted into a sensitive photoconductor by addition of the localized states formed by cadmium vacancies which is explained in below. The electron lifetime is then in the range of 10^{-2} to 10^{-3} sec, and the hole lifetime shorter than 10^{-8} sec. The crystal has been sensitized by the addition of recombination centers. The addition of recombination centers has increased the lifetime of one sign of carrier and decreased the lifetime of the other sign of carrier. The increase in lifetime by addition of recombination centers is contrary to the intuitive expectations, namely, that more recombination centers mean shorter lifetimes.

The intuitive expectation is borne out in semiconductors in which electron and hole lifetimes are equal. There, the only means for increasing the common lifetime of free pairs is to remove recombination centers. Similarly, in photoconductors in which electron and hole lifetimes are not equal, the addition of recombination centers of the same kind as those already present (assuming only one kind to be present) can only decrease the lifetimes of one or both carriers and cannot increase them. The remnant possibility is that the addition of recombination centers of a second kind can increase the lifetime of one sign of carrier. This is the model for sensitization.

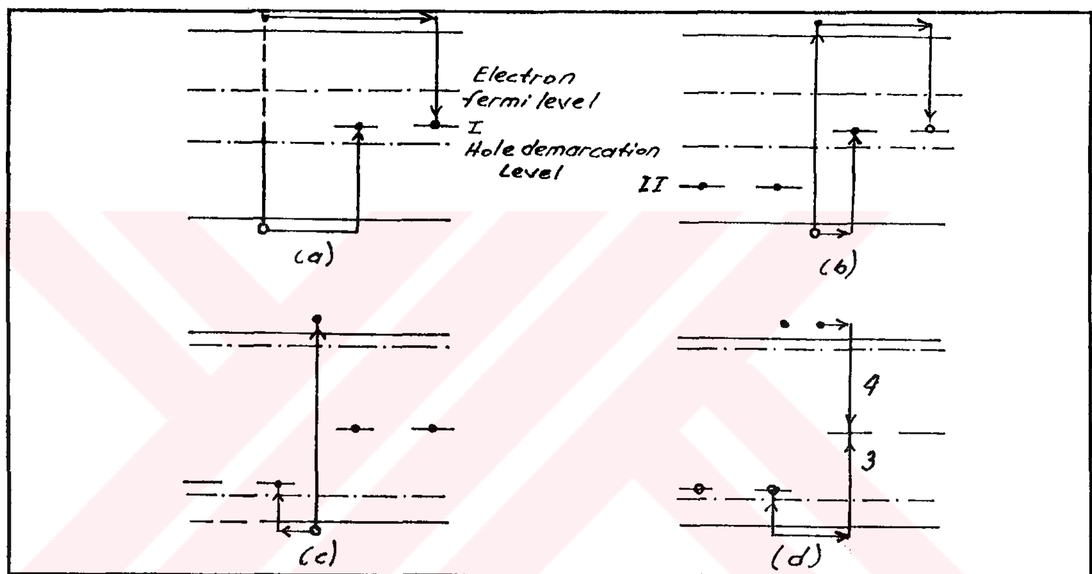

Figure 4.3-2 (a) Excitation and recombination processes in photoconductor with only type-I fast recombination centers; (b) excitation and recombination at high temperatures and/or low-light intensities for photoconductor with type-I centers and also type-II sensitizing centers; (c) excitation and recombination processes in photoconductor with both type-I and type-II centers, at low temperatures and/or high-light intensities; (d) infrared quenching transition for sensitized photoconductor.

Energy-level represantation of the sensitization process is shown in Figure 4.3-2. In an unsensitized material (Figure 4.3-2a) there are present recombination centers I of such a type as to produce a small free lifetime for photoexcited carriers. The identity of these centers is at the present time still largely unknown. We consider now the effects of adding compensated acceptor centers II. For low light levels and/or high temperatures such that the hole demarcation level for the II centers lies above the II levels, there is effectively no change in the sensitivity (Fig.4.3-2b). But for high light levels and/or low temperatures, such that the hole demarcation level lies below the II levels, the presence of the II centers has a sensitizing effect. This comes about in the following way: (1)Holes captured by the II centers have a longer life there before recombination than holes captured by I centers, because of the small cross section of II centers containing holes for capturing free electrons; (2) the II centers become occupied principally by holes, therefore, and, if the concentration of I and II centers is much larger than the density of free carriers, this means that the electrons initially in II centers are effectively transferred to I centers; (3) the lifetime of a free electron is increased because it now faces mainly centers with a small capture cross section and only few centers with a large capture cross section. If the concentration of I and II centers is not much larger than the density of free carriers, the incorporation of II centers provides effectively only additional recombination centers, and no sensitization result.

Figure 4.3-3a shows a photoconductor having one kind or class of recombination centers whose capture cross section for both electrons and holes is 10^{-15} cm^2. In general, electron and hole capture cross sections will be different. For simplicity of discussion we take them to be equal, without affecting the principle of the argument.

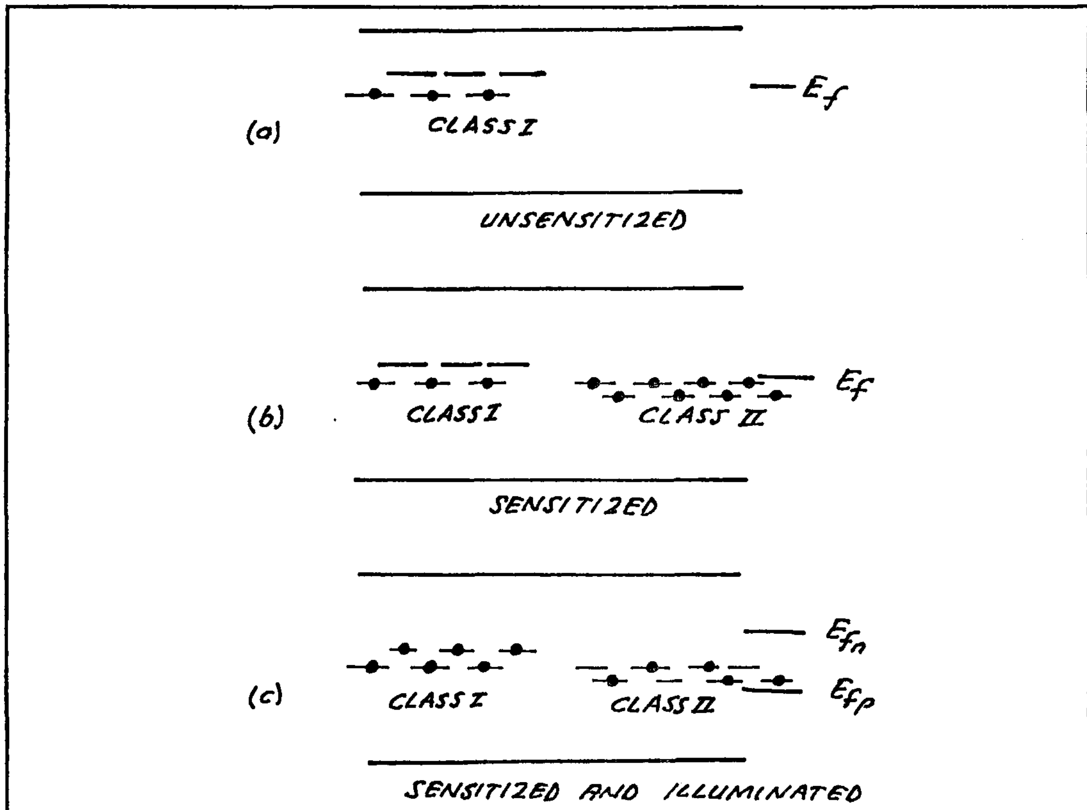

Figure 4.3-3 Schematic outline of sensitization.

Similarly, we take the densities of electron-occupied and hole-occupied centers to have the same value, $10^{15}/cm^3$. The principle of the model does not require this equality. Both electron and hole lifetimes will then have the rather "insensitive" value of

$$\tau_n=\tau_p=(vs_{n1}p_{r1})^{-1}=10^{-7}\ldots\ldots\text{sec} \qquad \textbf{(4.3-1)}$$

In figure 4.3-3b we have added $10^{16}/cm^3$ impurity states all filled with electrons and having a very small capture cross section for electrons, 10^{-20} cm^2, and a somewhat normal cross section for holes, 10^{-15} cm^2. In figure 4.3-3c we show the redistribution of electrons and holes that takes place among the recombination centers under illumination. Under illumination the following steady-state condition must be rigorously satisfied. This is the condition that the rate

at which free electrons pour into recombination centers (individually or collectively) must be precisely equal to the rate at which free holes pour in

$$np_{r1}vs_{n1}=pn_{r1}vs_{p1} \quad (4.3\text{-}2)$$

$$np_{r2}vs_{n2}=pn_{r2}vs_{p2} \quad (4.3\text{-}3)$$

or

$$\frac{p_{r1}s_{n1}}{n_{r1}s_{p1}}=\frac{p_{r2}s_{n2}}{n_{r2}s_{p2}}=\frac{p}{n} \quad (4.3\text{-}4)$$

In addition to, the particle conservation conditions are

$$n_{r1}+p_{r1}=N_{r1} \quad (4.3\text{-}5)$$

$$n_{r2}+p_{r2}=N_{r2} \quad (4.3\text{-}6)$$

Equation (4.3-4) becomes, for $s_{n1}=s_{p1}$,

$$p_{r1}=\frac{p_{r2}n_{r1}}{n_{r2}}\frac{s_{n2}}{s_{p2}} \quad (4.3\text{-}7)$$

We know that there will be a strong tendency to shift electrons from the N_{r2} states to the N_{r1} states, since free holes tend to accumulate in the N_{r2} states owing to the small capture cross section of these states for electrons.

$$n_{r1}\rightarrow N_{r1} \quad (4.3\text{-}8)$$

$$p_{r2}\rightarrow N_{r1} \quad (4.3\text{-}9)$$

With these approximation, equation (4.3-7) becomes

$$p_{r1}=N_{r1}\frac{N_{r1}}{N_{r2}}\frac{s_{n2}}{s_{p2}} \qquad (4.3\text{-}10)$$

Our assumptions that $N_{r1}/N_{r2} = 10^{-1}$ and $s_{n2}/s_{p2} = 10^{-5}$ then give

$$p_{r1}=10^{-6}N_{r1} \qquad (4.3\text{-}11)$$

The total rate at which electrons fall into the p_{r1} and p_{r2} states is

$$\frac{n}{\tau_n}=np_{r1}vs_{n1}+np_{r2}vs_{n2} \qquad (4.3\text{-}12)$$

from which

$$\tau_n=\frac{1}{N_{r1}vs_{n2}}=10^{-2}\text{sec} \qquad (4.3\text{-}13)$$

since $10^{-6}\ s_{n1} = 10^{-1}\ s_{n2}$.

We see by comparing equations (4.3-1) and (4.3-13) that the electron lifetime has been increased from 10^{-7} to 10^{-2} sec and the photoconductor sensitized by the same factor. Meantime, the hole lifetime has been decreased from 10^{-7} to 10^{-8} sec, owing to the addition of the N_{r2} states. The sensitization has come about by a redistribution of electrons and holes between the two classes of recombination centers. In a sense, the electron recombination traffic through the N_{r1} states has been snuffed out by filling the p_{r1} states with electrons from the n_{r2} states. The holes that were in the N_{r1} states and had a large cross section for electrons have now been shifted to the N_{r2} states where their capture cross section is smaller by five powers of ten.

In the illustration chosen here, about 90 % of the recombination traffic passes through the N_{r2} states since 90 % of holes go to these states. If s_{p2} had been chosen to be 10^{-17} cm^2 instead of 10^{-15} cm^2, the photoconductor sensitized by a large factor 10^4, but now only 10 % of the hole recombination traffic would pass through the N_{r2} states. If the density of N_{r2} states were considerably less than that of the N_{r1} states, they would have little effect on the sensitivity since no significant transfer of electrons from N_{r2} to N_{r1} could occur.

The other name for the recombination centers is sensitizing centers which lie at the Fermi level and exceed the number of electrons in the trapping states. If we wish to double the free-electron density by injection of space charge, we must also fill most of the empty recombination centers since a doubling of the free-electron density means that the Fermi level is raised by approximately kT. Hence, space-charge currents will not set until the applied voltage is sufficient to fill these recombination centers, that is, until

$$VC=\wp_r e \qquad (4.3\text{-}14)$$

where V is the voltage across the electrodes in the given photoconductor, C is the capacitance between the electrodes, $\wp_r$ is Hole-occupied total recombination centers in per unit cm^3 volume of the given photoconductor. This section will be explained in details at the last section of this thesis.

Finally, three characteristics of photosensitivity resulting from such a process follow directly from the considerations of Figure 4.3-2. (1) When the hole demarcation level is lowered through the II levels by increasing light intensity at fixed temperature, the sensitivity increases with light intensity, and therefore the measured photocurrent varies with a power of light

intensity greater than unity. (2) When the hole demarcation level is raised through the II levels by increasing temperature at fixed light intensity, the sensitivity decreases with temperature, i.e., temperature quenching of photoconductivity occurs. (3) If electrons are optically excited from the valance band to II levels occupied by holes (Figure 4.3-2d), the holes are freed and may be captured by I centers, thus reversing the sensitizing process, i.e., optical quenching of photoconductivity occurs.

4.4 Supralinearity

It is frequently found that the photocurrent increases as some high power (e.g., 3 to 5) of the light intensity over a short range of light intensities. Before and after transition, the photocurrent may vary approximately linearly with light intensity. Figure 4.4-1 shows a set of current-

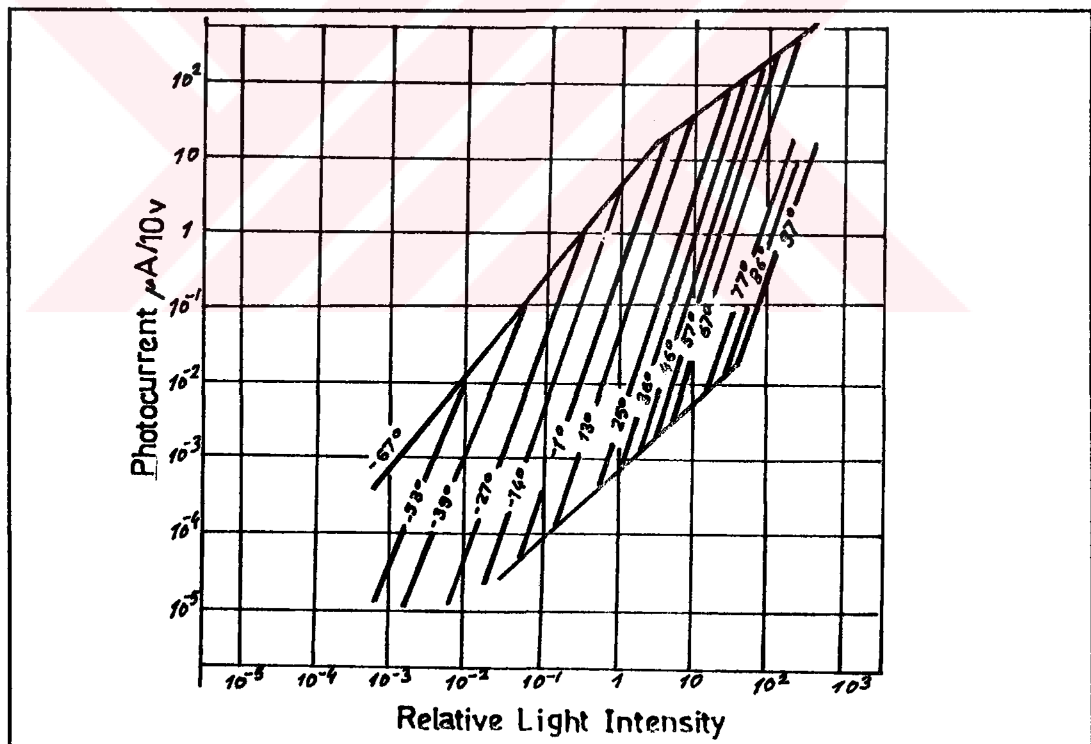

Figure 4.4-1 Data on supralinearity in CdS(R.H.Bube)

light curves obtained by R.H.Bube for CdS over a range of temperatures. The logarithmic shift of the sharp transition along the light intensity axis is approximately proportional to absolute temperature . The increase of photocurrent as a high power of the light intensity is called supralinearity.

Supralinearity is a particularly striking effect since most of the changes that one would except to occur at higher light intensities lead to sublinearity. Moreover, the supralinearity that is experimentally observed can occur at a relatively low light level where saturation of recombination centers is not likely to take place. Even so, most saturation effects also lead to sublinearity. In brief, the problem of accounting for supralinearity is not the usual one of choosing between a number of equally reasonable models but of finding even one model.

The model for supralinearity shown in Figure 4.4-2 follows easily from the two concepts: sensitization (Section 4.3) and "electron doping" (Section 4.1). In Figure 4.4-2a we show a photoconductor under low illumination such that

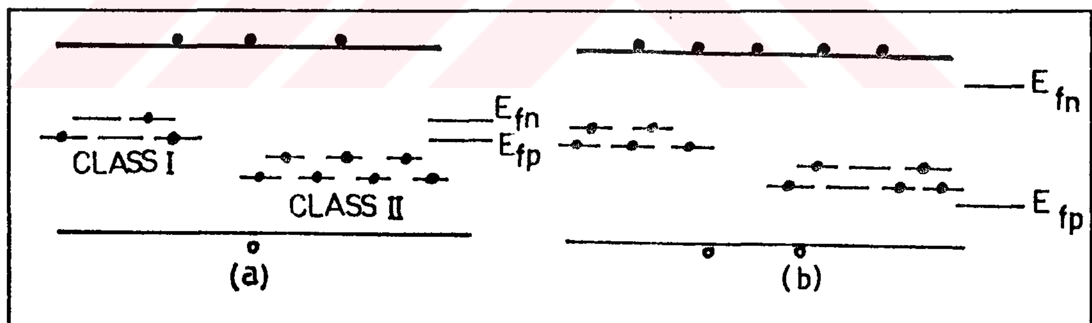

Figure 4.4-2 Schematic model for supralinearity. (a) Low level of excitation. (b) Intermediate level of excitation.

the two steady-state Fermi level embrace a set of recombination centers called class I states. These states have about equal capture cross section for electrons and

holes, i.e., 10^{-15} cm^2. If the density of these states is $10^{15}/cm^3$, the electron and hole lifetimes will be about 10^{-7} sec, as in the previous section. A second set of levels, class II states (sensitizing centers), is located below and outside the two steady-state Fermi levels sufficiently removed to qualify as hole traps rather than as recombination centers I. For the class II states the capture cross section for electrons is 10^{-20} cm^2 and for holes 10^{-15} cm^2.The density of the class II states is much less than the class I states.

Figure 4.4-2b shows that at some higher light intensity the steady-state Fermi levels have moved apart sufficiently to embrace the class II states as well as the class I states, so that there are now two sets of recombination centers just as in the sensitizing section. The result of incorporating the class II states in the category of recombination centers is to sensitize the photoconductor, that is, to increase the electron lifetime by some five powers of ten. This is an example of sensitization by "electron doping." While the class II states are being converted into recombination centers, the electron lifetime is continuously increasing and the photocurrent increases supralinearly with increasing light intensity. After full conversion, the photocurrent again increases linearly with light intensity.

A strict treatment of the transition of class II states from traps to recombination centers should take into account the demarcation levels, a separate set for each class of states.

4.5 Infrared and Thermal Quenching

A frequent observation is that a given photocurrent excited by light in the visible part of the spectrum can be considerably reduced or "quenched" by the addition of

infrared light. This is particularly true for the more sensitive photoconductors, CdS and Se are prominent example.

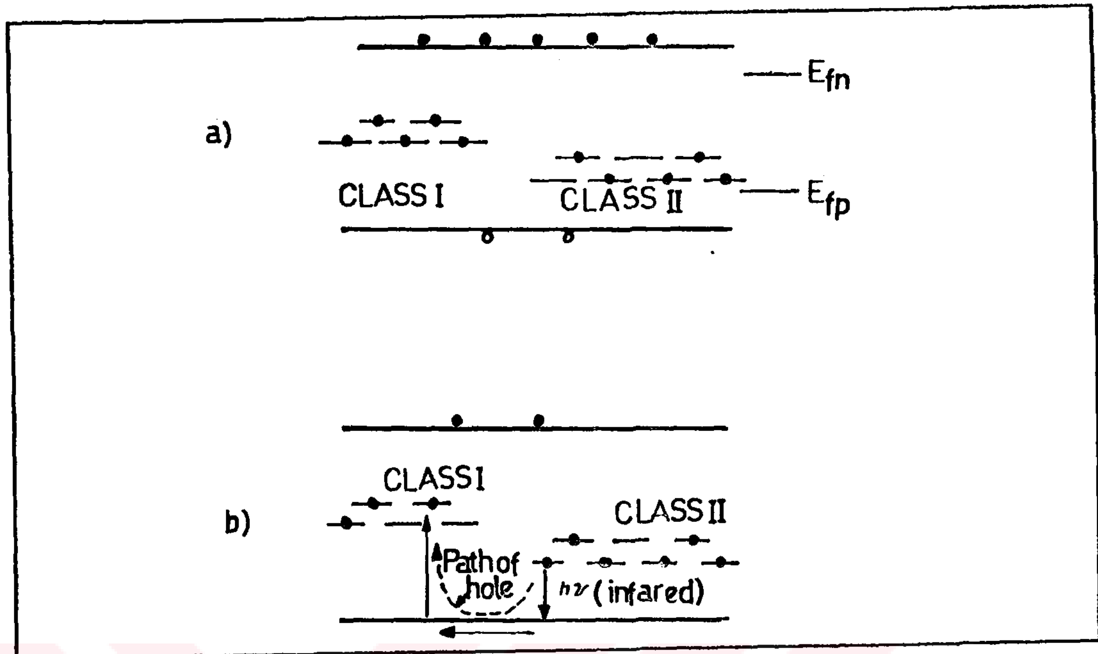

Figure 4.5-1 Model for infrared quenching. (a) Supralinear photoconductor illuminated with strongly absorbed light. (b) Addition of infrared light to (a).

The model for this effect (Figure 4.5-1) is the same as the model for supralinearity discussed in the previous section. Suppose that a supralinear photoconductor has been illuminated so that it has passed the supralinear transition and is now in the sensitive state. This means that the sensitizing class II states have been converted from traps to recombination centers. An increase in temperature at fixed light intensity will cause the photoconductor to revert to the insensitive state by shifting the steady-state Fermi levels farther from the band edges so that the sensitizing states become traps instead of recombination centers. This phenomenon is known as temperature quenching.

In place of heating the entire photoconductor, one can think of "heating" the sensitizing centers (class II states) selectively. This is accomplished by using infrared light that is selectively absorbed by the class II states. Electrons are thereby excited from the valance band into the class II states and the resultant free holes are captured by the class I (or insensitive) states. Since the process of sensitization had shifted holes from class I to class II states, this is the reverse process or one of desensitization. The infrared may be regarded as coupling the class II states closer to the valance band just as would occur with an increase in lattice temperature.

This model of infrared quenching can be used to define the energy interval between the class II states and the valance band. These data can also be consistent with the same energy interval from thermal quenching.

The decay of photocurrent after the cessation of excitation in any photoconducting materials, with trapping centers, large-cross-section recombination centers, and small-cross-section recombination centers, can be analyzed into the following components, listed in the order of decreasing decay rate.

(1) Direct recombination of free electrons with holes in large-cross-section recombination centers, without any trapping process involved.

(2) Emptying of shallow traps, the freed electrons recombining with holes in the large-cross-section centers.

(3) Transfer of holes from small-capture cross-section centers to large-capture cross-section centers.

(4) Emptying of deep traps.

The importance of each of these components in a measure of decay curve will depend strongly on the light intensity used. For very high light intensities, for which the density of free electrons is much larger than the density of trapped

electrons, the measured decay time will be equal to the lifetime as determined by component 1. For very low light intensities, the measured decay time will be determined almost completely by the faster of the (3) components alone.

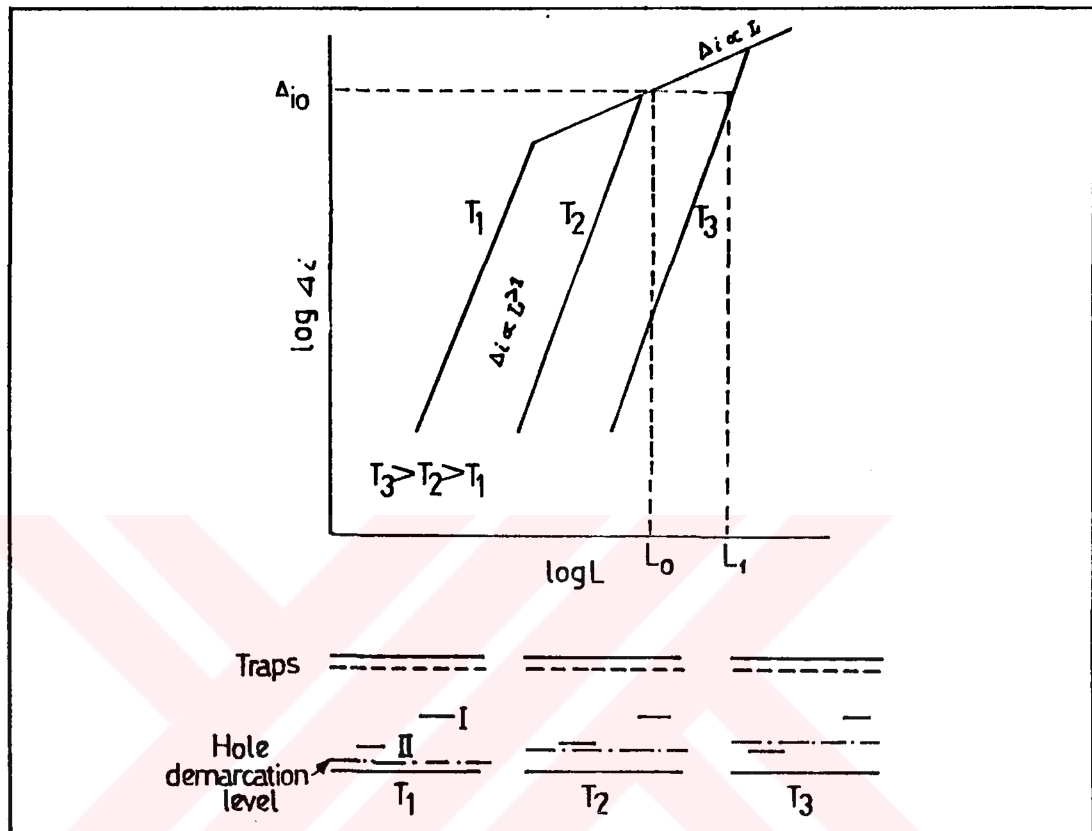

Figure 4.5-2 Typical variation of photocurrent with light intensity in the range in which the hole demarcation level passes through the sensitizing center level.

Consider the variation of photocurrent with light intensity shown in Figure 4.5-2 for the three different temperatures in such a material. The break from $\Delta i \propto L$ to $\Delta i \propto L^{>1}$ occurs when the hole demarcation level is at the small-cross-section levels II. At temperature T_1, a certain sensitivity $S_0 \propto \Delta i_0/L_0$ is obtained for a high light intensity L_0 giving a photocurrent Δi_0. In the steady-state condition under excitation, the hole demarcation level is well below the II levels. At the cessation of excitation,

the emptying of electron traps proceeds at a faster rate than the transfer of holes from II centers to large-cross-section I centers. Thus a slow decay is found, with component (3b) above dominant. At a temperature T_2, the same sensitivity S_0 is found, but now the hole demarcation level is just at, or just slightly below, the II levels in the steady state. At the cessation of excitation, thermal freeing of holes from the II centers takes place as well as thermal freeing of electrons from traps, and the thermal freeing of holes can be the rate-determining process. The effect of the transfer of holes from II centers to I centers during the course of the decay can be considered as a decreased in the lifetime of a free electrons as a function of time during the decay. This means that the decay will be more rapid than the decay determined by trap emptying alone. If there are p_{II} holes in II centers, lying E_{II} above the top of the valance band, and if there are n_t electrons in traps, lying E_t below the bottom of the conduction band, the condition for the rate of thermal release of holes from II centers to exceed the rate of thermal release of electrons from traps is

$$\frac{p_{II}S_{II}}{n_t S_t} > \exp\left(-\frac{E_t - E_{II}}{kT}\right) \qquad (4.5\text{-}1)$$

where S_{II} is the capture cross section of II centers for holes, and S_t is the capture cross section of traps for electrons. At a temperature T_3, the sensitivity has decreased to $S_1 \ \alpha \ \Delta i_0/L_1$, and only a portion of the II centers is acting as recombination centers even under steady-state excitation.

Thus, the decay is faster at T_3 than at T_1 for two reasons: (1) the initial lifetime at t=0 of the decay is less because of the decrease in sensitivity with increased temperature, and (2) the lifetime decreased during the decay

as holes are transferred from II centers to I centers.

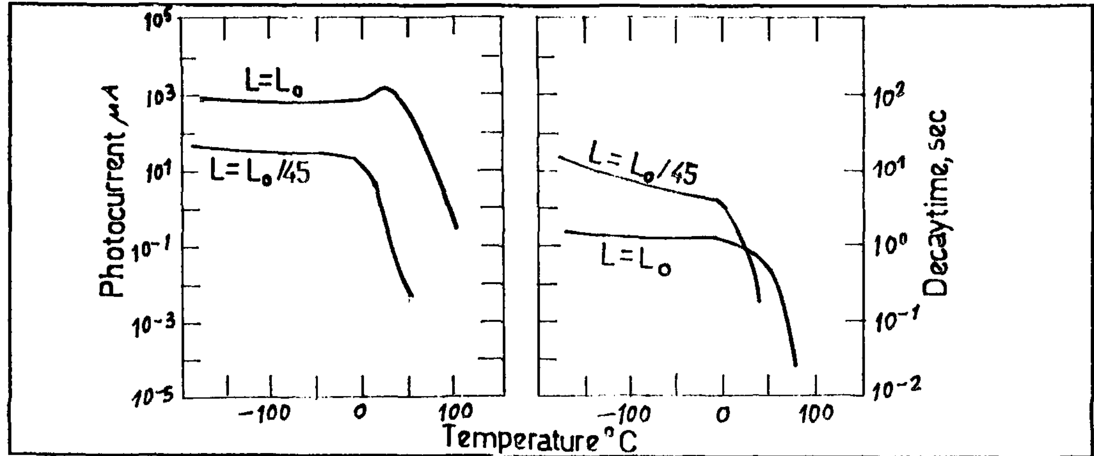

Figure 4.5-3 Temperature dependence of the photoconductivity and the decay time of a crystal for two different light intensities.

Figure 4.5-3 shows both the variation of photocurrent and of decay time with temperature for a crystal, for two different light intensities. The temperature for which temperature quenching of photoconductivity sets in, like the break from $\Delta i \; \alpha$ L to $\Delta i \; \alpha \; L^{>1}$ in Figure 4.5-2, marks the condition that the hole demarcation level is at the II levels. This condition occurs at a lower temperature, the lower the light intensity. As indicated in Figure 4.5-3, the measured decay time has approximately the same temperature dependence as the photocurrent, the decay time becoming actually shorter over a certain temperature range for the lower light intensity, because of the lower temperature at which freeing of holes from the II centers sets in at the lower light intensity.

4.6 Space-Charge-Limited Current with Ohmic Contacts

Measurements of the variation of space-charge-limited current injected into a crystal through an ohmic contact, as a function of the electric field applied to the crystal,

can also be used to give an indication of the total trap density, trap distribution with energy, and hence the actual location of fairly monoenergetic trapping levels.

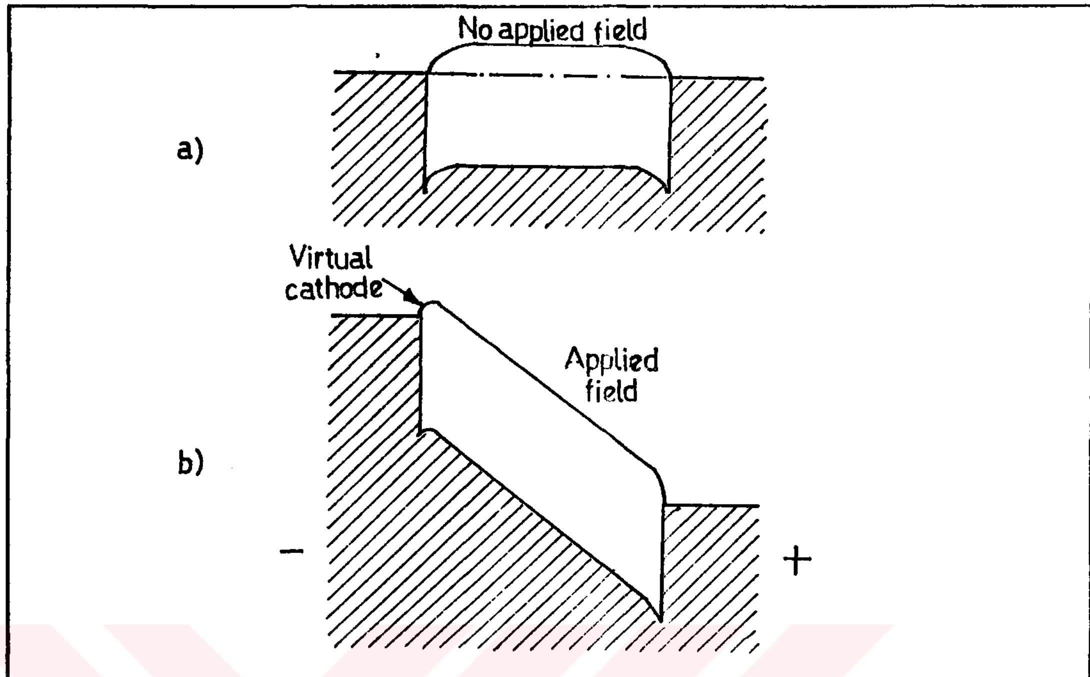

Figure 4.6-1 Energy-levels diagrams for a material with ohmic contacts, (a)in the absence of an applied field, and (b)in the presence of an applied field.

Figure 4.6-1 shows typical energy -band diagrams for an insulator or semiconductor with ohmic contacts. When an external field is applied, a virtual cathode is formed, a reservoir of electrons being present in the material, available for use as needed to replenish charge. If, however, the field is large enough, electrons will be injected into the bulk of the material to form a current which will be limited by space-charge considerations. A simple consideration of the magnitude of this current for a trap-free material shows that such space-charge-limited current can be quite large.

The observation of space-charge-limited current would seem most probable in an insulator (so that the intrinsic

material conductivity is much less than the space-charge-limited current) prepared with ohmic contacts. In this case, the measured current which increased with increasing applied voltage. These currents were interpreted to be space-charge-limited current, and the variation of current with voltage according to a power greater than 2 was attributed to the effects of traps. The existence of such space-charge-limited current is of basic importance for the determination of the maximum gain of a simple photoconductor with ohmic contacts.

If the voltage is increased, there is a sudden increase in the density of free electrons injected from the cathode. In time, however, most of these electrons are captured in traps. Finally a steady-state is set up, so that the rate of thermal excitation of electrons out of traps is equal to the rate of capture of free electrons by traps, i.e., the Fermi level is raised to a new position consistent with a higher density of free electrons. Most of the injected electrons are trapped, thus making the observed space-charge-limited current much smaller than they would be in a trap-free solid. For every kT that the Fermi level is raised, the density of free carriers increases by a factor of e, so that a rapid dependence of current on voltage is expected.

It remains to explore the effect of deep traps (i.e., below the Fermi level) and of recombination centers. The effect of deep traps is shown schematically in Figure 4.6-2. Here we have applied in the dark, sufficient voltage to raise the Fermi level from its dark value E_f to a higher steady-state value, E_{fn}.

With the gain of a simple photoconductor with ohmic contacts as defined previously,

$$G=\frac{\tau\mu V}{L^2} \qquad (4.6\text{-}1)$$

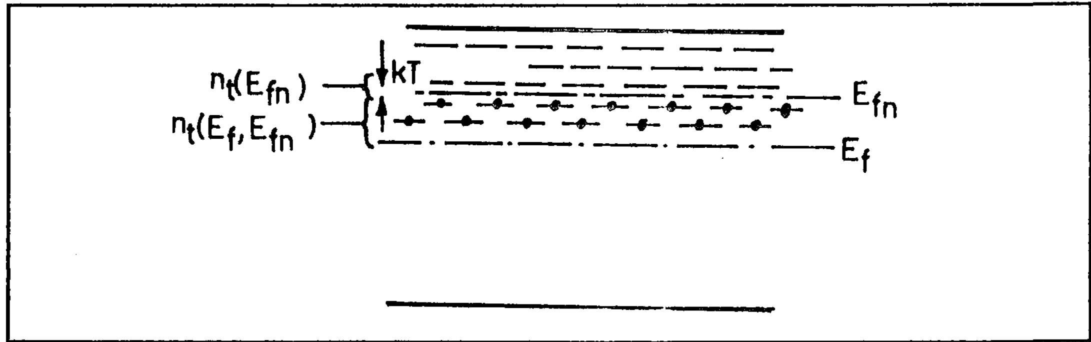

Figure 4.6-2 Definition of $n_t(E_f, E_{fn})$ and $n_t(E_f)$.

it might appear at first glance that the gain obtainable experimentally is unlimited, any desired gain being achievable by increasing V or decreasing L sufficiently. In practice, however, Rose has shown that a maximum gain is set by the fact that space-charge-limited current comparable in size to the photocurrents being measured being to flow when the applied field becomes high enough.

For photocurrents approximately equal in magnitude to the dark current, maximum gain will be obtained for a voltage given by

$$V_{max}C=e(n_t)_{kT}LA \tag{4.6-2}$$

where C is the total capacitance of the crystal, $(n_t)_k$ is the density of traps or recombination centers under the applying of voltages in the forbidden gap a kT wide portion at the dark condition, L is the interelectrode spacing, and A is the cross-section area and V_{max} is applied maximum voltages to the crystal.

4.7 Determination of Band Gaps

The values of the band gaps of insulators and semiconductors are commonly measured by one of six simple methods. These depend on the temperature dependence of the free-carrier density, the variation of absorption, photoconductivity excitation, and luminescence excitation as a function of wavelength, or the wavelength dependence of the emitted luminescence radiation resulting from recombination of free electrons and free holes.

(1) Temperature dependence of the conductivity in an intrinsic material, or in a temperature range in which intrinsic conductivity dominates.

(2) Temperature dependence of the Hall constant R in an intrinsic material, or in a temperature range in which intrinsic conductivity dominates.

These are two different ways of measuring the variation of the free-carrier density with temperature. When the conductivity is measured, the temperature dependence of the mobility introduces a further complexity. The Hall constant is simply proportional to 1/n and we may consider

$$n = A(T)\exp\left(-\frac{E_G}{2kT}\right) \qquad \textbf{(4.7-1)}$$

$$\frac{1}{R} = A^*(T)\exp\left(-\frac{E_G}{2kT}\right) \qquad \textbf{(4.7-2)}$$

In the simplest case, $A(T)=AT^{3/2}$ and $A^*(T)=A^*T^{3/2}$, where A and A^* are independent of temperature. If the temperature dependence of the mobility in the intrinsic range can be expressed $\mu \propto T^{-a}$, then a plot of $\ln(\sigma T^{a-3/2})$ or a plot of $\ln(1/RT^{3/2})$ as a function of 1/T gives a straight line, from the slope of which the value of E_G can be obtained. If E_G is

a linear function of T, i.e., if $E_G=E_{G0}+\beta T$, the value obtained from such slopes is E_{G0}. Of course if the absolute values of A(T) and $A^*(T)$ are known in terms of the effective density of states and the effective mass of the free carriers, a value for E_G can be obtained from each measurement of n or R at a given T.

(3) Variation of absorption as a function of wavelenght. The analysis of absorption spectra, both for direct and for indirect transition, can give values for the energy gap.

(4) Variation of photoconductivity excitation with wavelength.

(5) Variation of luminescence excitation with wavelength.

Methods 4 and 5 are two alternate ways of detecting absorption. Method 4 through the current (or voltage) caused by the free carriers created as the result of absorption, and Method 5 through the luminescence emitted when free carriers created by the absorption recombine radiatively. It is common for spectral response curves of photoconductivity and luminescence to show a fairly sharp maximum at a wavelenth slightly longer than that corresponding to the absorption edge. For wavelengths longer than the maximum, the excitation decreases simply because the absorption producing free carriers are decreasing. For wavelengths shorter than the maximum, the radiation is being strongly absorbed and produces excitation only near the surface of the crystal.

(6) Variation of luminescence emission with wavelengths, resulting from the recombination of free electrons and free holes. When the recombination of free electrons and free holes can be observed through a radiative transition, the maximum of the emission spectrum corresponds to the band gap.

It is clear that we cannot show all the absorption and excitation spectra characteristic of materials of interest for a discussion of photoconductivity. A few typical

examples of photoconductivity excitation spectra are shown in Figure 4.7-1

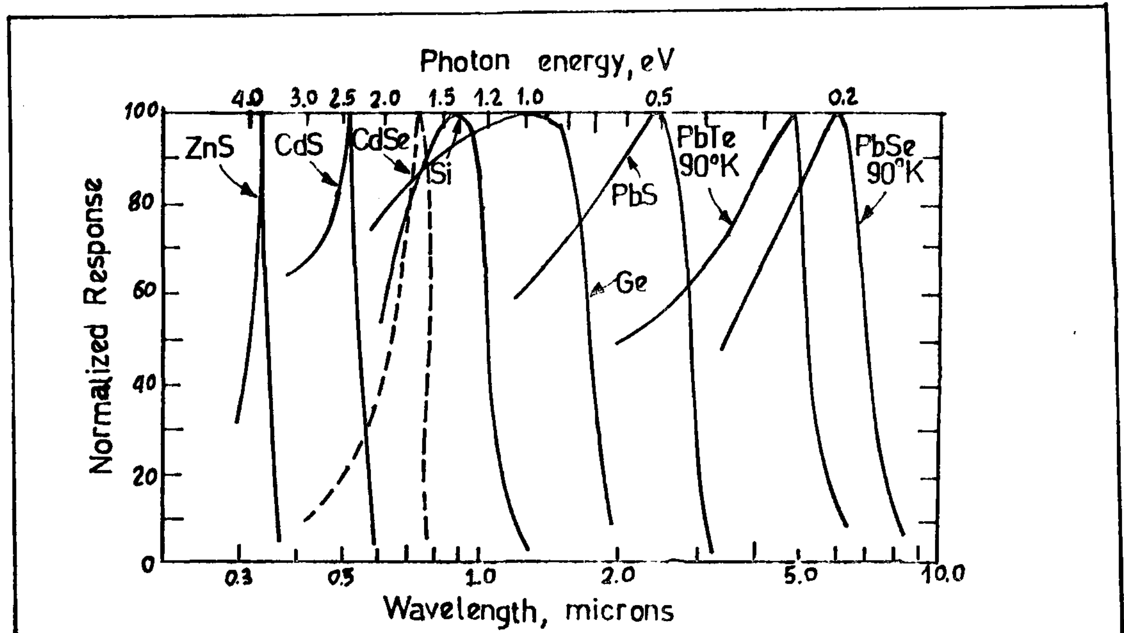

Figure 4.7-1 Photoconductivity response curves as a function of wavelength for a number of typical photoconductors.

The values of energy levels of sensitizing centers in the forbidden gap are determined by means of smaller peaks in the photoconductivity excitation spectra.

CHAPTER 5

EXPERIMENTAL SECTION

A perfect crystalline material has no energy states in its forbidden gap. But in real semiconductors or insulators there are always some imperfections associated with impurities or native crystallographic defects. In general, the exact nature of these centers is not well known and it is usual to classify them in terms of their observed behaviour. i.e., as donor or acceptor levels, recombination centers and sensitizing centers, majority or minority traps, etc.

Recombination centers can also be classified into two groups: class I and class II centers which are explained in detail in the previous chapters. Class I centers have large capture cross sections for both electrons and holes, while class II centers have small capture cross sections for electrons and have large capture cross sections for holes. The ratio of hole and electron capture cross sections for class II centers may be several orders of magnitude in which case the electron lifetime will be much longer than that of holes and the photosensitivity will be increased. Class II centers are also known as sensitizing centers and they are responsible for the photoconductivity.

In this study, the density of sensitizing centers in different type of photoconductors such as Selenium (Se) and ZnS will be investigated by using CV (Capacitance-Voltage)

junction capacitance technique and space charge limited current method. In addition to these methods, the density of sensitizing centers can be found by using thermally stimulated current method. In this method, the photoconductor must be investigated at low temperatures, for example, for semiconductor type photoconductors at 100^0K to 200^0K and for insulator type photoconductors at 150^0K to 300^0K. Because of the laboratory facilities are not available at the moment, thus this technique have not used, therefore we determine the density of sensitizing centers only by the other two techniques.

5.1 CV (Capacitance-Voltage) Method

The density of sensitizing centers can be found very easily by using CV methods. For this method, some electronic and photoconductive properties must be known. Some of these properties are explained in the previous chapters. In addition to these properties, some other properties must be also known to use C-V method.

Firstly, the photoconductor crystal growth can be obtained by using any one of the crystal growth techniques, such as evaporation techniques. These techniques are explained in the Chapter 3. In this study we used the evaporated layer method. And then for measurements, the crystal surfaces are covered with a metal (Metal-Semiconductor Contacts or Metal-Insulator Contacts). The top surface of photoconductor is covered with a metal and the bottom surface is covered with an another or same metal by using evaporation techniques. But,a small area at the center of top surface is not covered with the metal. Because of this, the light which impinges upon the surface generates electron-hole pairs. In this case, the photoconductor is like a capacitor and is shown in Figure 5.1-1.

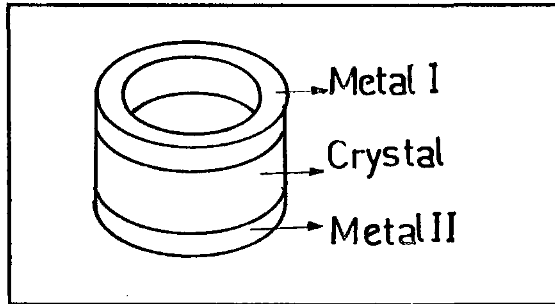

Figure 5.1-1. Representation of photoconductor like a capacitor.

If the light falls on the surface of a photoconductor, the electron-hole pairs will be generated in the valance band. These electrons gets excited and pass across the band gap of the photoconductor to move in the conduction band. The free electrons in the conduction band then go to the electrode (anode). However, the free holes are captured by means of sensitizing centers (Recombination centers II). The sensitizing centers (Recombination centers II) can capture only holes because of their small capture cross section. Thus, the holes are not exceed to the other electrode (cathode). Figure 5.1-2 shows electrons movement in the conduction band and holes captured by the sensitizing centers.

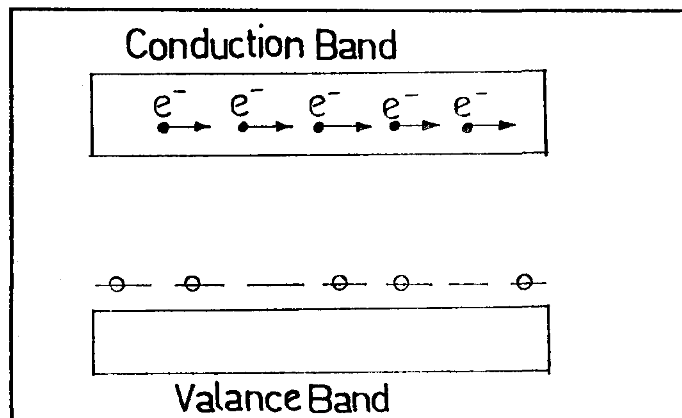

Figure 5.1-2. Representation of electron movements in the conduction band and holes captured by means of sensitizing centers in the forbidden gap.

The net charge in photoconductors is:

$$\partial n = n - p$$

where ∂n is the net charge, n is the number of free electrons and p is the number of free holes in the photoconductors. In the capacitor the voltages between the electrodes (anode and cathode) are due to this net charge. But in here, the free holes are captured by means of sensitizing centers. Thus, no free hole can reach to the cathode. Hence, the number of holes in the cathode is zero (p=0). In this case, the net charge is equal to

$$\partial n = n \qquad (5.1\text{-}2)$$

The number of electrons in the capacitor are found by its total charges, that is,

$$CV = Q = \partial n e \qquad (5.1\text{-}3)$$

where V is the voltage across the electrodes and C is the capacitance between the electrodes in capacitor, n is the number of free electrons on the electrodes per cm^3 and e is the electronic charge ($1.6*10^{-19}$ Coulomb). The same technique is used for measuring the number of sensitizing centers (Recombination centers II) in the any one photoconductor.

Secondly, we explain the exact nature of the centers in the forbidden gap in real semiconductors or insulators which of them sensitizing centers, traps and etc. and their functions in the forbidden gap. The functions of these centers are explained in detail in the previous chapters. In addition to these explanations, we see that if the light intensity is large enough, the all kind of centers in the forbidden gap are transformed from any one center such as

recombination centers I, majority and minority traps, etc., to the sensitizing centers (Recombination centers II) type. Again, this is also explained in detail in the section of previous chapters (see Chapter 4.2- 4.3). To measure the exact numbers of sensitizing centers in the photoconductors, a very large light intensity must be used. In this respect, in our experiment we used a light source (bulb) whose power is 500 Watts. Although light intensity from this light source is not enough to measure the exact number of sensitizing centers in the photoconductors (Se and ZnS) we see that density (number) of sensitizing centers are changed by the light intensity. The figures of experimental results will be represented in the last sections of this study.

When the light falls on the surface of photoconductors, the number of electrons generated are equal to the number of holes generated (n=p). If the every sensitizing center captures only one hole, then the number of sensitizing centers is equal to the number of holes. Hence, measuring number of electrons will yield the number of sensitizing centers, that is,

$$n=\rho_r \qquad (5.1\text{-}4)$$

where ρ_r is the density (number) of sensitizing centers.

Now we consider the case in which density of holes is less than the density of sensitizing centers. In this condition, all of the holes are captured by means of the sensitizing centers. This means that the number of holes captured is equal to the number of sensitizing centers. The other excess sensitizing centers do not captured holes, i.e., they are empty. These excess sensitizing centers are not measured by the experimental method. In this case, the measured density of sensitizing centers are less than its exact density. Therefore, we must use a light source with high intensity. In this case, the net charge between the electrodes are,

$$\partial n = n \tag{5.1-5}$$

and from the capacitor methods, the density of sensitizing centers are found as

$$CV = Q = \partial n e = \rho_r e \tag{5.1-6}$$

An other situation arises when the density of sensitizing centers is less than the density of holes. In this case, all of the sensitizing centers capture holes whose number is equal to the number of sensitizing centers. The other excess holes are moved in the valance band and they are exceeded to the electrode (cathode). Thus, the net charges between the electrodes are,

$$\partial n = n - p_1 \tag{5.1-7}$$

where p_1 is the free holes in the photoconductor. Again, in this condition, from the capacitor method the density of sensitizing centers are equal to,

$$CV = Q = \partial n e = \rho_r e \tag{5.1-8}$$

The capacitance and voltage of photoconductors are measured by using a C-V analyzer in our laboratory. Limits of the minimum capacitance and voltage range of C-V analyzer are 200 pF and 0 Volt respectively. Limits of the maximum capacitance and voltage range of C-V analyzer are 2nF and 20 Volts. Thus, if the capacitance value of photoconductor is decreased below the minimum limit of C-V analyzer, this capacitance value is not read by C-V analyzer and, vice versa, for maximum limit if the capacitance value of photoconductor is increased above of the maximum limit of C-V analyzer, this capacitance value is not read by this

analyzer. (see in detail information about C-V analyzer in the Appendix A). Also, a light source (bulb) is used to generate electron-hole pairs. The power of this light source is 500 Watts. This block diagram connections and experimental set up are shown in Figure 5.1-3 and 5.1-4 respectively.

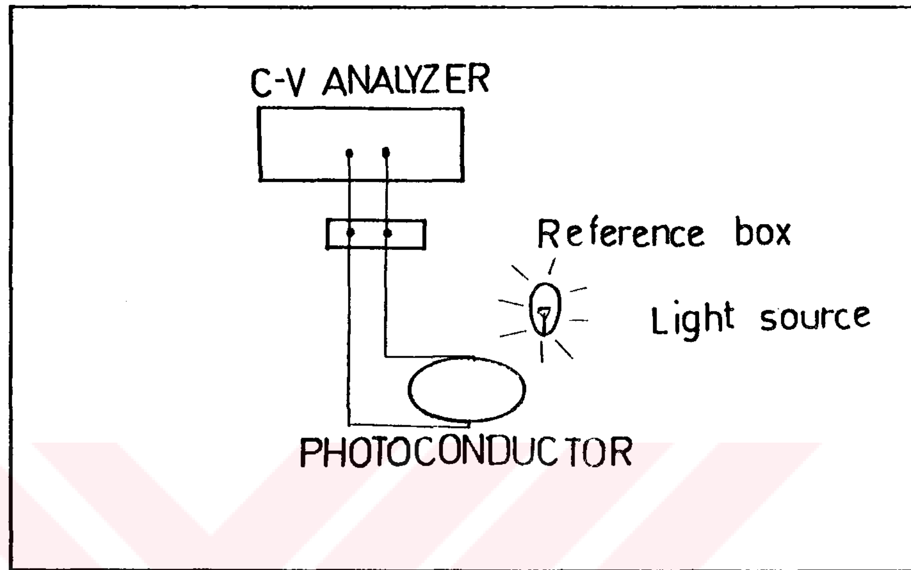

Figure 5.1-3 Block diagrams connections of C-V analyzer.

Figure 5.1-4 Experimental set up for measuring the density of sensitizing centers by the CV method.

5.2 Space-Charge-Limited Current Method

In the previous chapters the space-charge-limited current is explained in detail (see section 4.6). An emmission current is generated by means of free electrons which pass from the photoconductor when the light fall on the photoconductor surface. The generated holes are captured by means of sensitizing centers. The emmission current depends on the intensity of the light and decreases with decreasing light intensity. In the fixed light intensity, a variable electric field is applied to the electrodes of photoconductor with an increase in electric field. The emmission current (photocurrent) is decreased and at a certain voltage this current becomes zero. This voltage is the maximum voltage for a zero emmission current. If the applied electric field exceeds this maximum voltage, the current polarity is changed and then it starts to increase. Here, this current is defined as space-charge current and its starting point is the space-charge-limited current. The

Figures 5.2-1 show the transition from Emmission-Limited current to Space-Change-Limited current at a fixed light intensity.

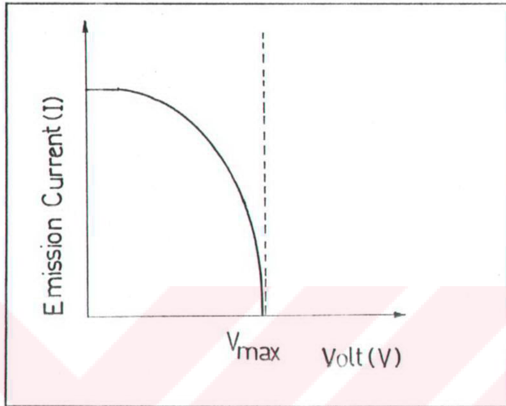

Figure 5.2-1 The trasition emission current to space-charge-limited current with applying voltage at fixed light intensity.

At the different light intensity,there is a fixed maximum voltage for different light intensity. i.e.,for L_0 , $V_{max}=V_1$, for L_1, $V_{max}=V_2$,etc.

The density of sensitizing centers are found from the following relation

$$V_{max}C=e(n_t)_{kT}LA \qquad (4.5-2)$$

where V_{max} is the maximum voltage for starting space-charge-limited current or transition from emmission-limited to space-charge-limited current, C is the total capacitance between the electrodes in the crystal, $(n_t)_{kT}$ is the density of traps under the appliyed voltage which is equal to the

sensitizing centers (Recombination centers II) under the illumination of photoconductor in the forbidden gap of a kT wide portion, i.e., $[(n_t)_{kT}=\wp_r]$, L is the interelectrode spacing, and A is the cross-sectional area which is shown in Figures 5.2-2.

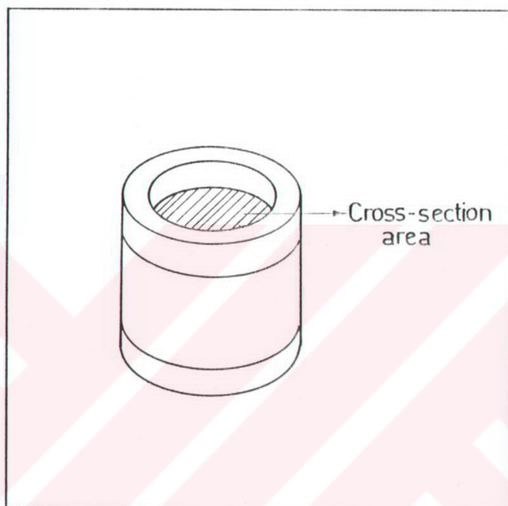

Figure 5.2-2 The cross-section represantation of a photoconductor.

At different light intensity the maximum voltages are measured by using a digital voltmeter, a digital ampermeter, and a digital voltage source. The experimental set up for this measurement is shown in Figure 5.2-3. Using the measured maximum voltages the total capacitance are measured by using a C-V analyzer. The experimental set up is shown in Figure 5.2-4 to measure the total capacitance between the electrodes in photoconductors.

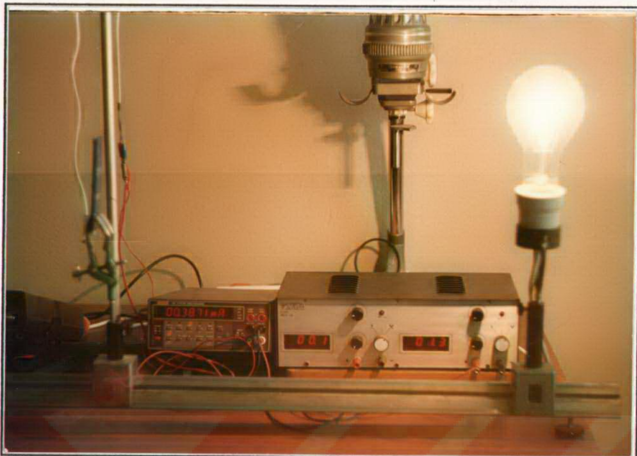

Figure 5.2-3 Experimental set up to measure V_{max} at different light intensity.

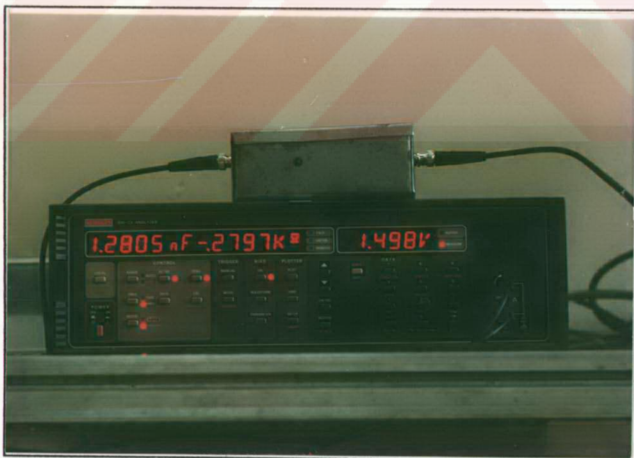

Figure 5.2-4 Experimental set up to measure C at different V_{max} and light intensity.

5.3 Determination of Band Gap

The band gap of crystals can be found by several different methods. These methods are explained briefly in the previous chapters (see section 4.6). In this study, we measured the value of the band gap of Se and ZnS photoconductor by using the variation of photoconductivity excitation with wavelenght method.

We know that if the light impinges on the photoconductor, the electrons in the valance band are excited to the conduction band. But, if the energy of the light is smaller than the band gap of the photoconductor, the electron can not be excited to the conduction band. The excited electrons are return to the valance band (see Figure 5.3-1a). Also, if the energy of the light is larger than the band gap of photoconductor, the electrons are not excited to the conduction band, In this case the excited electrons go above the conduction band (see Figure 5.3-1b).

The energy value of a light at a fixed wavelength is;

$$E_p = h\nu = h\frac{c}{\lambda} \qquad (5.3\text{-}1)$$

where E_p is the energy value of light, h is the Planck constant, ν is the frequency of the light, c is the velocity of light, and λ is the wavelenght of light.

If the wavelenght of incident light is changed, the energy value of light is changed. And at a certain wavelenght the electrons are excited from the valance band to the conduction band. This energy value of light is approximately equal to energy value of band gap($E_p=E_g$). Thus at this condition a small current or voltage pulse is generated on the photoconductor.

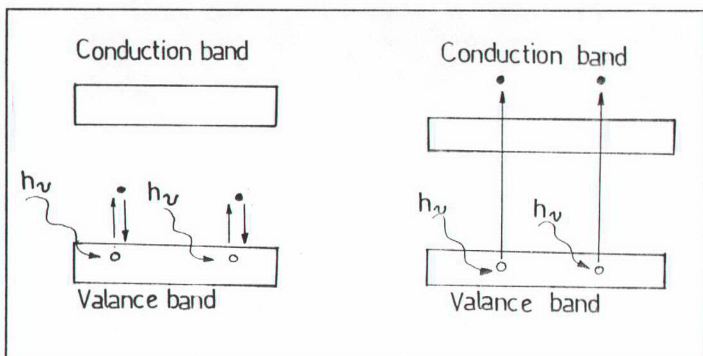

Figure 5.3-1 Motion of electrons (a) $E_p < E_g$ and (b) $E_p > E_g$

The wavelength of light can be changed by using a monochromator at a fixed light intensity. But in our laboratory, we have no monochromator. Therefore, we used a monochromator of a UV (Ultra-Violet) and Visible Spectroscopy (see Appendix B). The wavelength range of this monochromator changes from 200 nm to 1100 nm. Also we used an amplifier to amplify the small currents or voltage signals. A recorder is used to record the signals from the amplifier. The block diagram connections and experimental set up are shown in Figure 5.3-2 and Figure 5.3-3, respectively.

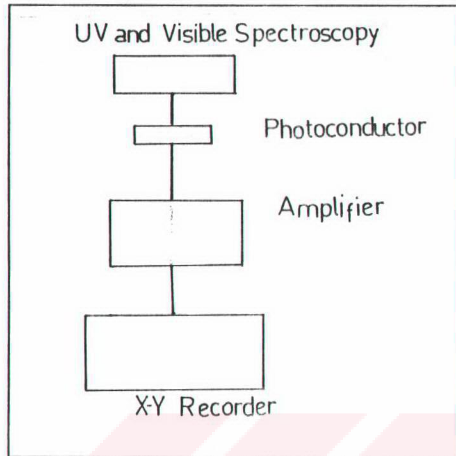

Figure 5.3-2 Block diagram connections of equipment to measure the band gap of a photoconductor.

Figure 5.3-3 Experimental set up to measure the band gap of a photoconductor.

CHAPTER 6

DISCUSSION OF RESULTS

6.1 Discussion of The Results Obtained by C-V Methods

In this section, we will present the results that we obtained from our experimental studies.

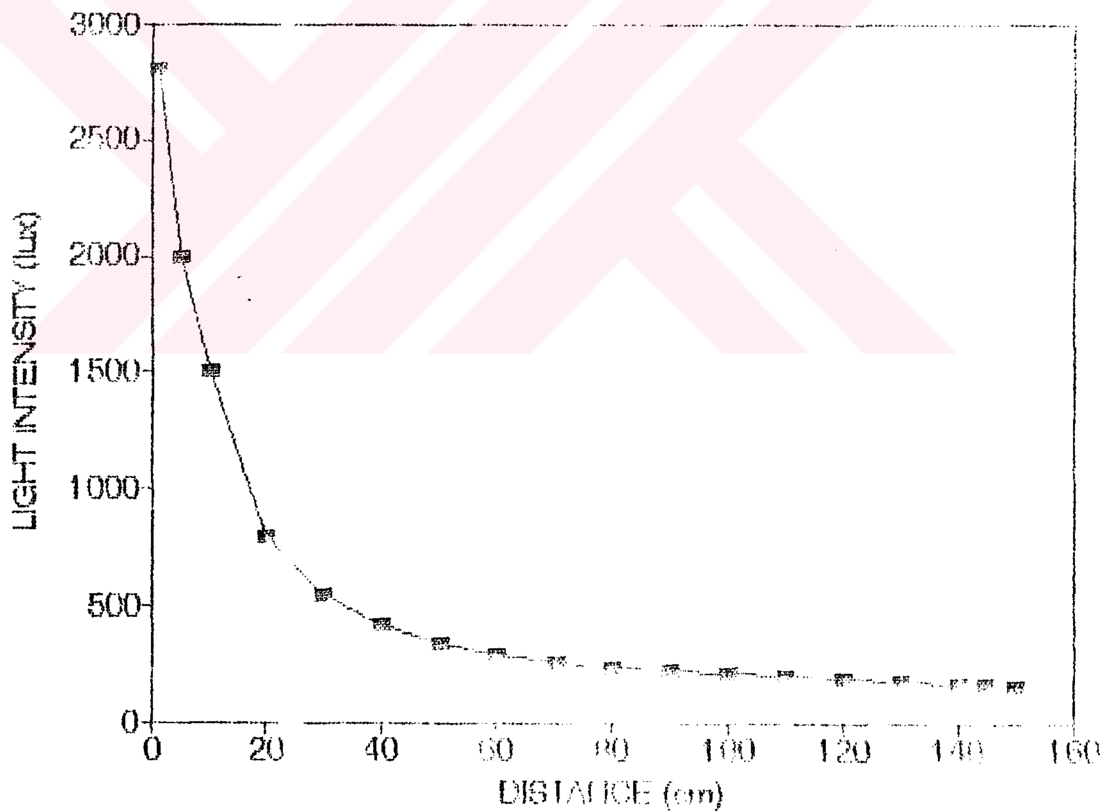

Figure 6.1 The variation of intensity as a function of distance between the light source (bulb) and low resistivity n-type Cl doped Selenium at 300^0 K.

Since the crystal selenium was doped by Cl atoms, it is a n-type photoconductor. The electrodes of photoconductors were made by Al metals which made a good contact with Se material. In Figure 6.1 the curve which was obtained from experimental studies shows the variation of intensity as a function of distance which is a length between the light source and photoconductor and can be adjusted by the distancemeter. The light intensity plays an important role in the determination of density of sensitizing centers in which photoconductivity increases with a power of light intensity greater than unity as the sensitizing centers change function from simple electron-hole traps to recombination centers II (sensitizing centers) with increasing light intensity. Thus, the light intensity measured as a function of distance at appropriate length. As seen in Figure 6.1, the light intensity abruptly decreased between 0 cm and 30 cm and then slowly decreased by increasing distance between the light source and photoconductor.

Figure 6.2 shows the variation of voltage as a function of light intensity. As seen in Figure 6.2, The voltage slowly changes between the 0 lux to 500 lux. Above the 500 lux of light intensity, approximately all sensitizing centers are essentially occupied by holes. The voltage increase abruptly but linearly the 500 and 3000 lux as a function of light intensity.

In Figure 6.3, the variation of photocurrent with light intensity is shown for Selenium photoconductor at 300^0 K. The break from $\Delta i \propto L$ to $\Delta i \propto L^{>1}$ occurs when the hole demarcation-level is at the small-cross-section level II at approximately 500 lux. The density of sensitizing centers can be determined from the fact that the photoexcited carrier density saturates at high light intensity when the sensitizing centers are essentially occupied by holes. Such an effect was observed for Cl impurity in Se. The actual density of electrons existing in the saturated condition

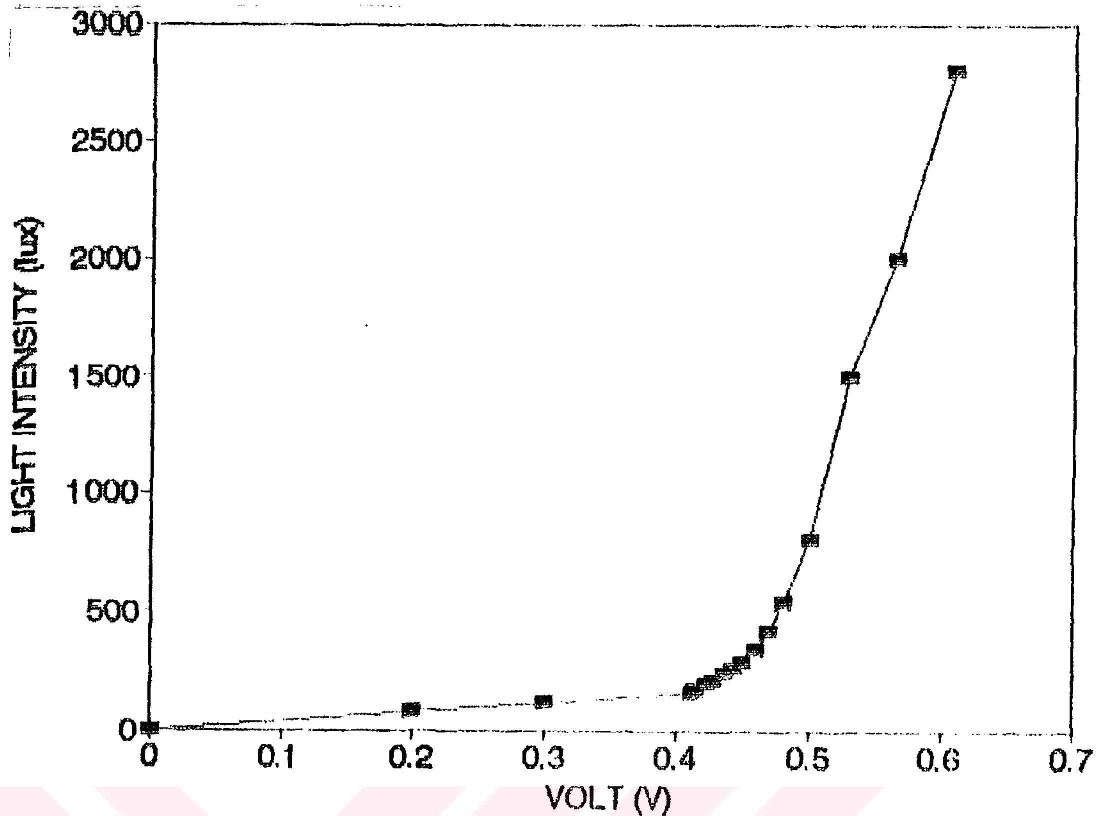

Figure 6.2 The variation of voltage as a function of light intensity in low-resistivity n-type Cl doped Selenium at 300^0 K.

is equal to the total density of sensitizing centers. In Figure 6.3, approximately above 1000 lux, all the sensitizing centers are saturated by holes. (see detailed explanation in Chapter 4).

Figure 6.4 shows the variation of capacitance as a function voltage in the low-resistivity n-type Cl doped Selenium photoconductor at 300^0 K. As seen from Figure 6.4 the capacitance between the electrodes of photoconductor slowly increases to the 0.4 Volt. Above this voltage, there is a rapid increase in capacitance of photoconductor. Between 0 volt and 0.4 volt a few sensitizing centers are saturated, and above 0.4 volt, the sensitizing centers slowly start to saturate. The light intensity at that point is approximately 500 lux.

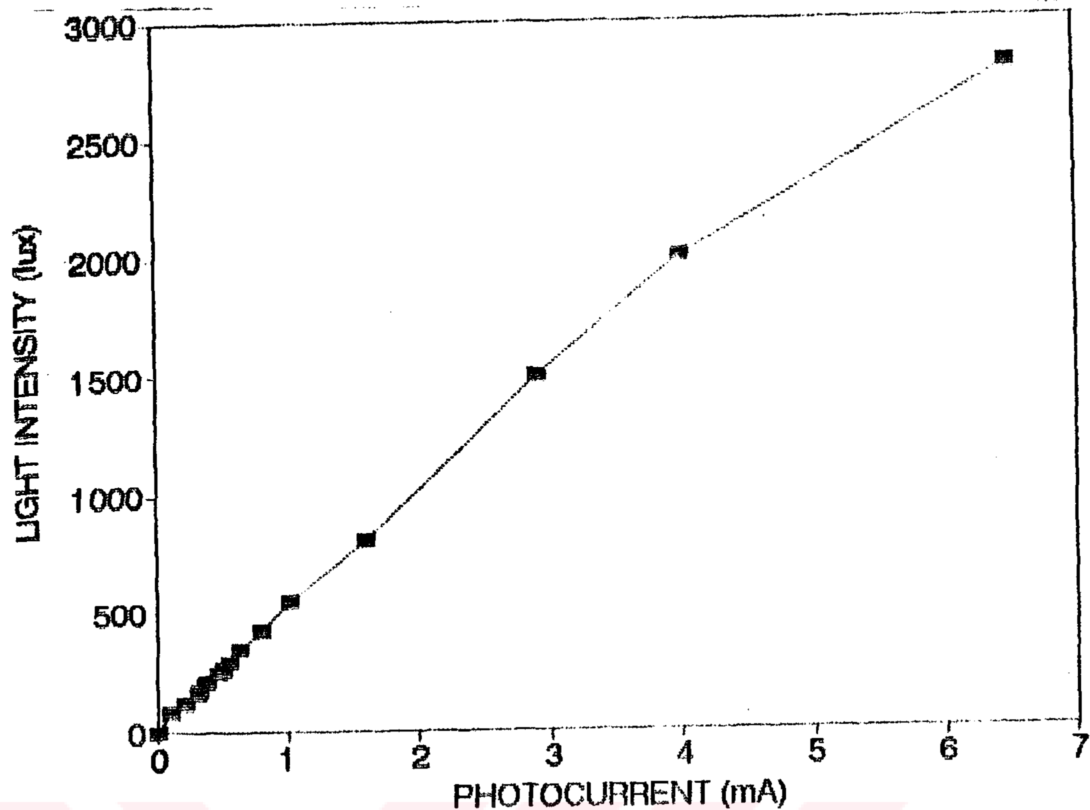

Figure 6.3 Variation of photocurrent as a function of light intensity in low resistivity Cl doped Se at 300^0 K.

Figure 6.5 shows the variation of capacitance as a function of voltage in the high-resistivity ZnCl doped ZnS photoconductor at 300^0 K. As seen from Figure 6.5 the capacitance between the electrodes of ZnS photoconductor slowly increases to the 0.2 mV. Again, above this voltage there is a faster increase in capacitance of photoconductor. Above the 0.2 mV., the sensitizing centers slowly start to saturate.

From Figure 6.4, we determined the density of sensitizing centers for any value of capacitance, voltage and intensity. The maximum density of sensitizing centers at per cm^3 was found at the available maximum value of light intensity, capacitance, and voltage that is approximately $8x10^9$ per cm^3.

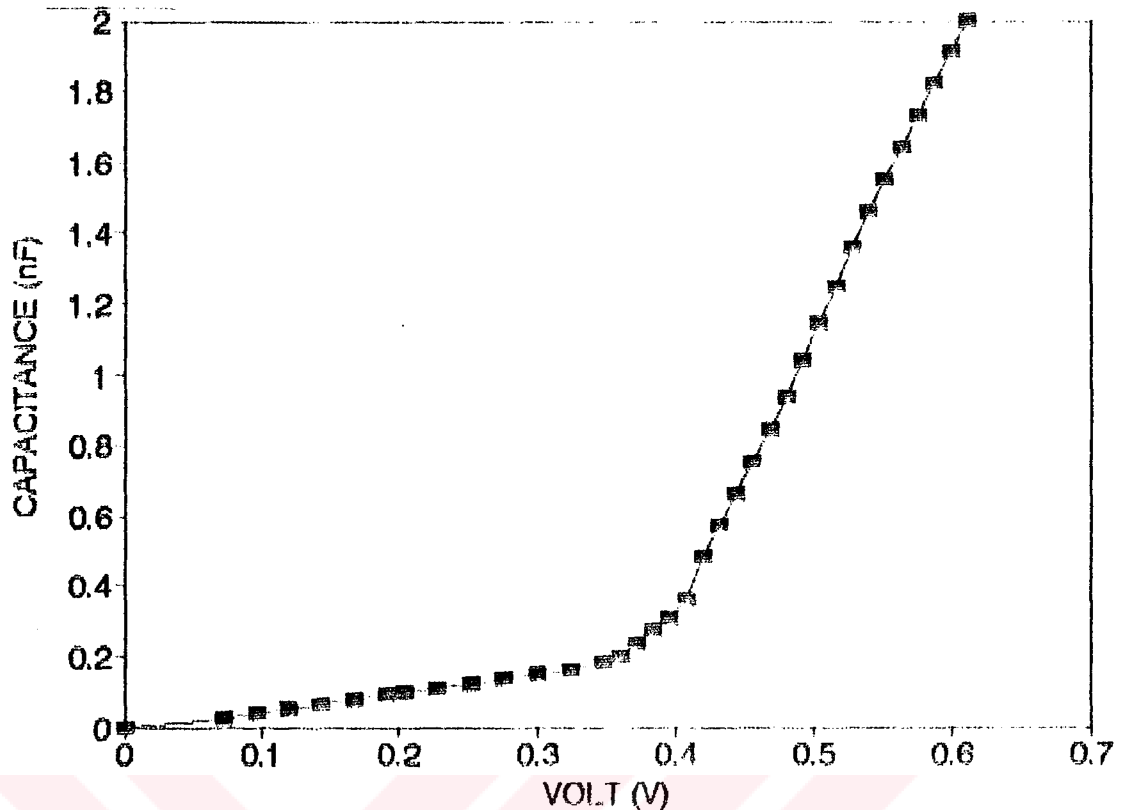

Figure 6.4 Variation of capacitance as a function of voltage between the electrodes in the low-resistivity n-type Se at 300^0 K.

The variation of density of sensitizing centers as a function of voltage between the electrodes of Se photoconductor and the variation of density of sensitizing centers as a function of light intensity are presented in Figure 6.6 and 6.7, respectively. As seen from the two curves, the maximum density of sensitizing centers is about $8x10^9$ per cm^3. If the light intensity is increased above the 3000 lux the density of sensitizing centers also increases and then they level off the their original value in the photoconductor material. At light intensity of 3500 lux, there is no increase in the value of density of sensitizing centers.

The variation of sensitizing centers as a function of voltage between the electrodes is shown in Figure 6.8. As seen from the curve, the maximum density of sensitizing

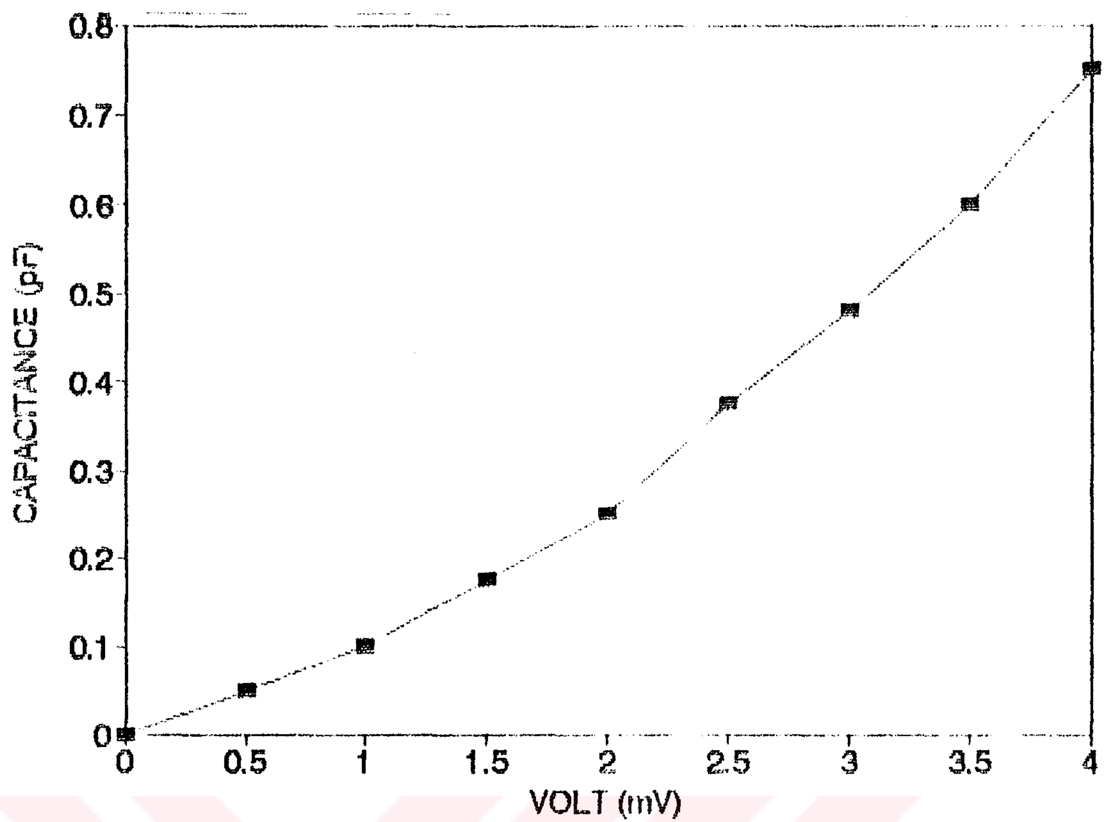

Figure 6.5 Variation of capacitance as a function of voltage between the electrodes in the high-resistivity ZnS at 300^0 K.

centers is about $2x10^5$ per cm^3. If the light intensity increased, the density of sensitizing centers also increases.

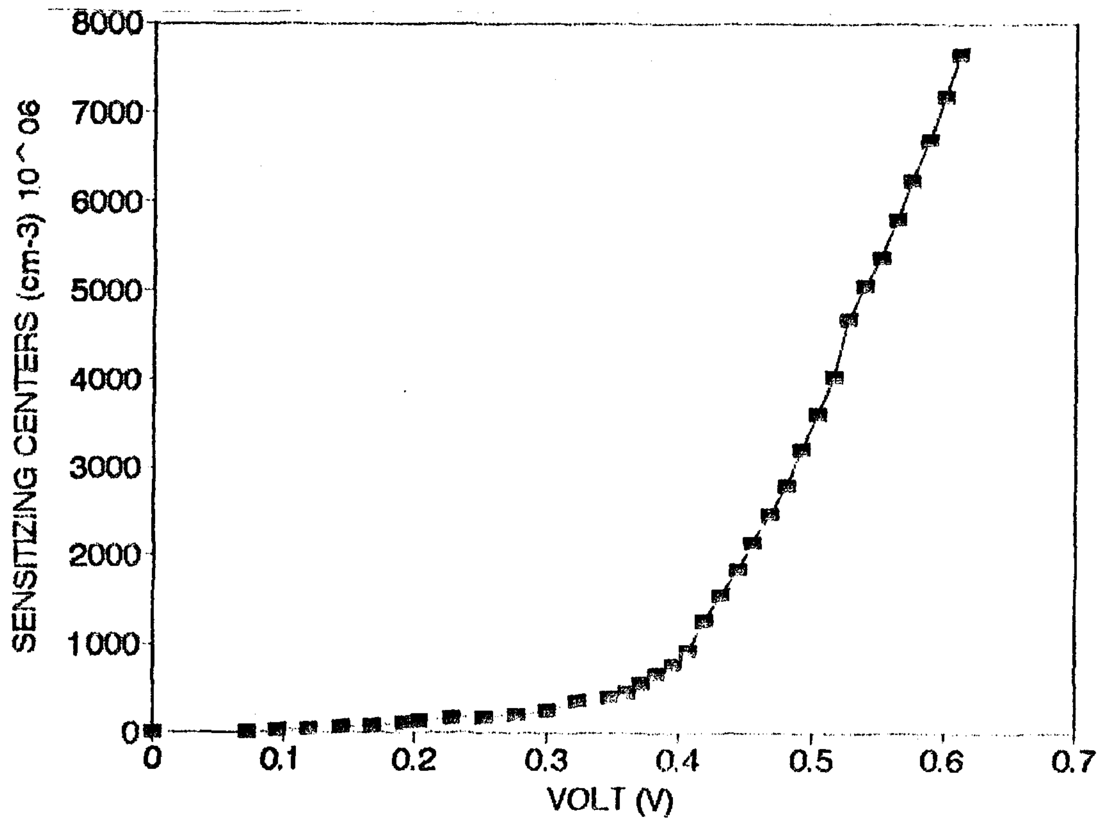

Figure 6.6 The variation density of sensitizing centers as a function of volt between the electrodes of n-type Cl doped low-resistivity Se photoconductor.

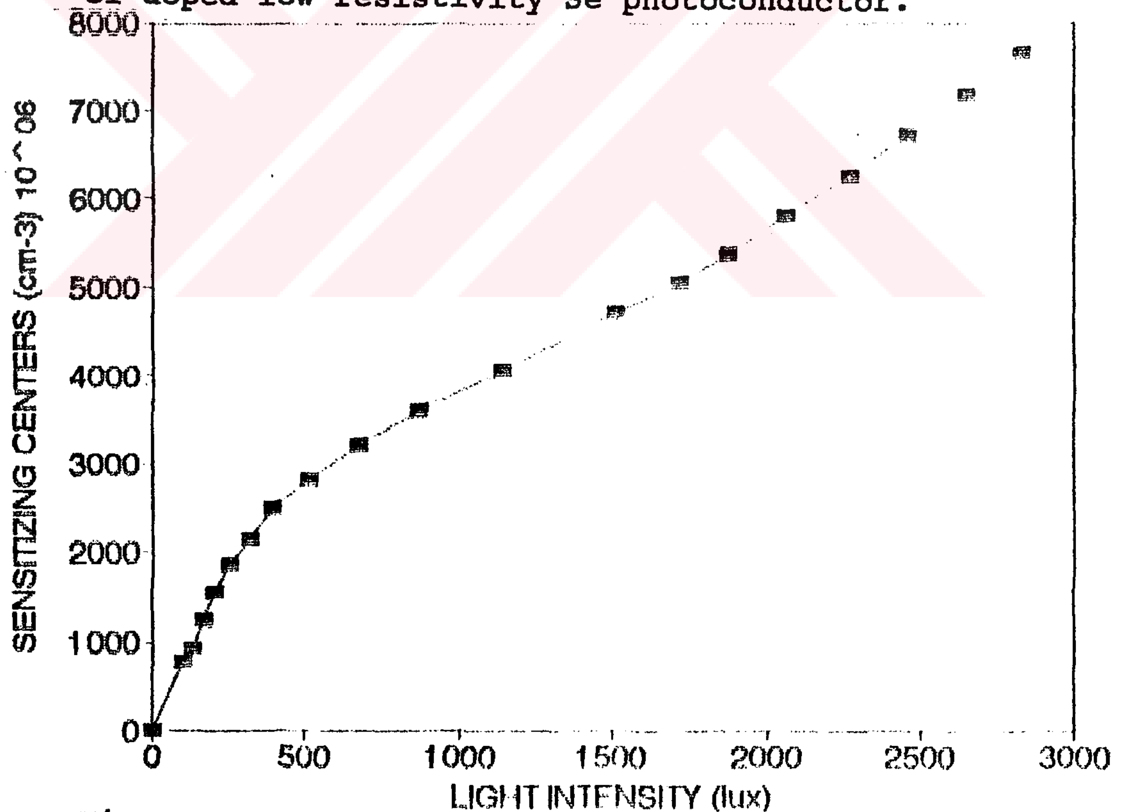

Figure 6.7 The variation density of sensitizing centers as a function of light intensity in n-type Cl doped low-resistivity Se photoconductor.

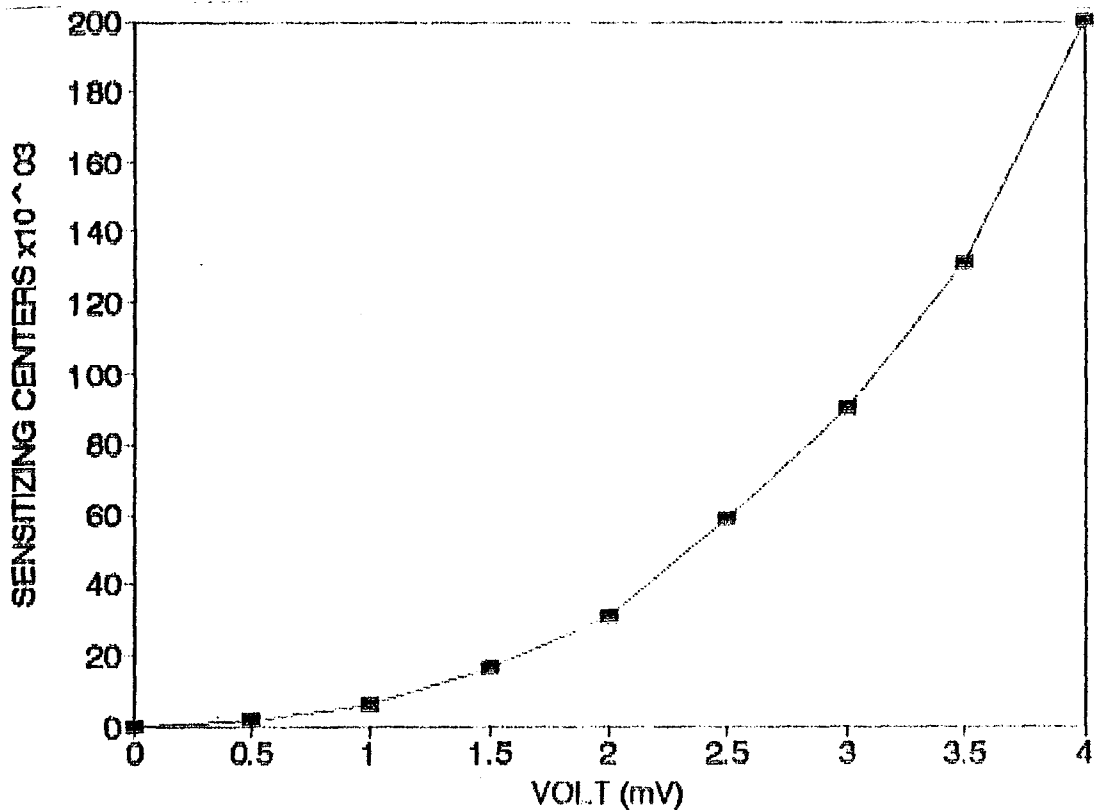

Figure 6.8 The variation density of sensitizing centers as a function of volt between the electrodes of ZnCl doped high-resistivity ZnS photoconductor.

6.2 Results and discussion of Space-Charge-Limited Method

In this section, we will present the results obtained from space-charge-limited method.

Firstly, at different light intensity, a variable voltage was applied to the elecrodes of photoconductor. This voltage is applied in the opposite direction of flow in the photocurrent. Then, the maximum voltages are found for emission current, i.e., when photocurrent decreased to zero. In Figure 6.9, the curve shows the variation of V_{max} as a function of light intensity. At this light intensity the emission current decreases to zero by the applied potential to the electrodes of photoconductor by using a voltage source.

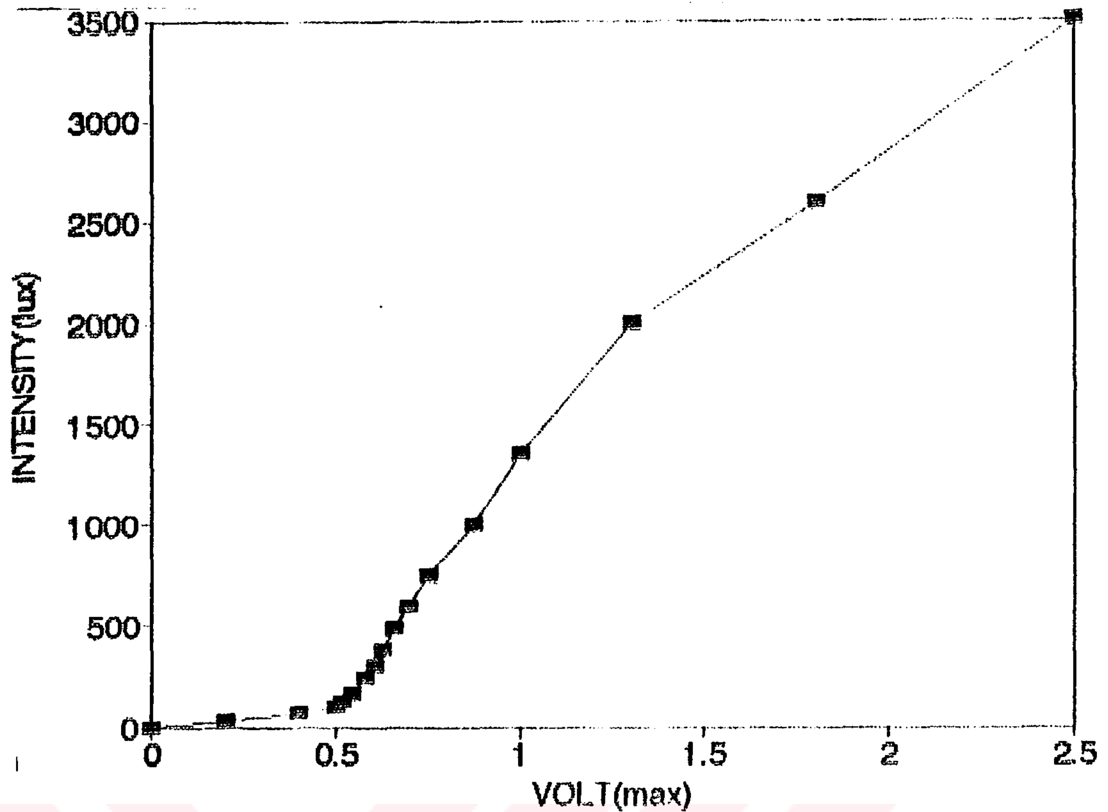

Figure 6.9 Variation of V_{max} as a function of light intensity in low-resistivity n-type Cl doped Se at 300^0 K.

By using the measured value of V_{max} at different light intensity, and by using the C-V analyzer, we measured the value of capacitance between the electrodes of Se photoconductor. Figure 6.10 exhibits shows the variation of C as a function of V_{max}.

Finally, by using the equation 4.5-2, we found the density of traps which are sensitizing centers under the illumination of photoconductors. The interelectrode spacing is 0.1 cm and the cross-section area is 21 cm^2. In the space-charge-limited method, the maximum value of density of sensitizing centers was found to be $2x10^{10}$ per cm^3.

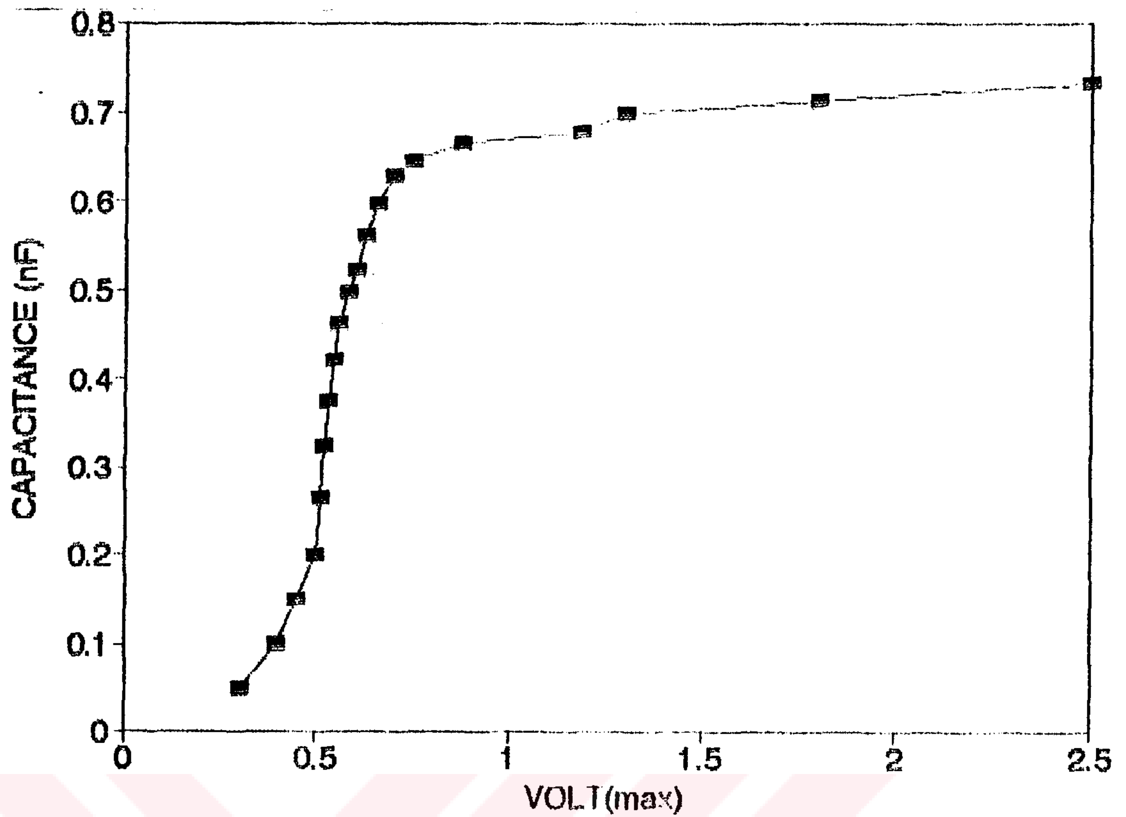

Figure 6.10 Variation of C as a function of V_{max} measured at the different light intensity in the n-type low-resistivity Cl doped Se photoconductor.

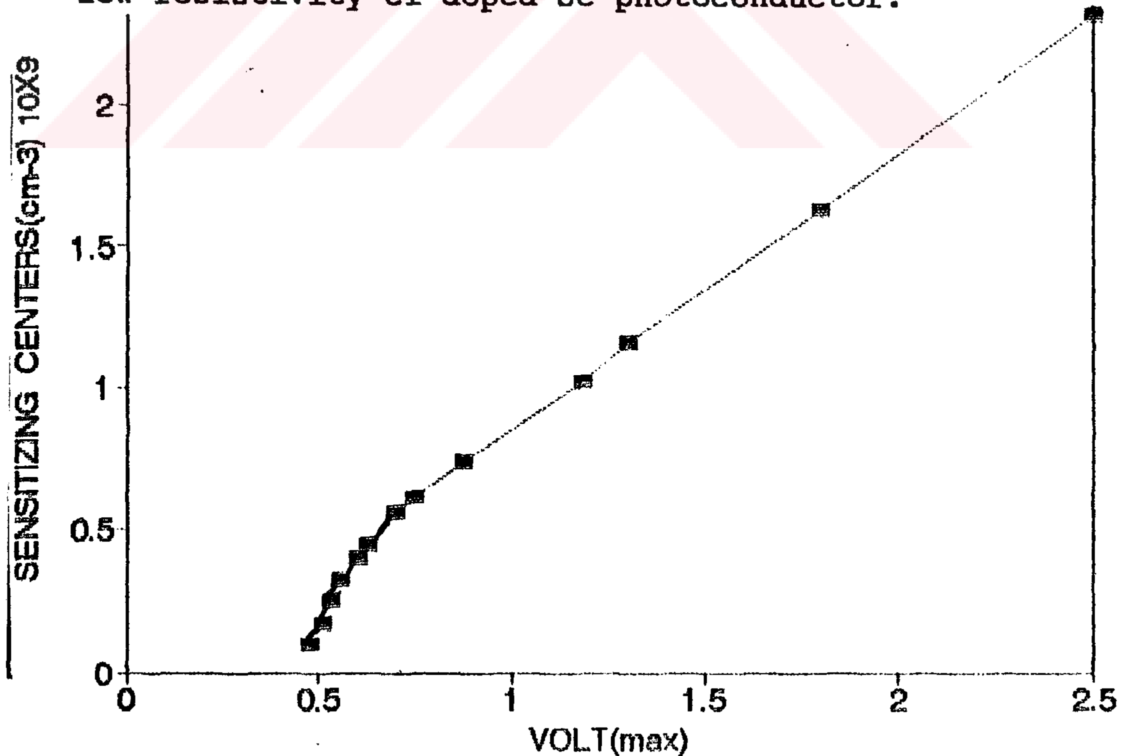

Figure 6.11 Determined density of sensitizing centers as a function of V_{max} in Se photoconductor.

6.3 Determination of Band Gap and Energy Level Values of Sensitizing Centers in the Photoconductors

The band gap determination of crystals was explained in the previous chapter. The photoconductivity excitation spectrum as a function of wavelength is presented in Figure 6.12. The maximum peak occured at 610 nm. This means that the maximum response of Se photoconductor to the light takes place at 610 nm. At this wavelength, the electrons get excited from valance band to the conduction band. By using equation 5.3-1, the band gap of Se photoconductor is found

$E_g=hc/\lambda=6.62x10^{-34}$(joule-sec)*$3x10^{8}$ (m/sec)/$610x10^{-9}$ (m)

$E_g=3.25x10^{-19}$joule

$E_g=2.03$ eV

The theoretical determination shows that the band gap of Se is 2.1 eV. The result obtained here by experimental method is close to the theoretical value of 2.1 eV. In Figure 6.12, the smaller peak shows that the excitation of electrons from the traps, which are the sensitizing centers under the illumination to the conduction band. The wavelength value of this peak is 730 nm, and its energy value is

$E_g=hc/\lambda=6.62x10^{-34}$ (joule-sec)* $3x10^{8}$ (m/sec)/$730x10^{-9}$ (m)

$E_g=2.72x10^{-19}$ joule

$E_g=1.7$ eV

The theoretical value of band gap of ZnS is 3.1 eV. The band gap determination of ZnS from its excitation spectrum is found 3.05 eV by means of bigger peak. The photoconductivity excitation spectrum as a function of wavelength of ZnS photoconductor is presented in Figure 6.13. In Figure 6.13 , the smaller peak shows that the excitation centers under the illumination to the conduction band. The wavelength value of this peak is 610 nm and its energy value is 2.1 eV.

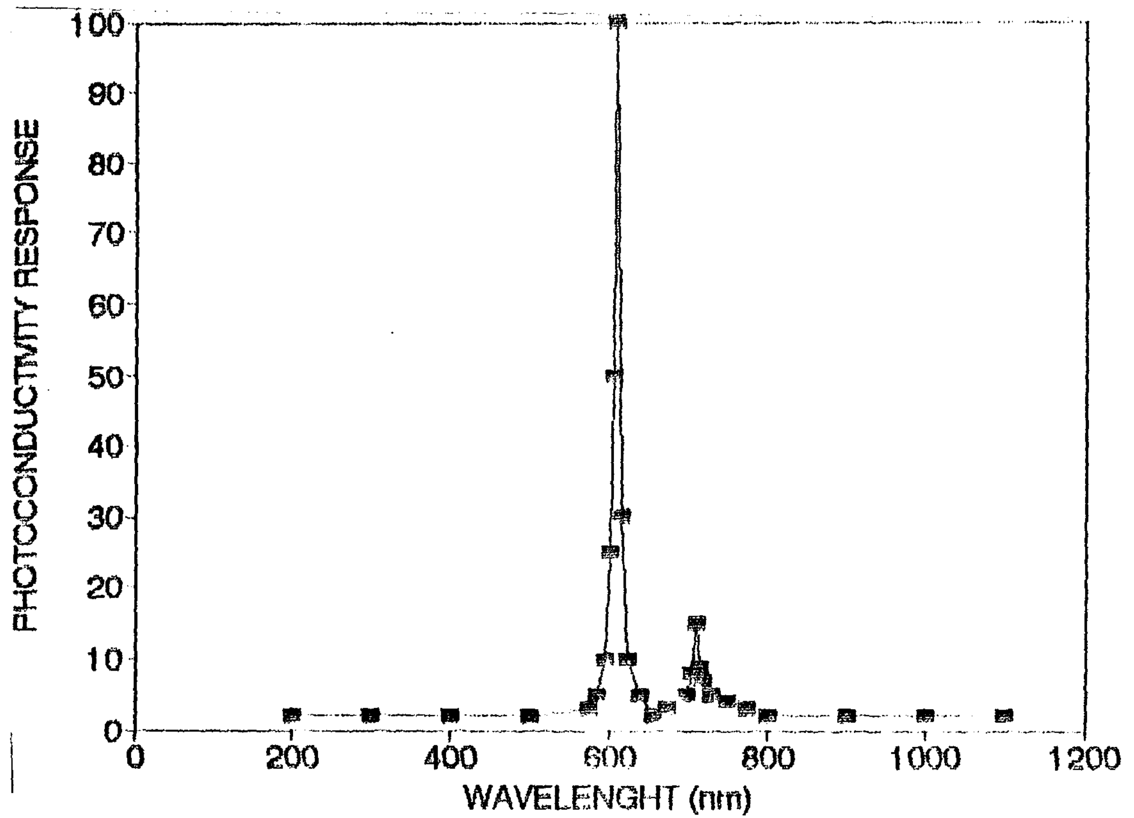

Figure 6.12 Photoconductivity excitation spectrum as a function of wavelength in low-resistivity Cl doped Se at 300^0 K.

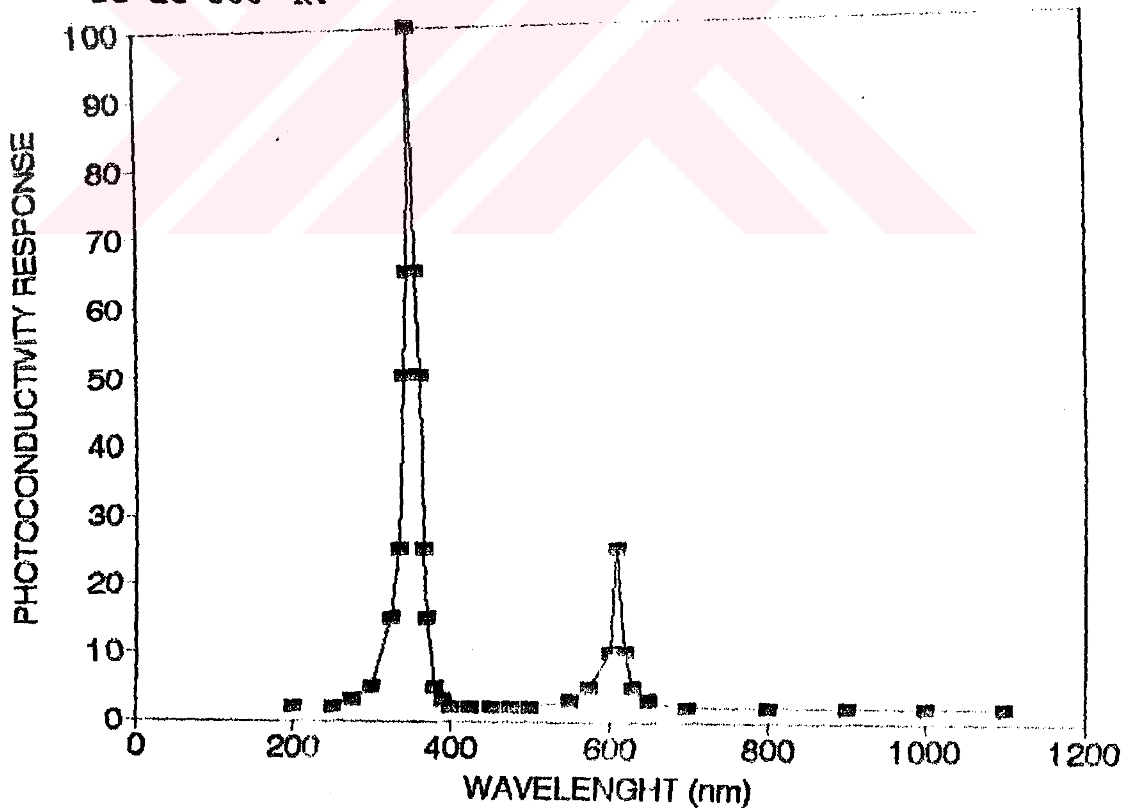

Figure 6.13 Photoconductivity excitation spectrum as a function of wavelength in ZnCl doped ZnS photoconductor.

CONCLUSION

In the first section of this study, the density of sensitizing centers was determined by the C-V method in the low-resistivity Cl doped n-type Selenium and high resistivity ZnCl doped ZnS photoconductors and then the density of sensitizing centers was determined by the space-charge-method as a function of light intensity in the low-resistivity Cl doped n-type Selenium photoconductor. We see that the density of sensitizing centers change linearly with the light intensity for the two methods. But all density of sensitizing centers saturate at the high light intensity, at which the density of sensitizing centers can be approximated.

In the second section of this study, the energy band gap of photoconductor and energy levels of sensitizing centers in the forbidden gap were determined by using UV and Visible spectrophotometer. The value of the energy band gap of Selenium photoconductor and ZnS are in good agreement with theoretical values,and therefore, the determined value of energy levels of sensitizing centers in the forbidden gap of selenium photoconductor and ZnS photoconductor should be approximately accurate.

The impurity incorporation to the photoconductor plays an important role in the semiconductor technology. Effectively, a photoconductor can be used for a variety of light and particle detection applications, as well as a light controlled switch. Other major applications in which sensitive photoconductor plays an essential role are television, cameras, normal silver halide emulsion photography, and the very large field of electrophotographic reproduction. Thus, a sensitive photoconductor must have sensitizing centers. These sensitizing centers

change the sensitivity of photoconductor against the light. If the density of sensitizing centers are very high in the forbidden gap of photoconductor, photoconductor is very sensitive against the light.

We recommend that a study should be done to see whether there are any disadvantages of sensitizing centers in the photoconductor.

APPENDIX A

If you want to use the Model 590 C-V analyzer by the local mode, you must press the local button in the front panel of analyzer. The other case, analyzer works in the IEEE mode.

The capacitance and resistance range of C-V analyzer can be changed by range button. Press RANGE button briefly to manually select range. Pressing and holding RANGE button for more than 1/2 second places the unit in autoranging.

If you want to use select readings rate per second , you must press RATE button up or down. The rate selection menu:1,10,75,1000 readings per second. But the slower rates will provide more resolution and quieter readings.

When press the ZERO button, the internal offset to maximize accuracy is available.

If you want to select the type of bias waveform to be programmed, use WAVEFORM button up or down to select the waveform type, then press ENTER button. The type of waveforms are

(0) DC Constant DC level in the range of ± 20
(1) STAIR Single staircase (step either up or down)
(2) DSTAIR Dual staircase (step up or down)
(3) PULSE Pulse train (constant level or step up or down)
(4) EXT Voltage from external source

The normal capacitance display is a 4.1/2 digit +21.999, -19.999 count value with engineering units in pF or nF. Display resolution is 3.1/2 digits at the 75 and 1000 readings per second rates.

The 4.1/2 digit voltage display indicates the programmed or actual measured value of the internal ± 20 volt bias source or the applied external bias voltage (± 200 V). When the unit displays reading or stored buffer values, the display will show the bias voltage as measured by an internal A/D converter.

Test INPUT and OUTPUT jacks connection as shown in Figure A. Use RG-58 coaxial cable for the best measurement at 1 MHz for optimum accuracy.

APPENDIX B

1- ULTRAVIOLET AND VISIBLE SPECTROPHOTOMETER

This instrument measures the transmittance and the absorbtion of a sample in the ultraviolet/visible/near infrared region of 200 to 1100 nm wavelengths to make quantitative analysis. It can also measure the absorbtion and the transition spectrum as a matter of course. It uses a deuterium lamp in the ultraviolet region and a tungsten iodine lamp in the visible-to-near infrared as the light source. The light from the source, after passing through a high order light cut-off filter, goes to the monochromator that uses a concave diffraction grating. The light is monochromated by the monochromator and is split into two beams by the beam splitter. One of the beams goes through the sample and other either goes through the reference sample such as a solvent or impinges on the silicon photocell detector. Figure B.1 shows the main unit of this instrument.

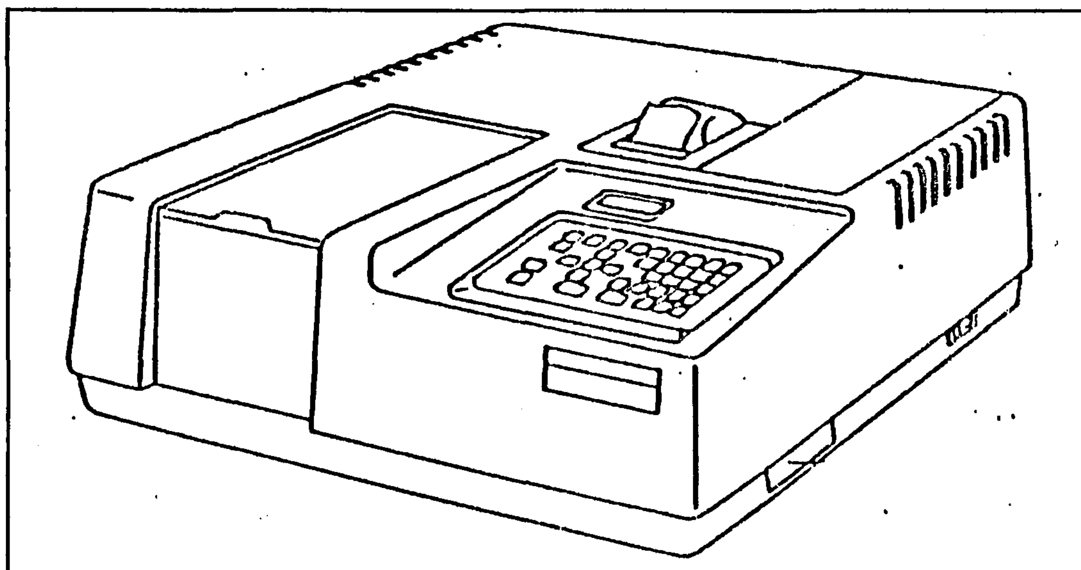

Figure B.1 Main unit.

2- SYSTEM OF THE UV AND VISIBLE SPECTROPHOMETER

Figure B.2 shows the block diagram of this system. After the light signal is converted into an electrical signal by the detector and amplified, it is subjected to A/D conversion. The data thus converted is subjected to necessary processing by a microcomputer.

In this study, we used only monochromator section of the UV and visible spectrophometer to obtain a fixed wavelength in the ultraviolet/visible/near infrared region. Monochromator, which is very important section for recording emission spectra, is used to supply a beam of light having some desired narrow range of wavelength.
In that case, it has the following component parts :(1) an entrance slit producing a well defined beam of heterochromatic radiation, (2) a prism or diffraction

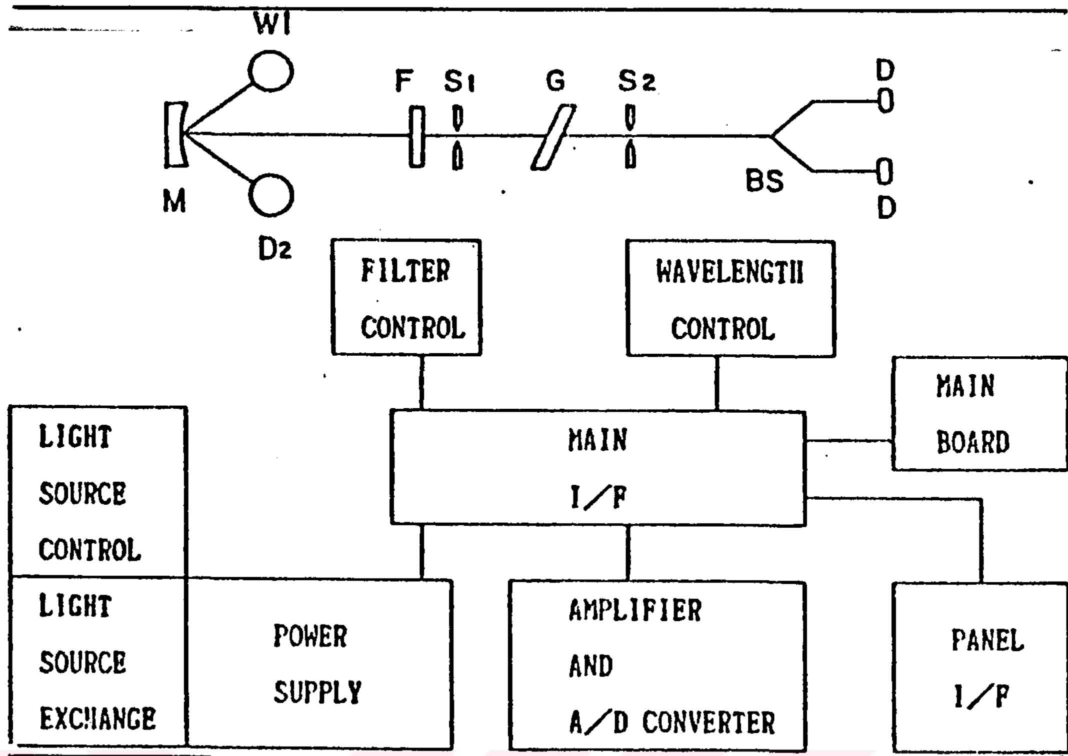

Figure B.2 Block diagram of the system.

grating dispersing the incident radiation into a continuous spectrum, (3) some device to rotate the prism or grating so that the desired wavelengths of exit radiation are obtained, and (4) an exit slit allowing a narrow band of wavelengths.

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