M.THESIS
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Department of Electrical Engineering

MASTER THESIS

MINORITY CARRIER LIFETIME MEASUREMENTS IN SILICON SAMPLES VIA PHOTOCONDUCTIVE DECAY METHOD

by

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ABSTRACT

MINORITY CARRIER LIFETIME MEASUREMENTS IN SILICON SAMPLES VIA PHOTOCONDUCTIVE DECAY METHOD

by

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The minority carrier lifetime in n-type and p-type silicon single crystals has been examined. In silicon samples, minority carrier lifetimes in the ranges of 68 µsec and 1464 µsec were measured by photoconductive decay (PCD) method which requires a four-step process: i) making the end contacts to the specimens, ii) resistivity measurement of that specimen, iii) conductivity type measurement of the specimen, iv) measurement of filament lifetime (τ_f). Using data obtained above, bulk lifetime (τ_B) is calculated.

Resistivities of silicon samples have been determined to vary from 11.69 Ω-cm to 7102 Ω-cm.

The aplication of the PCD method for minority carrier lifetime measurement in silicon samples is limited due to the following reasons: 1) Large cross sectional area of silicon samples is necessary, 2) relative excess carrier density ($\frac{\Delta n}{n_0}$ or $\frac{\Delta p}{p_0}$) must be less than 10^{-2}, 3) the maximum electric field applied across the sample must satisfy $E_0 \leqslant (kT/e)/\sqrt{D_{n,p}\,\tau_{n,p}}$, 4) surface recombination lifetime (τ_s) must be at least three times filament lifetime (τ_f), 5) diffusion and drift effects to the end contacts must be eliminated by $L_C \geqslant 4L_D$ and $L_C \geqslant 4d$.

Where L_C is the distance between the illumination boundary and nearest end contact, d is the drift length, and L_D is the diffusion length.

Keywords: Silicon, minority carrier lifetime, PCD method.

ÖZET

FOTOİLETKENLİK SÖNÜM METODUYLA SİLİKON NUMUNELERİNDE AZINLIK TAŞIYICILARININ YARI ÖMRÜNÜN ÖLÇÜLMESİ

K. ERSİN SEMEN

N ve p-tipi silikon tek kristallerinde azınlık taşıyıcılarının yarı ömür süreleri incelenmiştir. Aşağıdaki dört basamaklı işlemleri gerektiren fotoiletkenlik sönüm metodunu kullanarak 68 mikrosaniye-1464 mikrosaniye aralığında yarı ömür süreleri ölçülmüştür; i) numuneye omik kontak yapılması, ii) özdirencinin ölçülmesi, iii) iletkenlik tipinin belirlenmesi, iv) yarı ömür süresinin (τ_f) osilaskopla ölçülmesi. Yukarıda elde edilen verileri kullanarak, azınlık taşıyıcılarının hacım içindeki yarı ömür süresi (τ_B) hesaplanır.

Özdirençleri 11,69 Ω-cm - 7102,8 Ω-cm aralığında değişen silikon tek kristalleri ölçüm sırasında kullanılmıştır.

Fotoiletkenlik sönüm metodunu kullanarak silikonda azınlık taşıyıcılarının yarı ömür sürelerinin ölçülmesi aşağıdaki sebeplerden dolayı sınırlıdır; 1) kesiti büyük olan silikon numuneleri gerekmektedir, 2) nisbi fazlalık taşıyıcıların yoğunluğu 10^{-2}den küçük olmalıdır, 3) numuneye uygulanan maksimum elektrik alanı $E_0 \leqslant (kT/e)/\sqrt{D_{n,p}\ \tau_{n,p}}$ eşitsizliğini sağlamalıdır, 4) azınlık taşıyıcılarının yüzeyde kaybolma zamanı (τ_s), numunede ölçülebilen yarı ömür zamanı (τ_f)'nın en az üç katı olmalıdır, 5) uç kontaklara yayılma ve sürüklenme etkileri, $L_C \geqslant 4d$ ve $L_C \geqslant 4L_D$ eşitsizlikleri sağlanarak ortadan kaldırılmalıdır. Burada L_C aydınlatılan bölge ile en yakın uç kontak arasındaki uzaklık, d sürüklenme uzaklığı ve L_D ise azınlık taşıyıcılarının yayılabilecekleri ortalama mesafedir.

Anahtar sözcükler: Silikon, azınlık taşıyıcı ve yarı ömrü, fotoiletkenlik sönüm metodu.

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LIST OF SYMBOLS

A	Cross sectional area
C.F.	Correction factor
D	Ambipolar diffusion constant
D_n	Diffusion coefficient of electrons
$D_{n,p}$	Diffusion coefficient of either electrons or holes
D_p	Diffusion coefficient of holes
E	Electric field
E_g	Forbidden energy gap
E_i	Intrinsic Fermi level
E_0	Applied electric field
E_t	Trap energy level
E_x	Electric field in the X-direction
G	Generation rate
G_λ	Generation rate for the first pass of photons penetrating from the front surface
I	Radiation intensity
I_{SC}	Short-circuit current
J	Current density
K	The probability that an incident electron will create a new recombination centre
L	Length of sample
L_C	Distance between illumination boundary and nearest end contact
L_D	Diffusion length
N	Total number of carrier pairs
N_D	Donor concentration
N_e	Total number of bombarding electrons
N_{st}	Number of surface trapping centres per unit area at the surface
N_t	Trap density
N_{t0}	Concentration of recombination-generation centres before irradiation
P_{max}	Maximum power dissipation
R	Reflectivity of the illuminated surface
R_L	Resistance in series with voltage supply
R_0	Dark (specimen) resistance
T	Absolute temperature
U	Recombination rate

U_n	Recombination rate of electrons
V_0	Applied dc voltage
V_{0C}	Open-circuit voltage
α	Absorption coefficient
b	Ratio of electron mobility to hole mobility
d	Drift length
ΔG	Change in conductance
Δn	Excess electron carriers
$\Delta n/n_0$, $\Delta p/p_0$	Relative excess carrier
Δn_0	Excess electron carriers at time $t = 0$
Δp	Excess hole carriers
ΔR	Change in resistance
$\Delta \sigma$	Change in conductivity
ΔT	Change in temperature
ΔV	PCD voltage amplitude
e	Electronic charge
ϕ_M	Work function of metal
ϕ_s	Work function of semiconductor
i	DC current
i_0	Maximum dc current
i_s	Sample current
k	Boltzman constant
λ	Free space wavelength
m^*	Effective mass
μ_n	Mobility of n-type semiconductor
μ_p	Mobility of p-type semiconductor
n_i	Intrinsic carrier concentration
n_ℓ	Pair density of back surface
n_s	Pair density of front surface
p	Hole density
p_n	Hole density in n-region
p_{n0}	Hole density in n-region at time $t = 0$
p_0	Density of free holes
p_s	Hole density at front surface
r	Specimen radius
ρ	Resistivity
s	Surface recombination velocity
s_A	Surface recombination velocity for the x-face

s_B	Surface recombination velocity for the y-face
s_C	Surface recombination velocity for the z-face
s_0	Initial surface recombination velocity
s_1	Surface recombination velocity of front surface
s_2	Surface recombination velocity of back surface
σ	Capture cross section
σ_n	Electron capture cross section
σ_0	Dark (specimen) conductivity
σ_p	Hole capture cross section
τ	Minority carrier lifetime
τ_B	Bulk lifetime
τ_f	Filament in the limit as Δn approaches infinity
τ_n	Electron lifetime
$\tau_{n,p}$	Lifetime of either electron or hole
τ_0	Lifetime in the limit as Δn approaches zero
τ_s^{-1}	Surface recombination rate
τ_p	Hole lifetime
Θ	Hall angle
2A	Specimen length
2B	Specimen width
2C	Specimen thickness
2h	Height of right circular cylinder

CHAPTER 1

INTRODUCTION

Minority carrier lifetime is defined (1) as "the average time interval between the generation and recombination of minority carriers in a homogeneous semiconductor".

Why minority carrier lifetime measurement is important can be summarized as follows :

a) Measurements of excess carrier lifetime are a requirement in quality control in the production of semiconductors.
b) As a function of resistivity, injection level, and temperature, it furnishes means for checking carrier recombination theory.
c) The minority carrier lifetime of the base (or substrate) region of a p-n junction solar cell or diode is one of the most important material parameters which influences most performance. It limits the collection efficiency and power conversion efficiency achievable in a solar cell, and it controls the current-voltage characteristics in a long base (non-illuminated) diode.
d) Apart from the fundamental information that can be obtained from lifetime measurements, the design of devices (e.g., transistors) is impossible without some information on carrier lifetime.
e) It is of interest in studies of the basic energy level structure of semiconductors.
f) Since the density of the minority carriers being small may be more readily varied, many electronic processes in semiconductor technology are controlled by the minority carriers.

CHAPTER 2

LIFETIME MEASUREMENT TECHNIQUES

Various methods have been devised in the past for the measurement of carrier lifetime and employed with considerable success on crystals of germanium and silicon (2-8).

A. Transient Methods

1. Filamentary Transistor Method. The first method of measuring lifetime was used by Haynes and Shockley. A pulse of carriers is injected at a point contact biased as emitter and is swept along the filament by an externally applied electric field. The pulse is detected, then, at a second point contact biased as collector and the shape of the pulse is examined as a function of the time of travel. The field and the spacing between the emitter and the collector can be changed. In general, one expects that the total area under the pulse will decrease as exp $(-\frac{t}{\tau})$ with the time (t) of travel. However, the surface recombination often prevents an observation of a single exponential decay and the observed time constant τ_{obs} is actually composed of both surface and volume components. This method of lifetime measurement has one noticeable advantage. It is easy to perform checks concerning the mobility of the carriers constituting the travelling pulse. This in turn suggests whether trapping was important in the process.

2. Photoconductive Decay Method. Short pulses of light are used to introduce excess carriers, resulting in increase of the conductivity of the sample. This increase can be measured by passing a small dc current through the sample and through a resistor. The decay of the voltage across the resistor after termination of the pulse is always measured. The lifetime is the time necessary for this voltage to decay to $\frac{1}{e}$ of its original amplitude. The decay constant can be affected by surface recombination and by trapping of carriers. In Si, the former usually results in a sharp initial decay and can be minimized by the use of penetrating radiation. Trapping in Si has been studied by the use of this method. It usually affects the decay curve by contributing

a longtime constant tail, which however, can often be eliminated or reduced by dc illumination. This illumination produces carriers which fill the traps forcing the carriers produced by the pulsed light to recombine rather than be trapped. The photoconductivity decay method permits a resolution of lifetime limited by the sharpness of the cut-off of the light pulses. Photoconductivity decay also permits the investigations of surface recombination. It can also furnish information about lifetime in a localized portion of the sample if such a portion alone is exposed to light and provided the electric field E is small. There are several variants of this method, depending on the source of injection.

Navon et al has injected carriers electrically and has measured the decay of voltage during the time of travel of the carriers between two contacts. If the lifetime is shorter than the transit time, the analysis is similar to photoconductivity case.

Wertheim (9) has adapted the method for measurements of lifetime of the order of 10^{-8} second by the use of a pulsed electron beam from a Van de Graff accelerator.

P.C.D. method is most commonly used for homogeneous semiconductors and has been adopted as a standard by both the IEEE(10) and the ASTM (11). It requires resistivity and conductivity type measurement of a sample on which lifetime measurement will be performed.

B. Steady-state Methods

1. Diffusion Length Measurements: In these measurements the diffusion length L is usually measured and the result is converted to the lifetime. The simplest case is one in which the carriers injected optically are collected at a p-n junction. The distance between the collecting junction and the injecting light can be varied. The excess minority carrier density in n-type material can be expressed as:

$$\frac{d(\delta p)}{dt} = \frac{d(\delta p)}{\tau_p} + D_p \frac{d^2(\delta p)}{dx^2}$$

and the observed response in the simplest case is proportional to $\exp\left(-\frac{X}{\sqrt{D_p \tau_p}}\right)$.

Chopped light is usually used for reasons of sensitivity and

the rms voltage across a resistor in series with the detector is measured. The motion of carriers proceeds by diffusion as long as the applied electric field is small. Adam (12) improved this method by allowing for a simultaneous measurement of the diffusion constant. This is done by scanning a light spot across the junction.

The advantage of this method consists of its freedom from trapping effects, as the diffusion length rather than time is measured. However, several authors (13) report difficulties with measurement on Si due to surface conductance which upsets the exponential response. The experimental resolution in the diffusion length method is limited by the size of the light spot. The experimental arrangement requires sophisticated instrumentation if lifetimes shorted than 1 μsec are to be resolved (14) . The final resolution is of course dependent on the mobility of minority carriers, the higher the mobility the lower the resolved lifetime.

2. Photomagnetoelectric Effect. This is an effect similar to the Hall effect except that it is associated with the diffusion of optically injected carriers (15), (16). The direction of light and of the magnetic field are mutually perpendicular. The carriers produced by the light diffuse across the slab, but are deflected by the magnetic field in opposite directions. The electron and hole currents add and give a total PME short circuit current. In the open circuit condition this current is cancelled by a drift current in the opposite direction. The total current will be composed in varying degrees of the PME current and the drift current, depending upon the volume recombination. If the short circuit PME current is measured as well as the relative conductance increase without the field, then it is possible to calculate the lifetime of carriers without the necessity of measuring the light intensity or the recombination velocity of the surface (17) .

In particular in the case of a sample at least several diffusion lengths thick, and for injection which is not exceedingly high, one has:

$$I_{SC} = -\,\theta(\mu_n + \mu_p)^{-1}\left(\frac{D}{\tau}\right)^{\frac{1}{2}} \Delta G \qquad (2.1)$$

where θ is the Hall angle and ΔG is the change in the conductance.

Eq'n (2.1) implies that under identical experimental conditions the product of lifetime and mobility is constant. The PME method is

therefore able to resolve very low lifetimes in semiconductors with highly mobile carriers. Determinations of lifetime as low as 10^{-9}-10^{-10} seconds have been reported. Buck and McKim have investigated the PME effect in Ge finding a good agreement with the theory. The lifetimes obtained agreed well with those determined by photoconductivity decay methods. The method is also very versatile in its ability to measure the recombination velocities of both the illuminated and the dark surfaces.

3. Surface Photovoltage (S.P.V.) Method. It is most convenient for the direct measurement of the minority carrier diffusion length which is related to the carrier diffusion coefficient and lifetime by the relation $L = \sqrt{D\tau}$. SPV method has been used by a number of investigators during the past few years (18-28), and a tentative standard for this measurement has also been established by the ASTM (29) .

Whenever excess carriers are injected into a region of semiconductor in which there exists an electric field a separation of carriers occurs resulting in modification of the electric field and the generation of photovoltage. When the electric field occurs at the surface of a semiconductor the resulting voltage is termed the surface photovoltage, and appears as a change in potential between the surface and the bulk of the sample. Surface photovoltage is usually defined as the change in the surface barrier height ΔV_S, produced by illumination of the free semiconductor surface.

In S.P.V. method the specimen surface is illuminated with chopped monochromatic radiation of energy slightly greater than the band gap of the semiconductor, electron-hole pairs are produced and diffuse to the surface where they are separated by the electric field of the depletion region to produce a surface photovoltage.

C. Other Methods

1. Collection of Minority Carriers by Voc and Isc Method.
The open-circuit voltage or short-circuit current may be used instead of the SPV for the measurement of diffusion length in the base region of the device (30). The incident light intensity required to produce a given Voc or Isc is measured as a function of wavelength, and the diffusion length may be obtained from the extrapolation of the

intensity versus reciprocal absorption coefficient plot.

2. Open-Circuit Voltage and Short-Circuit Current Decay Method.
Open-circuit voltage decay method was originally applied to the Ge diodes (31).

3. Contactless Lifetime Measurement Techniques.
All the techniques given here, except microwave PCD technique, either require the use of mechanical probes which may be destructive to the material, or require the use of special device structures.

Originally contactless nondestructructive diffusion length measurement method, consisting optical excitation of excess carriers and simultaneous observation of infa-red absorption in Ge bulk materials due to these carriers, had been developed by Harrik (32).

4. The Drift Experiment.
Provided that the crystal filament is well ecthed and that dimensions of the small sides are at least two or three diffusion lengths, this experiment should yield the true lifetime independent of surface effects. Any trapping effects can be observed as an asymmetry of the collector waveform and eliminated by continuous illumination (13).

5. The Travelling Light Spot Experiment.
A method for which trapping processes have no effect on the measured distribution of carriers is desirable. Such a method is the travelling light spot experiment introduced by Goucher (1951), (33) and for which details have been given by Valdes (1952),(34). This method has the advantage that it can be used on a massive portions of crystals of irregular shape with one surface ground flat. Although reliable for the determination of τ in Ge, there are several difficulties to be overcome when measurements are made on Si.

a) Collector Non-linearity. By continuous illumination of the collector it can be forced to operate in the range where its conductance is a linear function of local minority carrier density.

b) Back-Scattered Light. If thin specimens are used there is a danger that incident light of wavelengths at or beyond the absorption edge may be scattered from the back surface, return to the front surface of the crystal, and generate charge carriers there. This effect would give an anomalously long value of diffusion length, but is only

important in crystals for which the dimensions of the short sides are about 1 mm or less.

c) Surface Recombination. With high quality Si crystals of type now available the large surface recombination velocity S causes a considerable modification to the distribution of injected carriers from the incident light spot.

The travelling light spot provides a ready method for the examination of regions of large ingots necessitating only grinding flat the area of surface to be investigated, fitting one base lead, and etching. Precautions have to be taken to correct for or to eliminate the effects of surface recombination and to linearize the collector. If these precautions are taken, the method provides a simple and accurate measurement of diffusion length and hence lifetime.

CHAPTER 3

PHOTOCONDUCTIVE DECAY METHOD

3.1. Introduction

The experimental arrangement for the measurement of minority carrier lifetime in semiconductors by P.C.D. method is shown in Fig. 3.1. A short pulse of light is commonly used (2 , 6) to excite non-equilibrium carriers in a sample across which an electric field is applied. The excess carriers produce an initial change in the conductivity, which returns to equilibrium value when the light is turned off and carriers recombine. Since the recombination rate depends on the number of excess carriers present at any time t, the number of excess carriers decays exponentially with time, i.e.,

$$\Delta n = \Delta n_o \exp\left(-\frac{t}{\tau}\right) \tag{3.1}$$

Where Δn_o is the number of excess carriers at time t=0 and τ is the minority carrier lifetime. The excess conductance of the sample under proper experimental conditions is directly proportional to the total number of excess carriers present. For a small conductance change the voltage change at the terminals of the constant current source is proportional to the conductance change. This voltage, therefore, decays back to its steady state value with the same time dependence as the number of excess carriers in the sample. The time dependence of the excess carrier density is obtained from the display of the voltage change on an oscilloscope. Analysis of the oscilloscope trace then yields the sample lifetime.

Many difficulties are encountered when an attempt is made to measure the carrier lifetime accurately. The decay constant can be affected by surface recombination and by trapping of carriers. In Si the former usually results in a sharp initial decay and can be minimized by the use of penetrating radiation (35). Trapping in silicon has been studied by the use of P.C.D. method (36). It usually affects the decay curve by contributing a long time constant tail, which however, can be eliminated or reduced by dc illumination. This illumination produces carriers which fill the traps forcing the carriers produced by the pulsed light to recombine rather than be

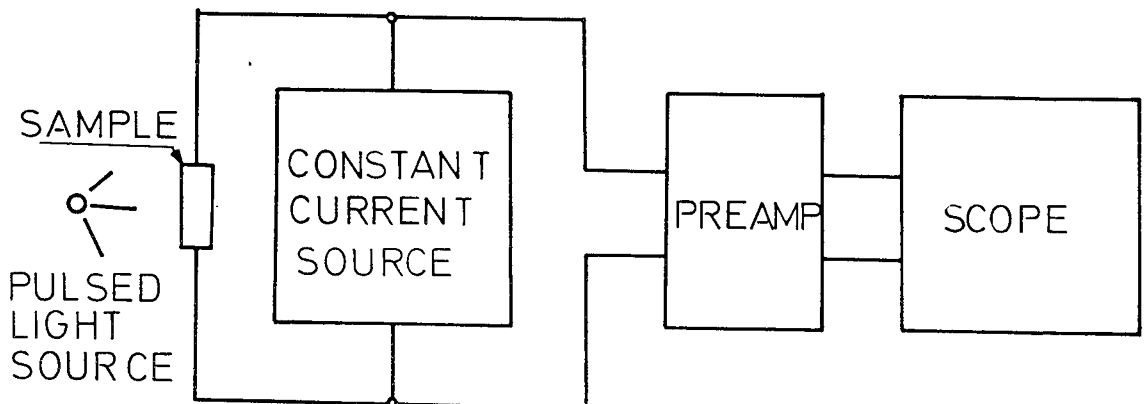


Fig.3.1. Experimental arrangement of PCD method.

trapped.

One of the major problems in interpreting P.C.D. lifetime measurements in silicon is the separation of the lifetime of carriers excited near the surface and that of carriers excited in the bulk of the crystal Navon, Bray and Fan evaluated the two lifetimes (3) by systematically studying the lifetime while changing the cross-sectional dimensions 2Bx2C of a rectangular sample. Since the surface lifetime τ_s is related to these dimensions such a procedure will separate the two lifetimes. The separation of the surface and the bulk minority-carrier lifetimes in silicon has been experimentally achieved by Carrol and Casper using the P.C.D. method (37).

Besides photoexcitation, other methods of injecting excess carriers have been developed. Wertheim and Augustyniak (38) have been able to measure very short lifetimes by the use of a pulsed electron beam from a Van de Graff accelerator. Curtis and Wickenhiser (39) irradiated samples with 150 kev xray pulses of 50 nsec duration. The sample penetration by these pulses is greater than that achieved with light sources and silicon filters. Lichtenstein and Willard (40) also used a pulsed x ray source, but they devised a contactless method of measuring the lifetime with an r.f. tank circuit. Naber and Snowden (41) have developed a microwave reflection technique. In these experiments, more penetrating radiation sources reduce surface effects significantly and should yield accurate values of the bulk lifetime.

Navon et al (3) has injected carriers electrically and has measured the decay of voltage during the time of travel of the carriers between the two contacts. If the lifetime is shorter than the transit time the analysis is similar to the P.C.D. case.

The P.C.D. method was studied in detail because of its wide acceptance and its adoption as a standard by both the IEEE (10) and the ASTM (11). There is no specification in the standards as to whether a chopped (steady-state) or pulsed (transient) light source is to be used (although pulsed light is given some preference). If the light is applied to the specimen for a time equivalent to many lifetimes, as in the case of chopped light, a steady-state excess carrier distribution is established. This does not occur under pulsed light excitation. A theoretical comparision of chopped and pulsed light was presented by Blakemore and Nomura (42) as part of a more general discussion of higher modes of recombination. They showed that the error

in τ caused by higher modes is greater for pulsed light excitation than for chopped light excitation under a variety of measurement conditions. This conclusion is also supported by a theoretical treatment reported by Ridley (43) . Because of this, a truer value for τ is obtained if chopped light rather than pulsed light is used. The experimental and analytical work relevant to the P.C.D. method has been summarized by Maltis and Baraody (44). They showed that, the chopped light measurement was more reproducible than the pulsed light measurements.

3.2. Photoconductivity

The conductivity of a semiconductor is expressed as

$$\sigma_o = e(n_o\mu_n + p_o\mu_p) \qquad (3.2)$$

where n_o and p_o are the densities of free electrons and holes, and μ_n and μ_p are the electron and hole mobilities respectively.

The formation of electron-hole pairs, through the absorption of radiation which causes band-to-band transitions, increases the number of charge carriers of both types. The change in conductivity is then given by

$$\Delta\sigma = e(\Delta n\mu_n + \Delta p\mu_p) \qquad (3.3)$$

where Δn and Δp are the excess electron and hole concentrations, respectively. The excess electron and hole concentrations can be given by the equations

$$\Delta n = G\tau_n \quad , \quad \Delta p = G\tau_p \qquad (3.4)$$

where G is the generation rate of electron-hole pairs per second per unit volume of semiconductor. If we assume that the number of traps is so small that $\Delta n = \Delta p (\tau_n = \tau_p)$; the change in conductivity $\Delta\sigma$ is then given by the equation

$$\Delta\sigma = e\,G\,\tau_n\,(\mu_n + \mu_p) \qquad (3.5)$$

This relation shows why the minority carrier lifetime is the key parameter in the photoconductivity. If trapping is present, however, one of the carrier may spend little time in its band before being trapped. From eq.(3.5), it is obvious that for maximum photoconductivity response, we need a crystal which has high mobility and long lifetime.

The phenomenon of photoconductivity consists of a few generic processes (1) generation, by external excitation of mobile carriers, (2) transport of those mobile carriers, (3) recombination.

Generation consists of exciting electrons across the forbidden gap, i.e, promoting charge from a nonconducting state (valence band) to a conducting state (conduction band). Both the electron in conduction band and the hole in the valence band are then free to contribute to the electrical conductivity. Transport occurs strictly in the extended band states. The free-like motion of the carriers are interrupted sporadically by scattering, among the band states, due to phonons or impurities. Direct recombination of electrons and holes (at moderate free carrier densities) is an improbable process. The recombination usually occurs through the intermediary of the impurity or defects levels in the gap.

3.3. Dependence of P.C.D. Voltage on Excess Carrier Density and Filament Lifetime.

When a section of the crystal (which is driven by a constant current generator) is illuminated with a pulse of light, the change $\Delta V(t)$ across the crystal is given by

$$\Delta V(t) = i \Delta R(t) \qquad (3.6\text{-a})$$

If the crystal is sufficiently uniform in cross-section and conductivity and if the density of added carriers is everywhere small compared to the density of majority carriers ($\Delta n, \Delta p << n_o, p_o$) the lines of current flow will not be disturbed appreciably by the injection. The total change in resistance can then be computed by integration along the X-axis. One finds

$$\Delta V(t) = \int_{\text{crystal}} \frac{<\Delta\sigma(x,t)>}{<\sigma_o(x)>} E(x)dx \qquad (3.6\text{-b})$$

where E is the electric field and the angular brackets in Eq.(3.6-b) denote an average done over the area of the crystal perpendicular to the lines of current flow. E is related to the specimen current density (J) where

$$J(x) = \sigma_o E(x) = \frac{i(x)}{A}$$

If trapping can be neglected, the light produces an equal number of minority carrier and majority carriers ($\Delta n = \Delta p$).
Then $\Delta V(t)$ becomes

$$\Delta V(t) = \int_{crystal} \frac{e(\mu_n + \mu_p)\Delta_n}{A\,\sigma_o^2}\, i\, dx \qquad (3.6\text{-c})$$

Integration of this equation gives

$$\Delta V(t) = -ie\,\frac{L}{A}\,\frac{\mu_n + \mu_p}{\sigma_o^2}\,\Delta n(t) \qquad (3.6\text{-d})$$

This shows that ΔV is directly proportional to excess carrier concentration.

Using Eq.3.1 into the Eq.3.6-d one can get

$$\Delta V(t) = \Delta V_o\, e^{-\frac{t}{\tau}} \qquad (3.6\text{-e})$$

where

$$\Delta V_o = -ie\,\frac{L}{A}\,\frac{\mu_n + \mu_p}{\sigma_o^2}\,\Delta n_o$$

- i is the constant current which flows through the sample,
- e is the electronic charge,
- L is the length of the filament,
- A is the cross sectional area of the filament.

Accordingly, the effective measured lifetime, ordinarily called the filament lifetime, τ_f at any instant is given by

$$\tau_f = -\Delta V\left[\frac{d(\Delta V)}{dt}\right]^{-1} \quad \text{if} \quad \Delta V \ll V_o \qquad (3.7)$$

where V_0 is the applied voltage across the filament. If the constant current is passed through the specimen by means of ohmic contacts at each end, and the specimen voltage is amplified and displayed on an oscilloscope, the analysis of the oscilloscope trace then yields the filament lifetime. The inverse dependence of ΔV on σ_0^2 means that the measurement becomes rapidly more difficult as the conductivity of the material increases.

The recombination mechanisms which jointly determine τ_f will include both volume and surface effects. It is necessary to take precautions to calculate the surface contribution if volume lifetime is to be measured adequately.

3.4. Recombination

Whenever the thermal-equilibrium condition of a physical system is disturbed, i.e., $pn \neq n_i^2$, there are processes by means of which the system can be restored to equilibrium, i.e., $pn=n_i^2$ (45).

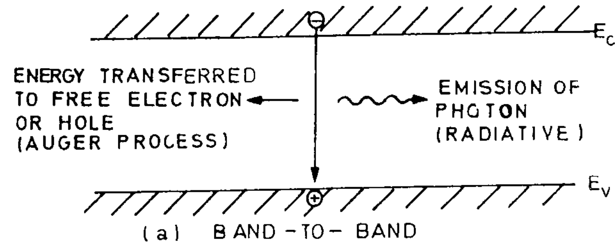
A- Band-to-Band Recombination :

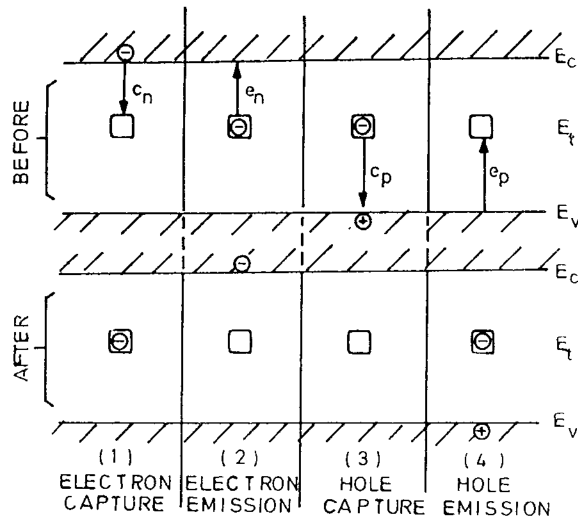
Fig.3.2-a illustrates the band-to-band recombination where an electron-hole pair recombines. Transition of the electron from the conduction band to the valence band is possible by the emission of a photon (radiative process) or by transfer of the energy to another free electron or hole (Auger process). The latter process is the inverse process to impact ionization, and the former is the inverse process to direct optical transitions, which are important for most III-V compounds with direct energy gaps.

B- Single-Level Recombination

It occurs when only one trapping energy level is present in the band gap as in Fig.3.2-b it consists of four steps: namely, electron capture, electron emission, hole capture, and hole emission. The recombination rate, U(in unit of cm^{-3} sec^{-1}), is given by

$$U = \frac{\sigma_p \sigma_n \nu_{th} (pn-n_i^2) N_t}{\sigma_n \left[n + n_i \exp\left(\frac{E_t - E_i}{kT} \right) \right] + \sigma_p \left[p + n_i \exp\left(-\frac{E_t - E_i}{kT} \right) \right]} \qquad (3.8\text{-a})$$





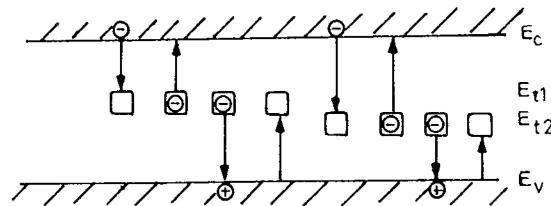


Fig.3.2. Recombination Processes

(a) band-to band recombination (radiative or Auger process)

(b) single-level recombination

(c) multiple-level recombination

where σ_p and σ_n are the hole and electron capture cross sections respectively, ν_{th} the carrier thermal velocity equal to $\sqrt{3kT/m^*}$, N_t the trap density, E_t the trap energy level, E_i the intrinsic Fermi level and n_i the intrinsic carrier density. It is obvious that under a thermal equilibrium condition, $pn = n_i^2$, $U = 0$. Furthermore, under the simplified condition that $\sigma_n = \sigma_p = \sigma$, Eq (3.8-a) reduces to

$$U = \sigma \nu_{th} N_t \frac{(pn - n_i^2)}{n + p + 2 n_i \cosh\left(\frac{E_t - E_i}{kT}\right)} \qquad (3.8\text{-b})$$

The recombination rate approaches a maximum as the energy level of the recombination center approaches midgap, i.e., $E_t \simeq E_i$. Thus the most effective recombination centers are those located near the middle of the gap.

Under low injection conditions, i.e., when the injected carriers ($\Delta n = \Delta p$) are much fewer in number than the majority carriers, the recombination process may be characterized by the expression

$$U = \frac{P_n - P_{no}}{\tau_p} \qquad (3.9)$$

where

$$\tau_p = \frac{1}{\sigma_p \nu_{th} N_t} \qquad (3.10\text{-a})$$

is the minority carrier lifetime (hole lifetime) in n-type semiconductor. Similarly for a p-type semiconductor, the electron lifetime is as follows :

$$\tau_n = \frac{1}{\sigma_n \nu_{th} N_t} \qquad (3.10\text{-b})$$

C- Multiple Level Case

Fig.3.2-c illustrates many level case where more than one trapping level is present in the band gap. The reciprocal of the resulting lifetime can be expressed as the sum of the reciprocal time constants due to several separate recombination levels only for the case of small density of centres.

D- Trapping

If the re-emission of the carriers from an energy level in the forbidden gap is more probable than the final step of recombination then an imperfection giving rise to this level is called a trap. Hornbeck and Haynes have studied trapping in silicon crystals (36). In Fig.3.3, the re-emission 2 of the electron will occur rather than recombination if the hole-capture cross section is very low. This could be the case for instance, if the level E_t represented a doubly ionized donor (with two positive charges). Such a level would be singly positively charged after step 1 and would have a very small attraction for a hole (low capture cross section for step 7). In this case the time spent by the carrier in conduction band is always the lifetime (mean life)of the electron and trapping affects only the time spent in the traps which can exceed by the order of magnitude of the lifetime of carrier. This effectively reduces the mobility of carrier and gives an apparent long decay constants (35).

E- Surface Recombination

The phenomenon of surface recombination as well as of trapping should be carefully distinguished from recombination in the volume of the material. It has been found that if free carriers are produced close to a surface, they may diffuse towards surface and consequently recombine at the surface rather than in volume. This will be influenced by several factors such as the geometry of the sample, the degree of penetration of photons (when photons are used to produce the carriers) as well as the effectiveness with which the surface reflects the carriers which approach it from the volume (35,46). Analogous to the low injection bulk recombination process, in which the reciprocal of the minority carrier lifetime $\frac{1}{\tau_p}$ is equal to $\sigma_p \nu_{th} N_t$, the surface recombination velocity is given by

$$S_o = \sigma_p \nu_{th} N_{st} \qquad (3.11)$$

where N_{st} is the number of surface trapping centres per unit area at the surface. However, the surface recombination velocity will be more complicated in form when a surface charge region is present; it will depend not only on N_{st} but also on the donor concentration and on the

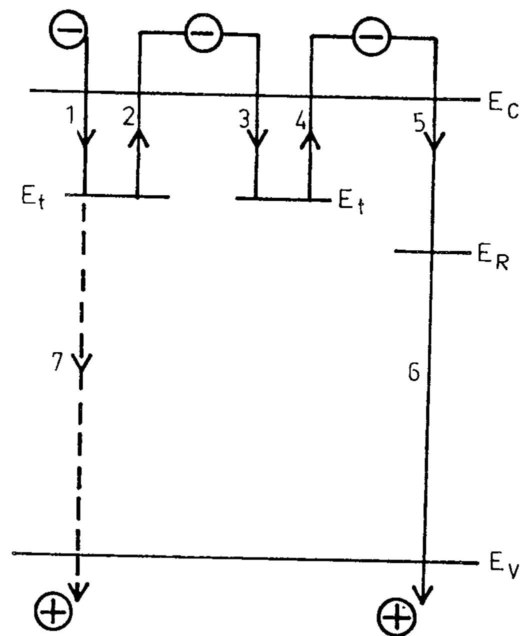


Fig.3.3. Trapping effects. The electron can be trapped at the levels E_t and released into the conduction band several times before recombining at E_R.

amount of surface charge which determines the electron and hole concentrations at the surface (n_s, p_s). In this case S will be given by (45,46)

$$S = S_o \frac{N_D}{n_s + p_s + 2 n_i} \qquad (3.12)$$

Surface recombination velocity (S) will go through a maximum when ($n_s + p_s$) is at minimum. This will happen when $n_s \simeq p_s \simeq n_i$. The maximum surface recombination velocity will then be given by

$$S_{max} = S_o \frac{N_D}{4 n_i}$$

F- Recombination Due to Specific Mechanism

i) Impurities

Many impurities have energy levels close to the middle of the band gap. These impurities may serve as efficient centres. A typical example is gold in silicon (47,48). It is found that the minority carrier lifetime decreases linearly with the gold concentration over the range of 10^{14} to 10^{17} cm^{-3} where τ decreases from about $2x10^{-7}$ second to $2x10^{-10}$ second. This effect is important in some switching device applications when a short lifetime is a desirable feature, but not for solar cells where a long lifetime is desirable.

ii) Radiation Damage

Another manner in which energy levels can be introduced into the forbidden gap is by high-energy particle irradiation (45,49-52,53) which causes displacement of host atoms and damage to lattices. These in turn introduce energy levels in the band gap and can act as acceptors, donors and recombination centres. For example (45), in silicon electron irradiation gives rise to an acceptor level at 0.4 eV above the valence band and a donor level at 0.36 eV below the conduction band, neutron irradiation creates an acceptor level at 0.56 eV; deuteron irradiation gives rise to an interstitial state with an energy level 0.25 eV above the valence band. The dependence of lifetime to the high energy electron radiation was given by (54)

$$\tau = \frac{\tau_o}{1 + \frac{KN_e}{N_{to}}} \qquad (3.13)$$

where N_{to} is the concentration of recombination-generation centres before irradiation, K is the probability that an incident electron will create a new recombination centre, N_e is the total number of bombarding electrons hitting a unit area of the surface of the sample. This equation predicts that the lifetime should decrease from its initial value τ_o in an inversely proportional manner with increasing radiation dose. The influence of radiation on the lifetime (49-53, 55,56) of semiconductors is important in solar cells for all space applications.

iii) Surface States

The existence of surface states has been predicted theoretically by Tamm and by Shockley (57). If some of these surface states should have energy levels near the middle of the band gap, we would expect them to act as efficient surface recombination centre.

It is generally believed that there exist two kinds of states on the surface of the semiconductor. The first type, the "fast" states are located at the interface of the semiconductor and almost always present oxide layer. The density of these states is about $10^{11} cm^{-2}$ and depends on the initial treatment of the surface. These states are believed to be responsible for surface recombination. It has been observed that the density of these states is increased if the surface is mechanically damaged, heated in a vacuum bombarded with ions, etched with HF(35). There exists another group of states, in densities exceeding 10^{13} cm^{-2}, so called "slow" states, which exhibit long decay times (35). These states are probably due to imperfections at the surface of the oxide or in the oxide layer. Their capture cross sections are orders of magnitude lower than of the "fast" states. These states are responsible for the variation of surface potential with the ambient gases, but not for the observed recombination velocities.

Finally, a given centre can act as a recombination centre or a trap centre depending on the relative magnitude of the capture cross sections for electrons and holes.

3.5. Excess Minority Carriers

A. Solution of Continuity Equation in Transient Case

The differential equation governing the excess carrier density Δn in the interior of a semiconductor with a uniform electric field E_x in the X direction is (58)

$$\frac{\partial \Delta n}{\partial t} = \frac{\Delta n}{\tau_B} + \mu E_x \frac{\partial \Delta n}{\partial X} + D \nabla^2 \Delta n \tag{3.14}$$

where τ_B is the bulk lifetime. The solution of this equation for the case of the rectangular parallel piped shown in Fig.3.4 is given by (59).

$$\Delta n(x,y,z,t) = G(\cos ax) \exp(\mu E_x X/2D_n)(\cos by)(\cos cz) \times \exp - \left[\frac{1}{\tau_B} + D (a^2+b^2+c^2) + \left(\frac{\mu E}{4D}\right)^2 \right] t \tag{3.15}$$

The boundary conditions on the faces of the sample are taken to be

$$D \frac{\partial \Delta n}{\partial x} = \pm S_a \Delta n, \quad D \frac{\partial \Delta n}{\partial y} = \pm S_b \Delta n, \quad D \frac{\partial \Delta n}{\partial z} = \pm S_c \Delta n,$$

where S_a, S_b and S_c are so-called surface recombination velocities for the x, y, and z faces, and the values of S_a, S_b and S_c, can be found from the transcendental equations which result when boundary conditions are substituted in Eq.3.15. Then Δn can be written

$$\Delta n(x,y,z,t) = G \left(\cos \frac{\xi x}{A}\right) \exp(\mu E_x X/2D) \left(\cos \frac{\eta y}{B}\right) \cos\left(\frac{\zeta z}{C}\right) \times \exp - \left[\frac{1}{\tau_B} + D\left[\frac{\xi^2}{A^2} + \frac{\eta^2}{B^2} + \frac{\zeta^2}{C^2}\right] + \frac{(\mu E)^2}{4D} \right] t \tag{3.16}$$

where $\xi \tan \xi = \frac{S_a A}{D}$, $\eta \tan \eta = \frac{S_b B}{D}$, and $\zeta \tan \zeta = \frac{S_c C}{D}$

The time dependent term in Eq.3.16 can be separated into three parts. The first term is the reciprocal of the bulk lifetime. The second term which we can abbreviate by $\left(\frac{1}{\tau_s}\right)$ is the contribution to the total decay constant arising from the additional diffusion

current caused by the distortion of the distribution by the electric field. For the lifetime measurements the last term should be kept small compared with the sum of the first two, i.e.,

$$\frac{(\mu E)^2}{4D} \ll \frac{1}{\tau_B} + \frac{1}{\tau_s} \qquad (3.17)$$

To find the change in conductance of the sample we need the total number of carriers added and hence Eq.3.16 must be integrated over the volume of the sample. The result is

$$\int_{volume} \Delta n . \Delta V = \Delta n_o \exp\left(-\frac{t}{\tau_f}\right) \qquad (3.18)$$

where τ_f is the filament lifetime which is measured from the P.C. decay.

The magnitude of the surface term $(\frac{1}{\tau_s})$ depends on S_a, S_b, and S_c. We shall discuss two cases here.

Case 1: If S is very large on all faces $(S_a = S_b = S_c = \infty)$, then ξ, η, and ζ take the simple form

$$\xi = \eta = \zeta = \frac{\pi}{2}$$

and $\frac{1}{\tau_s}$ becomes

$$\tau_s^{-1} = \frac{\pi^2 D}{4}\left[\frac{1}{A^2} + \frac{1}{B^2} + \frac{1}{C^2}\right] \qquad (3.19)$$

Case 2: If S is very large on faces perpendicular to the x-axis and equal to some intermediate value on the other faces $(S_a = \infty,\ S_b = S_c = S)$, then $\frac{1}{\tau_s}$ becomes

$$\tau_s^{-1} = \frac{\pi^2 D}{4A^2} + D\left[\frac{\eta^2}{B^2} + \frac{\zeta^2}{C^2}\right] \qquad (3.20)$$

Finally, the bulk lifetime τ_B is found by

$$\frac{1}{\tau_B} = \frac{1}{\tau_f} - \frac{1}{\tau_s} \qquad (3.21)$$

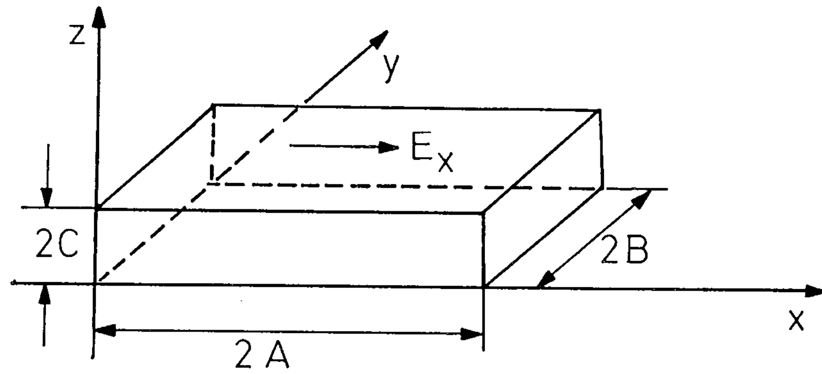


Fig.3.4. Sample geometry.

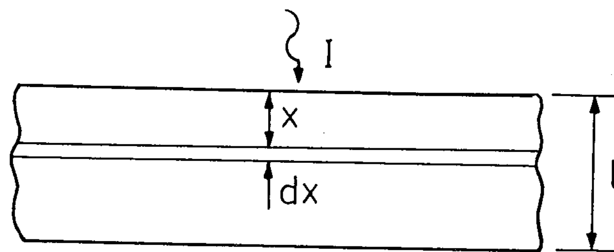


Fig.3.5. Schematic arrangement ℓ = sample thickness, I = incident photon flux.

B- Solution of Continuity Equation In Steady-State Case

The required continuity equation is

$$\frac{\partial \Delta n}{\partial t} = G_{\lambda} - U_n + D_n \frac{d^2 \Delta n}{dx^2} \tag{3.22}$$

For simplicity, consider the photoconductor to have the form of large sheet with thickness ℓ as in Fig.3.5.

Let it be illuminated on one face by radiation having intensity I(photon/second). The charge carriers produced by illumination will diffuse in the positive or negative X direction because of the concentration gradient. It is assumed that carrier pairs recombine in the volume of the material at a rate determined by τ and further that they will recombine at the surface at a rate which is represented by the surface recombination velocity s. For steady state condition, $\frac{\partial(\Delta n)}{\partial t} = 0$, and Eq.3.22 becomes

$$D_n \frac{d^2 \Delta n}{dx^2} = \frac{\Delta n}{\tau} - (1-R)\, I\, \alpha\, e^{-\alpha x} \tag{3.23}$$

For convenience, let $\frac{1}{D\tau} = \beta^2$, and $\frac{(1-R) I \alpha}{D} = \gamma$

$$\frac{d^2 \Delta n}{dx^2} = \beta^2 \Delta n - \gamma\, e^{-\alpha x} \tag{3.24}$$

The general solution of this equation is given by

$$\Delta n = B e^{-\beta x} + C\, e^{\beta x} + \left[\frac{\gamma}{\beta^2 - \alpha^2}\right] e^{-\alpha x} \tag{3.25}$$

Boundary conditions are

$$\begin{aligned} \left[i_R \right]_o &= -D \frac{d\Delta n}{dx}\bigg|_{x=0} = -n_s S_1 \\ \left[i_R \right]_\ell &= -D \frac{d\Delta n}{dx}\bigg|_{x=\ell} = n_\ell S_2 \end{aligned} \tag{3.26}$$

where n_s is the pair density at the front surface and S_1 is the surface recombination velocity of the front surface; n_ℓ is the pair density at the back and S_2 is the back surface recombination velocity respectively.

Substituting these in Eq.3.25 and solving for the constants B and C, we obtain

$$B = \frac{\gamma}{\beta^2-\alpha^2}\left[\frac{(S_2-a)(b-S_1)e^{-\alpha\ell} + (S_1+a)(b+S_2)\,e^{\beta\ell}}{(b-S_1)(b-S_2)\,e^{-\beta\ell} - (b+S_1)(b+S_2)e^{\beta\ell}}\right] \tag{3.27}$$

$$C = \frac{\gamma}{\beta^2-\alpha^2}\left[\frac{(S_2-a)(b+S_1)\,e^{-\alpha\ell} + (S_1+a)(b-S_2)\,e^{-\beta\ell}}{(b-S_1)(b-S_2)\,e^{\beta\ell} - (b+S_1)(b+S_2)\,e^{\beta\ell}}\right] \tag{3.28}$$

where $\alpha D = a$ and $D\beta = b$

We assume that the increase in conductivity caused by the radiation is proportional to N, the total number of carrier pairs:

$$N = \int_0^\ell \Delta n(x)\,dx = \frac{1}{\beta}\left[B(1-e^{-\beta\ell}) + C\,(e^{\beta\ell}-1)\right] + \frac{\gamma(1-e^{-\alpha\ell})}{(\beta^2-\alpha^2)}$$

Finally N becomes

$$N = \frac{(1-R)I\alpha}{D(\frac{1}{L^2}-\alpha^2)}\left[\frac{1-e^{-\alpha\ell}}{\alpha} - L\left[\frac{\left[(S_1+S_2\,e^{-\alpha\ell})+\alpha D(1-e^{-\alpha\ell})\right]\left[\frac{D}{L}\sinh\frac{\ell}{L}\right] + \left[(S_1S_2(1-e^{-\alpha\ell})+\alpha D(S_2-S_1e^{-\alpha\ell})\right]\left[\cosh\frac{\ell}{L}-1\right]}{(\frac{D^2}{L^2}+S_1S_2)\,\mathrm{Sinh}\frac{\ell}{L} + \frac{D}{L}\,(S_1+S_2)\cosh\frac{\ell}{L}}\right]\right]$$

If $S_1 = S_2 = S$, N can be rewritten as

$$N = \frac{(1-R)I\tau}{1+K\coth\frac{W}{2}}\,(1-e^{-Z})\left[1+\frac{WR\left[W\coth\frac{W}{2} - Z\coth\frac{Z}{2}\right]}{W^2-Z^2}\right].$$

where $W = \frac{1}{\sqrt{D\tau}} = \frac{\ell}{L}$

$$Z = \alpha\sqrt{D\tau} = \alpha L$$

$$K = S\sqrt{\frac{\tau}{D}} = S\,\frac{L}{D}$$

Representative curves of photoconductivity $\left[P \rightarrow \frac{N}{(1-R)\,I\,\tau}\right]$ versus Z as a function of W and K parameters were computed by D_e Vore (60), when the parameters have these ranges: $Z=10^{-2} - \infty$, $W= 10^{-1}-10^{5}$, and $K = 10^{-4}-10^{2}$.

CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1. Introduction

Measurement of minority carrier lifetime is quite important as explained in Chapter 1.

The decay of excess carrier concentration in semiconductors has been measured in a number of ways. Most commonly known, perhaps, is the photoconductive decay method. In epitaxial layers and in thin single crystal wafers, surface recombination modifies lifetime measured by PCD method and PCD method requires ohmic contacts to the specimen. This method may be difficult if (1) the minority carrier lifetime is too short to measure conveniently, (2) and trapping effects give misleading results.

4.2. Photoconductive Decay Method

4.2.1. Apparatus

A block diagram of the apparatus used to observe the decay of photoconductivity is shown in Fig.4.1. The elements of the apparatus are explained as follows.

Light Source

There is presently no specification in the standards (61,62) as to whether a chopped or pulsed light source is to be used.

The difference between chopped light and pulsed light measurements is related to the carrier distribution at the beginning of decay. If light is applied to the specimen for a time equivalent to many lifetimes,as in the case of chopped light, a steady-state excess carrier distribution is established. This does not occur under pulsed light excitation. A theoretical comparision of chopped and pulsed light was presented by Blakemore and Nomura (63).

The desired features of the light source are (1) turn-off time should be shorter than measured lifetime, (2) intensity of light source should not be too excessive, (3) penetrating light source should be used to reduce the effect of higher modes of surface recombination, (4) the radiation wavelength should not be longer than

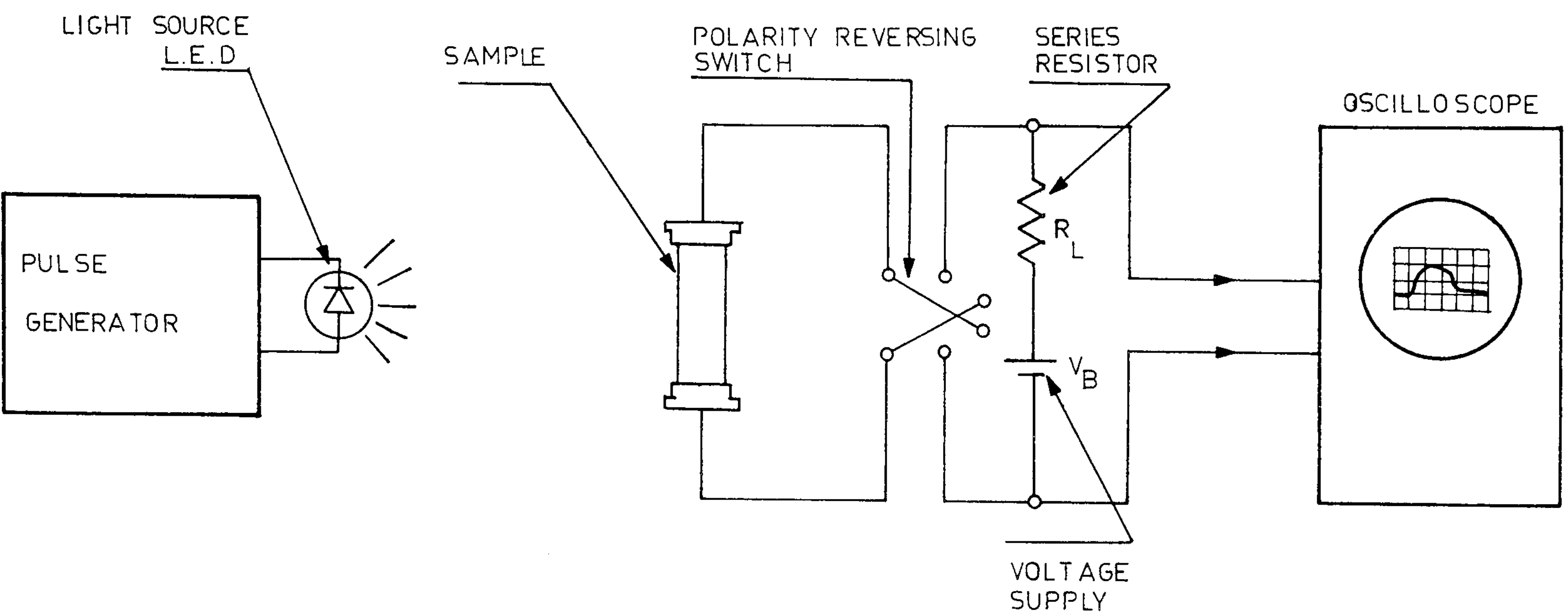


Fig.4.1. Schematic diagram of apparatus used in photoconductive decay method.

the absorption edge ($\lambda = 1.1\ \mu_m$ for S_i) where no electron-hole pairs are produced.

Infrared light emitting diode was used as the light source to produce uniform excess carriers throughout the specimen volume.

Pulse Generator

Pulse generator (Model 180) provided a pulsed field and delayed trigger for the photolight and oscilloscope. The frequency range of the pulse generator was 0.1 Hz-2 MHz, maximum output pulse was about 12.8 V.

Oscilloscope

The photoconductivity pulse was displayed with Textronix 5103N oscilloscope, the choice depends on the lifetime being measured. The frequency response of the detecting system must be adequate to display the decay curve without distortion. The time base of the oscilloscope was 0.1 μs - 2 sec. The Textronix 5103 N was equipped with an 5A20N plug-in unit detecting 0.5 mV-50V to amplify the photoconductivity pulse.

Constant Current Generator

The battery, V_B, could be replaced by a well-filtered and regulated power supply. The resistor, R_L, must be non-reactive with a resistance higher than the specimen resistance to provide essentially constant current conditions. The present standards (10,11) suggest $R_L \geqslant 20\ R_{specimen}$. When this is so, and when small-signal conditions prevail, the PCD signal amplitude ΔV is directly proportional to the excess carrier density Δn. To permit the measurement of specimens of various sizes, R_L and V_B may be variable. A reversing switch was used to observe the P.C.D. signal for both polarities of the constant current source. All connections were made with shielded cables and as short as possible.

Sample Holder

Sample Holder is mounted on a track, and can be moved in a plane perpendicular to the path of the pulsed light. Hence the, lifetime can

be measured as a function of distance along the crystal. Since trappings of excess carriers is sensitive to the ambient light level, the crystal holder is contained in a light tight box which also provides electrical screening.

4.2.2. Sample Preparation

A. Sample Shape and Size

Specimens used for lifetime measurement by PCD method are usually as grown crystals or rectangular parallelpipeds from these crystals. If no knowledge of the lifetime is available before measurement, the largest possible specimen should be used to minimize the contribution of surface recombination to the observed value (τ_f).

B- Surface Preparation

Two types of surface treatments were used for the lifetime measurements.

i- Lapped Surfaces

Specimens were lapped with Carborandum on each surface to produce a reference surface. The surface recombination rate may be calculated by

$$\tau_s^{-1} = \pi^2 D \left[\frac{1}{(2A)^2} + \frac{1}{(2B)^2} + \frac{1}{(2C)^2} \right] \quad (4.1)$$

for the case of a rectangular parallelpiped, and

$$\tau_s^{-1} = \pi^2 D \left[\frac{9}{16r^2} + \frac{1}{(2h)^2} \right] \quad (4.2)$$

for the case of a right circular cylinder. Where (2A) is the specimen length, (2B) is the specimen width, (2C) is the specimen thickness, r is the specimen radius, 2h is the height of the right circular cylinder, and D is the ambipolar diffusion coefficient given by

$$D = \left[\frac{n_o + p_o}{\frac{n_o}{D_p} + \frac{p_o}{D_n}} \right] \quad (4.3)$$

where D_n and D_p are the diffusion coefficients of excess electrons and holes, n_o and p_o are the equilibrium electron and hole concentrations. For extrinsic materials, D reduces to the minority carrier diffusion coefficient.

ii- Etched Surfaces

Except two end faces where ohmic contacts were made, all other faces were etched with HNO_3:HF: CH_3COOH (16:2:1) for three minutes at room temperature. According to the literature (64) this treatment gives S = 100 cm/sec. Surface recombination rate can be calculated by

$$\tau_s^{-1} = \frac{\pi^2 D}{4A^2} + S\left[\frac{1}{B} + \frac{1}{C}\right] \tag{4.4}$$

for the case of rectangular parallelpiped, and

$$\tau_s^{-1} = \frac{\pi^2 D}{4h^2} + \frac{2S}{r} \tag{4.5}$$

for the case of a right circular cylinder.
Where S is the surface recombination velocity.

C- Specimen End Contacts

End contacts should cover the entire ends of the specimen and should be nonrectifying. A variety of procedures has been developed for producing end contacts in silicon. In the present experiments, ohmic contact were formed by lapping the specimen ends with carborandum and plating with nickel.

The quality of end contacts should be tested by observing the voltage across the sample corresponding to each polarity of the constant current source. If the specimen voltages for the two polarities agree to within five percent, the contacts will be considered as nonrectifying.

4.2.3. Experimentation

A- Determination of Conductivity Type

Conductivity type defines the nature of the majority carriers in the specimen. There are four methods to determine conductivity type of extrinsic semiconducting materials. Two of them were used during the

experiment, and therefore those two will be explained in a more detailed manner (65).

i) Hot Probe Technique

This method gives dependable results in n-and p-type silicon having a room temperature resistivity up to 1000 Ω-cm (Fig. 4.2).

The sign of the thermal emf generated between two metal probe contacts to the specimen held at different temperatures is used to determine conductivity type. One of the probes is maintained at room temperature while the other is heated. The warmer probe will be positive with respect to the cooler probe when the specimen is n-type and negative when the specimen is p-type. The polarity is observed on a center zero meter or a fluke. Since most of the temperature difference occurs in the region of the probe which is not at room temperature, the sign observed is governed by the type of the portion of the specimen at this probe contact.

ii) Cold Probe Technique

It gives a dependable results for n-and p-type germanium having a room-temperature resistivity of 20 Ω-cm or less and for n-and p-type silicon having a resistivity up to 1000 Ω-cm.

iii) Point Contact Rectification Technique

It gives a dependable results for n-and p-type silicon with room-temperature resistivity between 1 and 1000 Ω-cm. This method is not recommended for germanium.

iv) Type-All System

It has two modes, so called rectification and thermoelectric modes. Model 530 (Keithley instrument) which has been used during experiment had a unit with type-all system.

iv-a) Rectification Mode

It is appropriate for use on n-and p-type silicon having a room-temperature resistivity between 0.1 and 1000 Ω-cm, inclusive.

Rectification is the mode of operation initially used. An ac voltage is imposed across two of the probe points as shown in Fig.4.3a. A second set of probe points is used to sense the polarity of the generated voltage. The polarity depends on how the voltage is generated

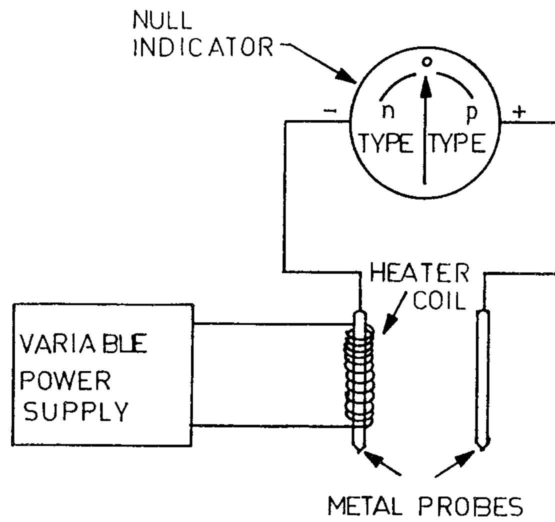


Fig.4.2. Hot probe technique apparatus.

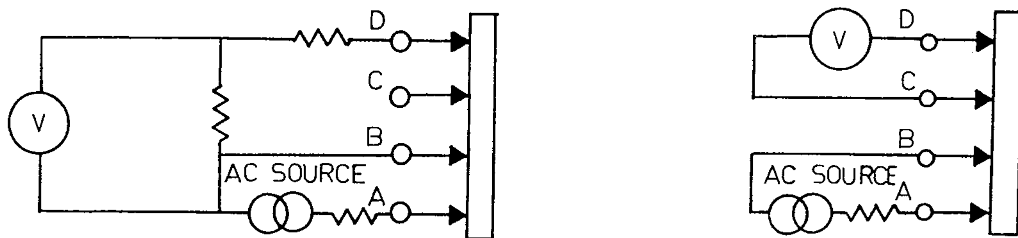


Fig.4.3.a) Rectification mode. b) Thermoelectric mode.

and on the conductivity type of the material. If the probe points are providing a rectification effect at the point contact to the semiconductor then a dc voltage between points B and D will result. The polarity of the rectification depends on the conductivity type of the material. Back biasing is achieved on a metal-to-n-type semiconductor diode when the semiconductor is at a positive potential with respect to the metal. A negative potential results in a back-biased junction for p-type semiconductor. Thus the semiconductor type is simply a function of the polarity of the voltage. For certain resistivities the quality of rectification degenerates such that the usefulness of this mode decreases. An acceptable rectification action for Model 530 occurs for voltage readings above 0.5 mV. Therefore, for voltages less than 0.5 mV the thermoelectric mode was used.

iv-b) Thermoelectric Mode

In this mode the ac voltage impressed across the input probe points increases the temperature near the point of contact by joule heating of the semiconductor. A Seebeck voltage is generated between a hot and cold probe point where ΔV is the voltage generated across two regions of material whose temperatures differ by ΔT. The physical process that generates the Seebeck voltage is the diffusion of the thermally generated carriers from the hot region of the material to the cold region. The carriers will diffuse from high-to-low-concentration regions, in particular from the hot to the cold probe. This diffusion creates a non-equilibrium carrier concentration in the cold region which generates an electric field, opposing further diffusion. This diffusion of carriers from the hot to the cold probe continues until the generated electric field is sufficient to overcome the tendency of carriers to diffuse. For example, in p-type material, the thermally generated electrons diffuse to the cold probe, building up a negative space charge which retards further diffusion. As a result, the hot probe is more positive than the cold probe. The use of four probe points permits a separation of the ac power source and the voltage-detection functions.In the Model 530 the voltage sensing is performed by the Model 163 digital voltmeter which provides speed and convenience of a digital display with automatic polarity indication. The thermoelectric mode utilizes all four probe points as shown in Fig.4.3-b.

B- Measurement of Resistivity

The resistivity (ρ_l) is defined as the proportionality constant between the electric field and the current density. The resistivity of a semiconductor is an important material acceptance requirement. It is widely used for quality purposes during device fabrication. There are two standard methods which can be applied directly to the Si and Ge. Application of these to other semiconductor materials may require the use of different probe material and probe attachment.

Method A, Two-Probe :

This method requires a bar specimen of measurable cross section and with cross-sectional dimensions small in comparision with the length of the bar. For materials for which no specific ASTM (American National Standard Measurements) referee method has been developed, this method is recommended for material acceptance purposes.

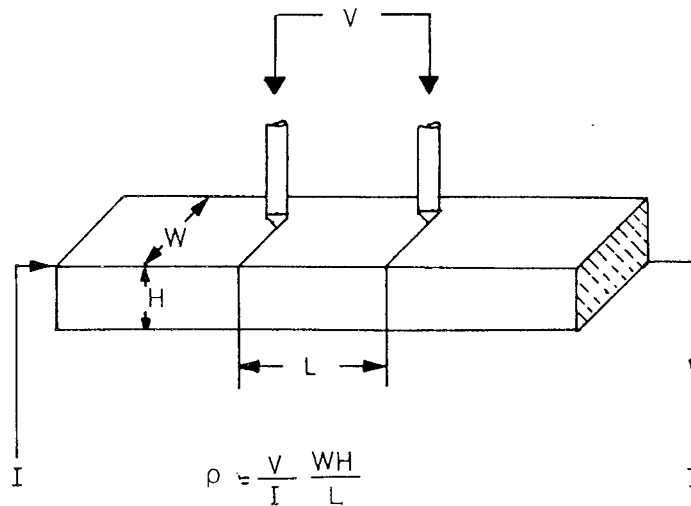
A direct current is passed through ohmic contacts at the ends of a bar specimen and the potential difference is determined between two probes placed along the current direction (Fig.4.4-a). The resistivity is calculated from the current and potential values and factors appropriate to the geometry.

Method B, Four-Probe :

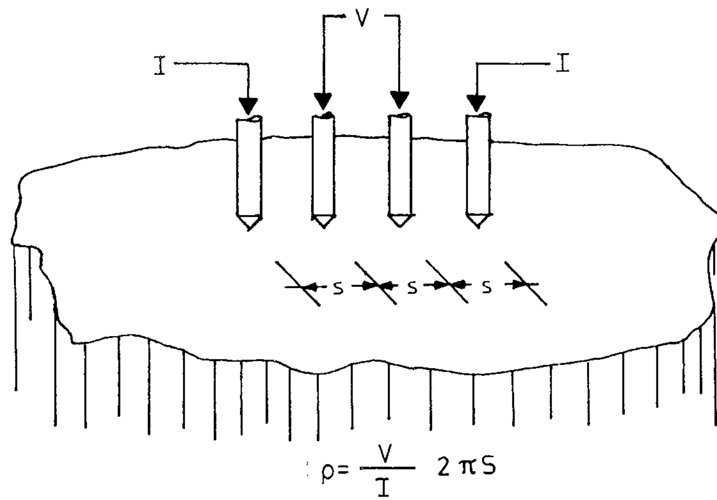
This method is rapid and does not require a specimen of regular cross-section. This method may be used on irregularly shaped specimens, provided a flat region is available for the contacting probes. This method is applicable only to the specimens such that the thickness of the specimen and the distance from any probe point to the nearest edge are both at least four times the probe spacing. (Fig.4.4-b).

C- Calculation of Surface Recombination Rate

Surface recombination rate is a sensitive function not only of size, but also diffusion constant and surface recombination velocity which vary from crystal to crystal. Knowing the conductivity type and the resistivity of the specimen, diffusion constants of carriers were deduced from curves in (45). Then surface recombination rate. τ_S^{-1}, were calculated using the equations in section 4.2.2.B.



(a)



(b)

Fig.4.4.a) Two-probe method
b) Four-probe method

D- Measurement of Filament Lifetime

A block diagram of the apparatus used to observe the decay of photoconductivity was shown in Fig.4.1. Sample prepared as mentioned before was held in place by either screw type contacts or pressure type contacts (for thin samples). The photolight was shaped by the pulse generator and was directed to the silicon crystal. Direct current was passed through the specimen by means of ohmic contacts at each end.

D.C. current source (0-6 volts battery) was connected in series with a non-reactive resistor R_L, whose resistance was greater than the sample resistance so that a constant current was preserved during illumination. V_B and R_L were adjustable in steps. The output photoconductive decay signal was taken to the preamplifier and oscilloscope from the side of reversing switch remote from the specimen, so that the oscilloscope display was not inverted when the specimen current was reversed. The oscilloscope was triggered from the rise of the photoconductivity signal ΔV. Very wide range of pulse heights was applied to the light source. The stable PCD signals were usually found between 10-150 Hz by changing the frequency of pulse generator.

Under small-signal conditions, the specimen voltage change (ΔV) and excess carrier density are inversely proportional (refer Eq.3.6-d) when the light is turned off, the filament lifetime τ_f is defined by the rate of decay of Δn or ΔV. Thus

$$\frac{1}{\tau_f} = -\frac{1}{\Delta V}\left(\frac{d\Delta V}{dt}\right) = -d(\ell n\Delta V)/dt \qquad (4.6)$$

or

$$\Delta V = V_o \exp\left(-\frac{t}{\tau_p}\right) \qquad (4.7)$$

The filament lifetime was measured from the logarithmic decay slope of ΔV. This is simple when τ_f is constant for which the curve is purely exponential which has the same logarithmic slope throughout. In the present case, however, the logarithmic slope changed through the course of the decay, i.e., τ_f was a function of ΔV, It was still possible to measure lifetime, but the filament lifetime should be described by a series of pairs of values for τ_f and ΔV.

The sequence of the operations at room temperature (~ 300° K)

was as follows: First display the total photoconductivity signal on the oscilloscope screen changing the time-base-sweep and vertical voltage amplification rates. Bring the peak point of PCD signal on the middle line of the oscilloscope i.e. at $x = 0$, using the horizontal shift control knob and note the peak value of PCD signal. Shift the peak point of the signal to the $x = -0.2$ cm (1 cm was divided to 5 equal parts on the oscilloscope screen) and read the amplitude of the PCD signal at $x=0$ and continue this operation until the PCD signal amplitude becomes unreadable even the biggest vertical voltage amplification is used. When the PCD signal amplitude versus time is plotted on the semi-logarithmic graph paper, it will be a linear after a suitable delay. The slope of the line is found from the best curve fitting and gives directly the filament lifetime.

The magnitude of maximum PCD signal depends on a number of parameters which is given by:

$$\Delta V_o = - ie \frac{2A}{(2Bx2C)} \frac{\mu_n + \mu_p}{\sigma_o^2} \Delta n_o \qquad (4.8)$$

where i is the constant current which flows through the sample, e is the electric charge, 2A is the length of the sample, (2Bx2C) is the cross-sectional area of the sample, μ_n and μ_p are the mobilities of electrons and holes respectively, σ_o is the dark conductivity, and Δn_o is the number of electron-hole pairs produced at $t = 0$.

The inverse dependence of ΔV_o on σ_o^2 makes the measurement rapidly more difficult as the conductivity of the material increases. For a given sample, μ_n, μ_p and σ_o^2 are constants. So ΔV_o can be increased, either increasing the intensity of the light source (this was done by changing the amplitude of the current pulse), and constant current passed across the filament. To change each of those parameters put some limitations on the measured filament lifetime.

If the filament measurement is to be accurate, i) the density of excess carriers (Δn), must be small compared to the majority carrier density in the region of the crystal where the lifetime is measured. ii) the electric field applied across the sample must be small so that the excess carriers do not drift into the region of different field, conductivity or lifetime during the measurements. Both conditions limit the signal level in the experiment in which

signal-to-noise ratio is invariably a problem.

The light output of infra-red lamps used is intense at about 0.9 μm wavelength. The absorption coefficient of silicon at that wavelength is such that the injected carrier density is sharply peaked at the illuminated surface of the crystal. Therefore, even if the average density of injected carriers is small compared to the majority carrier density, the injection level may be high near the illuminated surface. Under such conditions higher modes of surface recombination occur in the early stages of decay and produce a distorted trace. ΔV is rapid function of time at first, approaching the behaviour of the lowest mode as the decay proceeds. The influence of higher modes is directly related to the penetrating depth of the light source, type of surface preparation, and turn on portion (pulse length) of the light source, and illuminated area. Moreover, the rate of decay of the PCD signal will also be small until such time as the "saturation" of the PCD response is relieved by recombination and diffusion of excess carriers. Typical decay curve influenced by over injection is shown in Fig.4.6.

To get filament lifetime, over-injection should be avoided at the surface, and the portion of the decay curve should be ignored until it becomes exponential. With the present system no measurement of decay slope was made until the signal has decayed to less than 60 percent of the peak value.

Photovoltage can also be detected by the present system and be similar in amplitude and time dependence to the PCD signal. Hence, one should check that illuminating the crystal does not give rise to a signal if constant current generator is set at zero. Photovoltage effects can be reduced by making good ohmic contacts to the ends of the sample and keeping the pulsed light away from the end contacts. The presence of end contact resistance can be seen as a photocurrent noise and as the presence of the photovoltaic effect. The amplitude of any photovoltaic signal should be less than one percent of the desired PCD signal.

Carrier recombination at the end contacts caused by the drift under applied electric field is called sweep-out. In order to relate bulk lifetime τ_B with the measured filament lifetime τ_f as stated in equations in Sec.4.2.2., it is necessary the photoinjected carriers neither diffuse nor drift to the end contacts. Such diffusion or drift

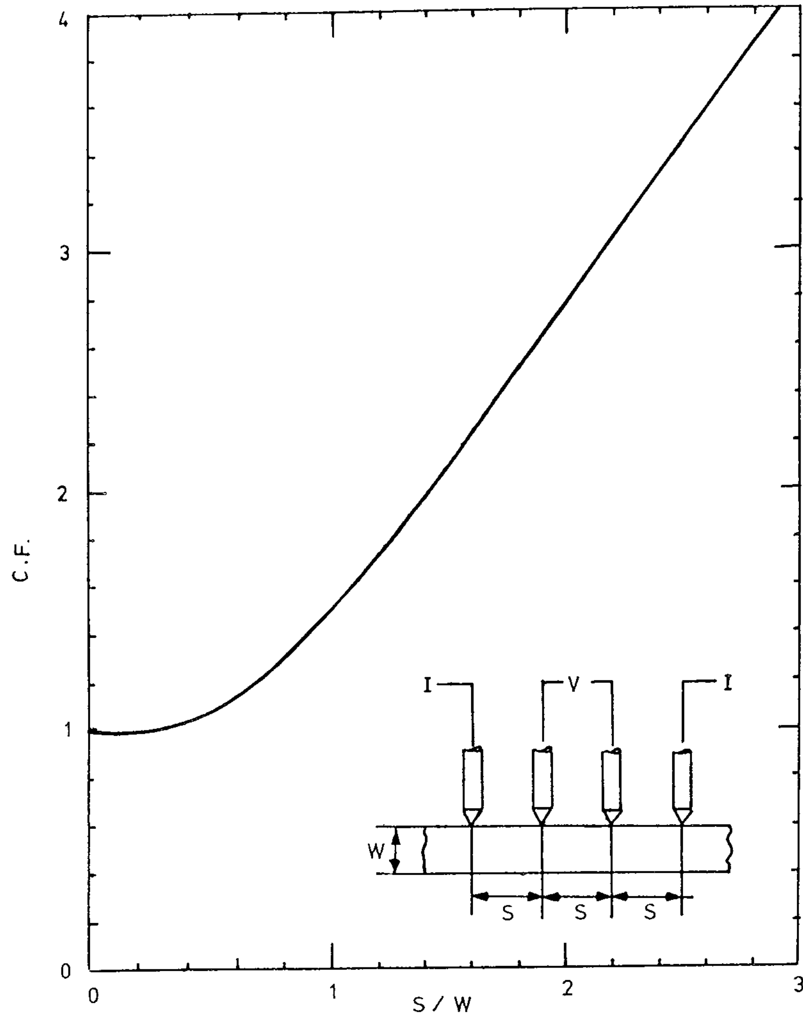


Fig.4.5. Correction factor, C.F. as a function of the ratio of slice thickness (w) to probe separation (s).

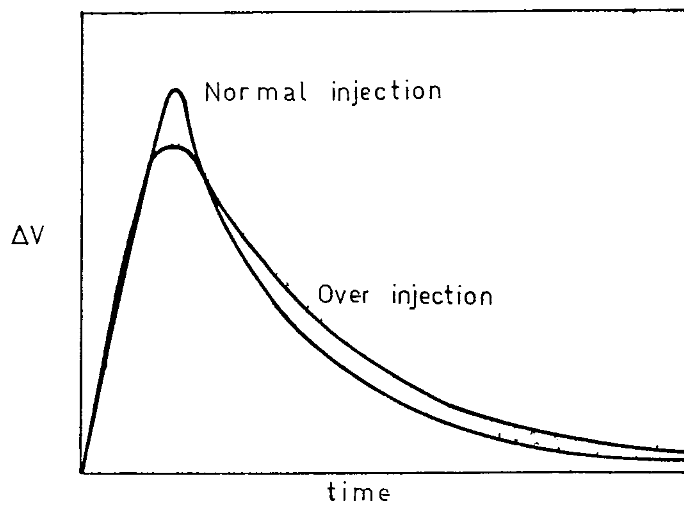


Fig.4.6. The effect of injection level on photoconductivity signal decay.

would result in a short τ_f, since recombination occurs almost immediately at the end contacts of the filament.

For the case of uniform generation of the entire specimen, Stevenson and Keyes (59) suggested that the electric field E be such that

$$\frac{(\mu E)^2}{4D} << \frac{1}{\tau_B} + \frac{1}{\tau_S} \qquad (4.9)$$

This expression forms the basis for the specification in the standards (10,11) that E be such that

$$E \leqslant \frac{300}{\sqrt{\mu\tau_f}} \qquad (4.10)$$

where E is in volts per centimetre, μ is in square centimetre per volt second, and τ_f is the filament lifetime in microseconds.

In practice it is not preferable to illuminate the entire specimen because i) the photovoltages are often generated at metal-semiconductor end contacts and given misleading results; ii) the calculation of τ_B from τ_f is simplified if the regions near the specimen end contacts are masked from the incident light and electric field is selected such that photogenerated carriers do not diffuse or drift to the end contacts. To assure this condition, the distance L_C between the illumination boundary and the nearest end contact should be large compared to both the drift length, d; and the diffusion length L_D. The quantities d and L_D are defined by

$$d = \mu E \tau_B \qquad (4.11)$$

$$L_D = \sqrt{D\tau_B} \qquad (4.12)$$

Diffusion to the end contacts can be made insignificant by illuminating only the centre (half) of the specimen or making the specimen sufficiently long. If the excess carriers do not diffuse to the end contacts and the sweep-out is the limiting factor in determining the maximum allowable specimen current, then it can be derived from the drift length d for the case of $L_C = 4\,d$

$$i_S = \frac{L_c}{4\,\mu\tau_B R_o} \tag{4.13}$$

where R_o is the dark resistance of the filament which is

$$R_o = \rho \frac{(2A)}{(2Bx2C)} \tag{4.14}$$

If the specimen current and resulting power dissipation are sufficiently large, the specimen temperature increases, resulting in a possible increase in τ_f. To prevent power dissipation and ohmic heating of the sample, the sample current i_s must be such that

$$i_s << \sqrt{\frac{P_{max}}{R_o}} \tag{4.15}$$

where P_{max} is the maximum power dissipation for silicon. In preferred size of silicon specimen by standards (11) the total power dissipation should not exceed 5 mWatt (58) then the maximum specimen current will be given by

$$i_s = \sqrt{\frac{5x10^{-3}}{R_o}} \tag{4.16}$$

In practice it is usually necessary to calculate a maximum specimen current for both the power dissipation and the sweep-out limitations. The lowest current should then be used in the PCD measurement.

If the trapping effects are present, $\Delta n \neq \Delta p$ and $\tau_n \neq \tau_p$. Trapping affects the final stages of decay and gives a long-time constant tail. The tail can usually be eliminated by either heating the sample or using steady-state background light. These treatments can create steady-state carrier density larger than the equilibrium carrier density so that the measurement is no longer a low level measurement. Under these conditions PCD measurement may have poor reproducibility.

The specimen resistivity should also be uniform and the lowest resistivity value should not be less 90 percent of the highest value.

Finally the lowest measurable filament lifetime value by the

present set-up was determined by the turn off characteristic of the pulsed light source, while the highest values were determined by diffusion constant D and the sample dimensions.

E- Calculation of Bulk Decay Time

Bulk decay time, τ_B, can be calculated by the relation

$$\tau_B = \left[\tau_f^{-1} - \tau_s^{-1}\right]^{-1} \tag{4.17}$$

If the following assumptions are valid:

1- Trapping is not significant so that the electron and hole lifetimes are equal.

2- Photoinjected carriers do not diffuse or drift to the end contacts. If recombination occurs at the end contacts, τ_f should be modified to include a term involving the specimen length or a term involving the applied electric field or both.

3- The initial stages of decay is ignored to reduce higher modes of surface recombination.

4- Specimen is characterized by a simple bulk decay time. Inhomogeneous distribution of impurity centres causes τ_B to vary with position in the crystal. This can result in poor measurement reproducibility unless the same portion of the specimen is illuminated consistently.

5- Conductivity modulation is not significant, $(\Delta V/V_o) \ll 1$ (10) . If the above assumptions are valid $\tau_f > \frac{\tau_B}{3}$, τ_B can be calculated from the measured filament lifetime. Otherwise τ_B may be imprecise since it is calculated from the difference between two large numbers.

CHAPTER 5

RESULTS AND DISCUSSION

5.1. Introduction

Minority carrier lifetime measurements were made by photoconductive decay method on n-type and p-type silicon materials. All the results to be reported here were obtained at room temperature. The optimum conditions for the determination of minority carrier lifetime have been investigated.

5.2. The Photoconductive Decay (PCD) Results

Experimental results of PCD method are analysed in terms of the number of quantities and conditions. Some of these are related to the nature of semiconductor material and recombination process, while the others are related to the instrumentation and sample preparation. Theoretical and experimental studies were conducted to determine suitable conditions under which the minority carrier lifetime measurement could be made. In order to define suitable measurement conditions the following parameters were studied;

i- The dependence of filament lifetime, T_f, to the resistivity of the specimen.

ii- The dependence of surface lifetime, T_s, to the specimen dimensions, surface preparation, diffusion constants of excess carriers.

iii- The change of filament lifetime, T_f, with T_s.

iv- Drift and diffusion effects on T_f and the PCD signal amplitude.

v- Determination of bulk lifetime, T_B, from measured T_f under suitable conditions.

5.2.1. Filament Lifetime

A- Filament Lifetime, T_f, and Resistivity

The filament lifetime measurements were made on samples with large rectangular cross sectional areas cut from n-type and p-type single crystal silicon. All surfaces were lapped to produce reference surfaces. Experimental conditions were so adjusted that drift and diffusion effects

to the bulk lifetime were insignificant. Surface contribution to the bulk lifetime was also reduced by choosing specimens with large cross sections. Under all these conditions the change of PCD signal amplitude with time on a number of specimens was plotted on a semilogarithmic graph paper as in Fig.5.1. It can be seen that the PCD signal is not purely exponential. Calculated filament lifetimes from the slope of the curve are also given for each specimen in Fig.5.1. The reduction of minority carrier lifetime with resistivity has been observed.

B- Recombination Process in the Bulk of Silicon

The change of minority carrier lifetime with changes in resistivity due to the recombination of minority carriers via recombination centres is well-known. This type of recombination dominates the recombination process in silicon. However, the magnitude of this recombination rate is less known. It is determined by the saturation lifetime which dominates at low resistivities. They are controlled by the capture cross section of the recombination centres and by their density.

C- Filament Lifetime and Excess Carrier Density

In order to verify the dependence of lifetime to the injected excess carrier density, the filament lifetime was measured as a function of photoconductive signal amplitude. Under small signal conditions ($\Delta n = \Delta p < p_o$ for p-type and $\Delta n = \Delta p < n_o$ for n-type specimen), the change in voltage across the illuminated portion of the filament is proportional to the change in excess carrier density and given by

$$\Delta V = -V_o \frac{e(\mu_n + \mu_p)}{\sigma_o} \Delta n \tag{5.1}$$

The variation of Δn can be deduced from the change in conductivity $\Delta\sigma$. Thus for n-type sample the relative excess carrier density is

$$\frac{\Delta n}{n_o} = -\frac{\Delta V}{V_o}\left[\frac{b}{b+1}\right] = -\frac{\Delta\sigma}{\sigma_o}\left[\frac{b}{b+1}\right] \tag{5.2.a}$$

and for p-type sample, it is

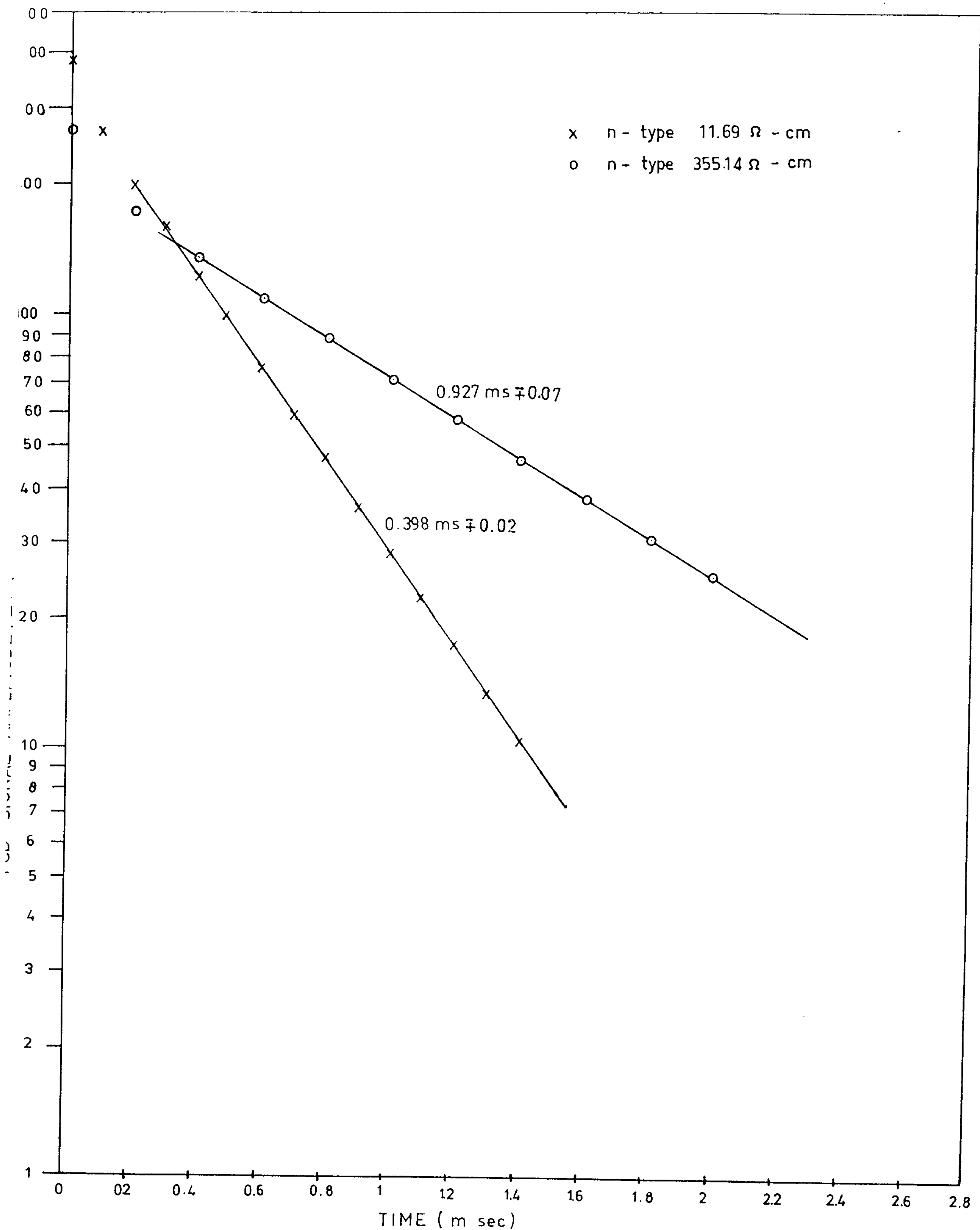


Fig.5.1. The change of PCD signal amplitude with time. Filament lifetime τ_f is calculated from the regression line.

$$\frac{\Delta n}{p_o} = - \frac{\Delta V}{V_o}\left[\frac{1}{b+1}\right] = - \frac{\Delta\sigma}{\sigma_o}\left[\frac{1}{b+1}\right] \qquad (5.2.b)$$

where b is the ratio of electron mobility to hole mobility, ΔV is the maximum PCD signal level, V_o is the d.c. applied voltage across the filament. The values of $\frac{\Delta V}{V_o}$ used for PCD measurements and calculated values of $\frac{\Delta n}{n_o}$ values are shown on table 5.1. Conductivity types of specimens were determined both by hot-probe thermal emf and by type-all system and the sample resistivities were measured by four-point probe technique (sec 4.2.3). The density of majority carriers are taken from graph in (66) to compare with the density of injected excess carriers. To calculate relative excess carrier density from Eq.5.2-a and b, the appropriate values of mobilities are deduced from graph in (66).

D- Recombination and Excess Carrier Density

Mathematical models which describe the recombination process under certain idealized conditions have been developed. One such model was developed independently by Shockley and Read (67) and by (68). According to the Shockley-Read-Hall (SRH) recombination model, the lifetime τ is related to the excess carrier density Δn(assumed equal to Δp) by

$$\tau_f\left[1 + \frac{\Delta n}{n_o + p_o}\right] = \tau_o + \tau_\infty\left[\frac{\Delta n}{n_o + p_o}\right] \qquad (5.3)$$

where τ_o is the lifetime in the limit as Δn approaches zero and τ_∞ is the lifetime in the limit as Δn approaches infinity. Filament lifetime, τ_f, as a function of excess carrier density has been reported by many authors (44,69). Although the linear relationship of Eq.5.3 is sometimes observed, experimental data of τ_f as a function of Δn more often give a non-linear plot. This indicates that the recombination process of most specimens is too complex to be described by the relatively simple SRH model. An extensive discussion of the SRH model is given by Blakemore (69).

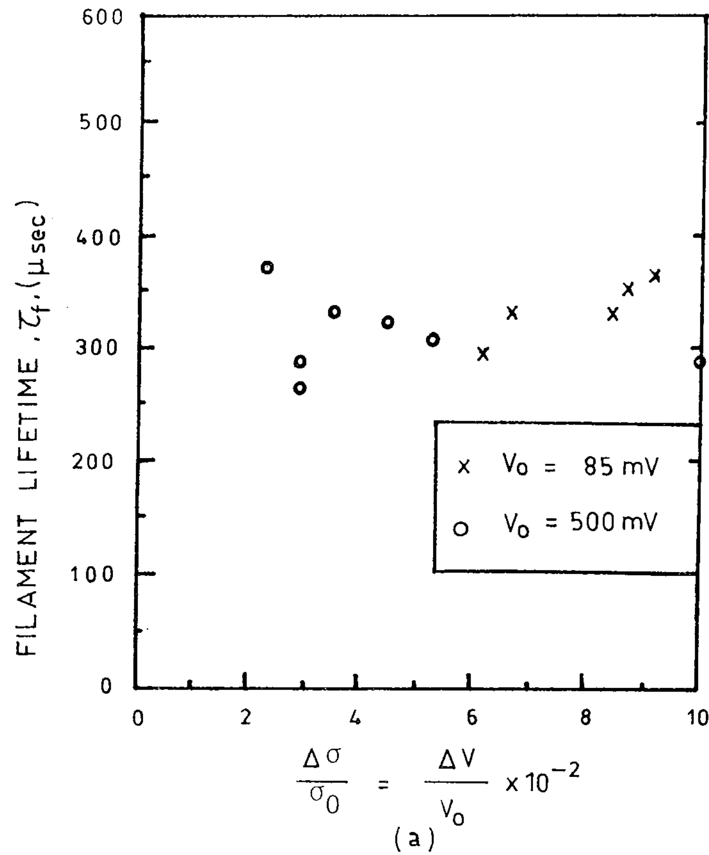
Experimentally measured filament lifetime was plotted as a function of $\Delta\sigma/\sigma_o$ on Fig.5.2. If $\Delta\sigma/\sigma_o$ value is multiplied by a factor of 0.75 for n-type specimens and by a factor of 0.25 for p-type specimens, $\Delta\sigma/\sigma_0$ is converted to $\Delta n/(n_o + p_o)$. Also, if the time scale (τ_f) is

Table 5.1. Calculated relative excess carrier densities from the relative conductivity changes at which τ_f measurements were made.

Conductivity Type	Resistivity ρ (Ω - cm)	Cross Section 2B x 2C (cm^2)	Measured $\Delta V/V_o$	Calculated $\Delta n/n_o$* or $\Delta n/p_o$*
N	483.4	1.5 x 0.33	82.4×10^{-3}	30.6×10^{-3}
	355.14	1.85 x 0.55	2.25×10^{-3}	1.72×10^{-3}
	321.6	0.7 x 0.47	0.39×10^{-3}	0.1×10^{-3}
	357	0.5 x 0.37	1.5×10^{-3}	0.21×10^{-3}
	11.69	1.3 x 0.25	0.09×10^{-3}	0.022×10^{-3}
P	483.4	1.05 x 0.2	0.51×10^{-3}	0.027×10^{-3}
	7102.8	1.05 x 0.2	0.4×10^{-3}	0.021×10^{-3}
	355.14	1.15 x 1.05	19.8×10^{-3}	6×10^{-3}
	1109.8	0.65 x 0.3	30.5×10^{-3}	1.49×10^{-3}

* $\Delta n/n_o$ or $\Delta n/p_o$ = (2B x 2C) . $\Delta V/V_o$. C.F.

C.F. = 0.75 for n-type Si, C.F. = 0.25 for p-type Si.



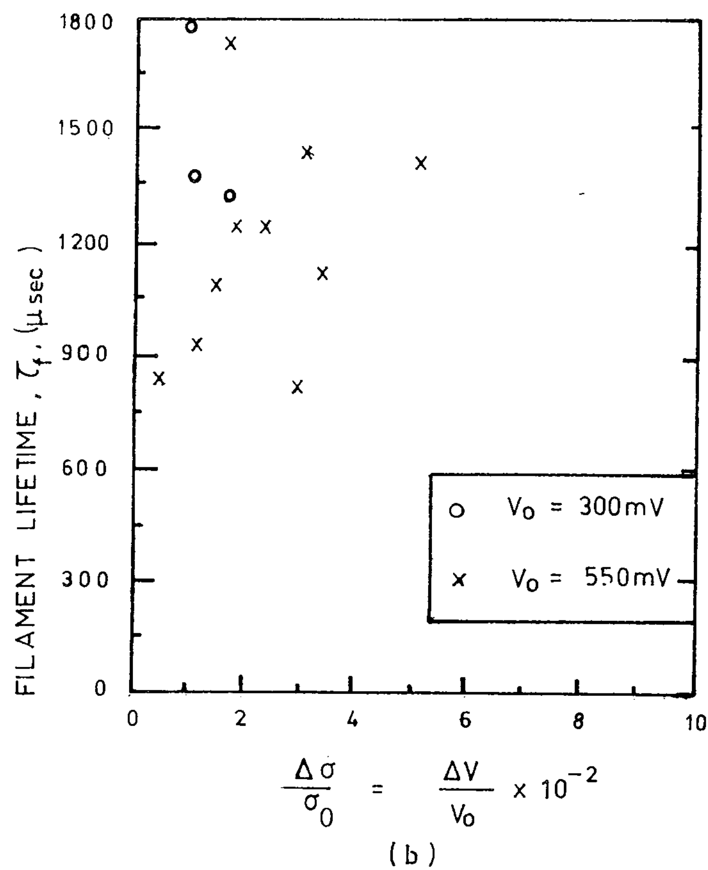


Fig.5.2. Measured filament lifetime τ_f as a function of conductivity modulation $\Delta\sigma/\sigma_0$: a) n-type, 483.4 Ω-cm Si single crystal, b) p-type, 355.14 Ω-cm Si single crystal.

multiplied by a factor of $1+\Delta n/(n_o+p_o)$, then the results will be analysed according to (Eq.5.3) the SRH model.

5.2.2. Surface Recombination Rate, τ_s^{-1}

It is necessary to pay considerable care in the interpretation of experiments in terms of recombination process in the bulk of the material. The phenomena of surface recombination can be carefully distinguished from recombination in the bulk of the material by the PCD method. Surface recombination rate is influenced by several factors such as geometry of the sample, the penetrating depth of incident photons, photon intensity, surface recombination velocity and diffusion constants of minority carriers.

A- Sample Geometry, and Diffusion Constants of Excess Carriers

One of the ways to increase the PCD signal amplitude for a given resistivity is to reduce the cross sectional area of the filament (sample), but the reduction in cross-sectional areas puts some limitations on the measured filament lifetime. The change of filament lifetime with the change of sample dimensions was experimentally verified on a number of p-type and n-type specimens. 360 Ω-cm, n-type single crystal silicon cut was used to three different cross-sectional areas, which have typically (1.85×0.55 cm^2), (0.7×0.47 cm^2) and (0.5×0.37 cm^2). Firstly, all surfaces were lapped and filament lifetime measurements were made. Surface recombination rate for each filament was also calculated by Eq.4.1 and both measured τ_f and calculated τ_s values are included on table 5.3 at the end of this section. Two other p-type specimens with (1.05×0.2 cm^2) and (1.15×1.05 cm^2) rectangular cross-sections whose resistivities were almost equal to 400 Ω-cm were used for measurement of τ_s values. About three times higher τ_s value in n-type silicon than p-type silicon for the same cross-sectional dimension is explained with three times lower diffusion constant (mobility) of excess holes in n-type specimens. In order to relate the bulk lifetime, τ_B, to measured τ_f, calculated τ_s values must be at least two times higher than τ_f and at least three times higher than τ_B. This implies that high bulk lifetime measurements require larger sample sizes to reduce the surface contribution to the

measured lifetime.

The other two important parameters; surface recombination velocity and the light source will now be discussed since they affect the measured filament lifetime.

B- Surface Recombination Velocity

To verify the importance of surface treatment on surface recombination rate, a few specimens with different cross-sectional dimensions were etched except two end faces where ohmic contacts were made. According to the literature (64) the etching solution gives S= 100 cm/sec. Using this appropriate value of surface recombination velocity, surface recombination rates were calculated from Eq.4.4 for each specimen and given on table 5.3.

Surface recombination velocity is an extremely sensitive function of surface treatment. Values ranging from 10^5 cm/sec on lapped surfaces to 10^2 and even 10 cm/sec on etched or otherwise treated surfaces have been reported on Si (57). Small magnitude of S implies that a large fraction of carriers approaching to the surface is reflected, while S large means that most carriers are captured at the surface. Two types of traps are known to exist at the surface of a semiconductor and acts as recombination centres.

C- Light Source

In the case of bulk lifetime measurement, it would be helpful to use sufficiently penetrating radiation in order to generate the excess carriers in the volume of the sample. Since a smaller percentage of the carrier injection is near the surface, surface recombination will be less important in determining the initial rate of decay. In the present experiments, the light source used was an infrared light emitting diode (GaAs) with an intense radiation at about 0.9 μm wavelength. The measured absorption spectrum of silicon near the band edge (66) shows that the penetration depth of the radiation at that wavelength is 35 μm($\alpha \sim 290$ cm^{-1}). Hence injected carriers density will be large in a 35 μm layer beneath the illuminated surface of the crystal. Therefore, surface recombination occurred in the early stages of the decay and produced a distorted trace on the oscilloscope.

Shockley (58) showed, even if the injection were uniform the decay would not be describable by a simple time constant, and the largest time constant (τ_B) is influenced by surface recombination. It is also known that the rate of the electron-hole pair generation is proportional to the incident photon energy and corresponding absorption coefficient of the material at that energy. Virtually no electron-hole pairs will be produced if the incident radiation energy is less than the minimum band gap of silicon ($Eg = 1.1$ eV). However the inverse dependence of the PCD signal amplitude ΔV, on dark conductivity, σ_0, makes the measurement rapidly more difficult as the conductivity of the material increases. Thin specimens require non-penetrated light source to eliminate the possibility of excess carrier recombination at the back surface.

The other important specification for the PCD measurements is such that the intensity of the light source should not be too excessive. The straightforward calculations of $\Delta n / n_0$ or $\Delta n / p_0$ (Δn is assumed to equal to Δp) taking the measured $\Delta V/V_0$ values from Fig.5.2 and using Eq.5.2-a and -b were given on table 5.1. To get filament lifetime, over injection at the surface must be avoided by ignoring the early portion of the decay which is about 20-30 percent of the peak value. If over injections are present in the bulk material, then the effect can be analysed according to the SRH model.

5.2.3 Diffusion and Drift Effects

A. Diffusion and Sweep-out

Another important contribution to the total decay constant arises from additional diffusion current caused by the distortion of carrier distribution via the electric field. In order to relate bulk lifetime τ_B with measured filament lifetime τ_B as stated in Eqs. in Sec. 4.2.2, it is necessary that photoinjected carriers neither diffuse nor drift to the end contacts. Such diffusion and drift affect the PCD signal amplitude and measured filament lifetime.

The effect of electric field on PCD signal amplitude and measured filament lifetime is verified on a number of filaments. Under certain assumptions the PCD signal level, ΔV, is given by an integral (3.6-c), the integrand of which is proportional to the electric field,

inversely proportional to the (average) conductivity. As it is seen from Fig.5.3, the linear dependence of ΔV on applied field breaks up almost 0.21 V/cm in n-type filaments while the linear relationship breaks up almost 0.13 V/cm in p-type filaments. However, the change in the τ_f in both types filaments was large beyond these limits. The same critical points were also observed on the same etched specimens.

It is known from theory that the total filament current is composed of drift and diffusion terms. For the lifetime measurements , the drift and diffusion current of excess carriers should be small compared to the drift current of majority carriers and drift current of excess carriers must also be less than diffusion current of excess carriers to prevent the distortion of excess carrier distribution at injected point. The majority carriers are either electrons or holes, their drift and diffusion currents at injected point must be satisfying the following relation,

$$e\Delta n \ \mu_{n,p} \ E_o \leqslant eD_{n,p} \frac{\Delta n}{Ln,p} \tag{5.4}$$

where the term in the left side represents the drift current of excess carriers and the term in the right side corresponds to diffusion current of excess carriers. Using the Einstein relation in the above equation, the critical electric field, E_o, can be deduced which is

$$E_o \leqslant \frac{kT/e}{\sqrt{D_{n,p} \tau_{n,p}}} \tag{5.5}$$

where $D_{n,p}$ and $\tau_{n,p}$ represent the diffusion constant and minority carrier lifetime. The experimental result on Fig.5.3, almost fits Eq.5.5. This implies that maximum usable electric field in the PCD measurements without distortion of excess carriers by the electric field is limited by the minority carrier bulk lifetime and diffusion constant of excess carriers.

For the case of uniform generation in the entire filament with rectangular cross-section, Stevenson and Keyes (59) derived an equation which is given by

$$\tau_f^{-1} = \tau_B^{-1} + \tau_S^{-1} + \frac{(\mu E)^2}{4D} \tag{5.6}$$

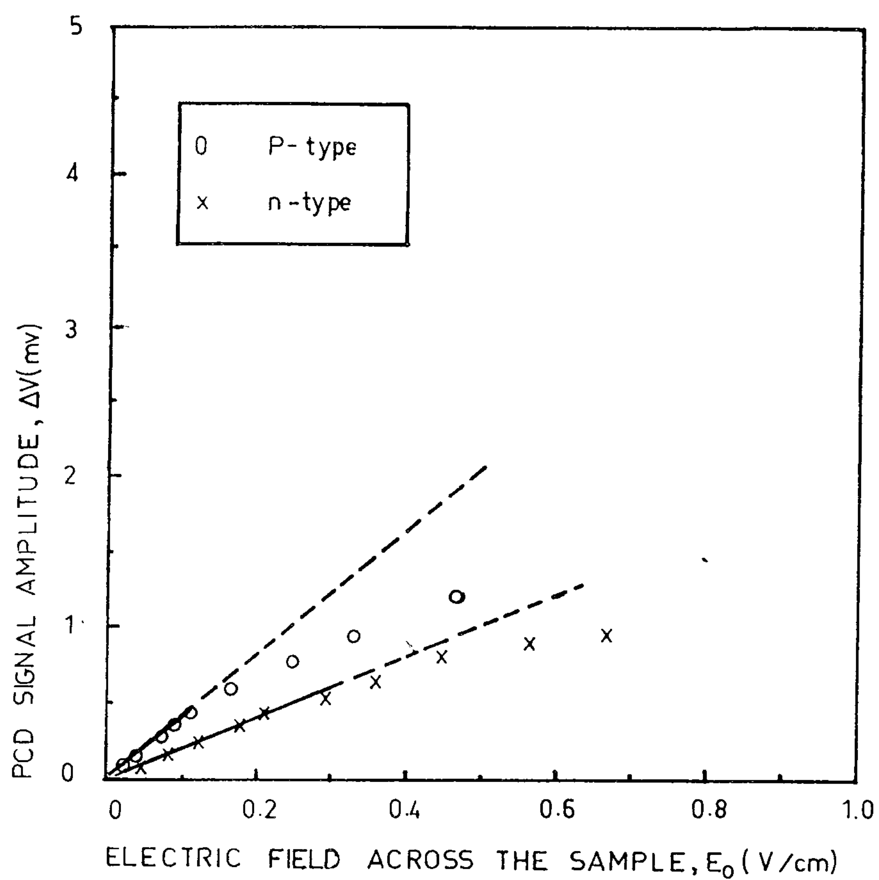


Fig.5.3. The change of PCD signal amplitude with applied electric field across the sample at constant injection level.

The last term represents excess carrier recombination resulting from drift to the end contacts under applied electric field. μ and D are effective mobility and diffusion constants respectively. For the case of lifetime measurements, this last term must be kept small compared with the sum of the first two, i.e.,

$$\frac{(\mu E)^2}{D} << \frac{1}{\tau_B} + \frac{1}{\tau_S} \quad (5.7)$$

Under low electric field the term in the right side will be equal to τ_f^{-1}, then Eq.5.7 can be used to detect the maximum value of electric field for the lifetime measurement. Taking the Einstein relationship into account the critical field becomes

$$E_o \simeq \frac{300}{\sqrt{\mu\tau_f}} \quad (5.8)$$

This last expression is recommended in standards (10,11) where E_o is V/cm, μ is cm^2/V-sec, and τ_f is the filament lifetime in microseconds. Comparison of Eq.5.5 with 5.8 shows that while in the former case the maximum electric field is limited by the bulk lifetime, the latter case is limited by the filament lifetime.

In practice it is not preferable to illuminate the entire specimen, because, i) the surface photovoltages are often generated at metal-semiconductor end contacts and gives misleading results; ii) calculation of τ_B from τ_f is simplified if the regions near the specimen ends are masked from incident light. In the present experiments, only the centre of the filament surface was illuminated. If the distance L_c between the illumination boundary and the nearest end contact is large compared to both the drift length, d, and the diffusion length L_D which are given by,

$$d = \mu E \tau_B \quad (5.9)$$

$$L_D = \sqrt{D\tau_B} \quad (5.10)$$

If $d \leqslant L_D$ these two equations reduce to Eq.5.5. If L_C is many times of L_D, the excess carriers do not diffuse to the end contacts. Then choosing the electric field which gives the drift length $d \leqslant L_D$, the last term in Eq.3.16 was eliminated. It can be assumed that the excess carrier density Δn established in the illuminated region of the sample drifts a distance d in a time τ_B under applied field. If the end contact is at a distance of 4d from the illumination boundary, only a small fraction of the total number of excess carriers ($\Delta n/e^4 = 0.02$) will be swept out. Hence they will have insignificant effects on the measured τ_f. Analogous to the drift to the end contacts, diffusion to the end contact is eliminated if L_C is about four times the diffusion length.

B- Specimen Current and Power Dissipation

If the specimen current (applied field) is sufficiently large, the specimen temperature increases, resulting in a possible increase in the measured filament lifetime. Mattis and Baroody (44) suggested that total power dissipation in silicon specimens should not exceed 5mW and if the contact resistance is very small than bulk resistance, the maximum specimen current is given by

$$i_s = \sqrt{\frac{P_{max}}{R_0}} = \sqrt{\frac{5 \times 10^{-3}}{R_0}} \tag{5.11}$$

where R_0 is the dark (sample) resistance.

The maximum usable current or electric field without distortion of excess carriers was calculated for a number of specimes on which lifetime measurements were made and summarized on table 5.2. Calculations are more easily based on the bulk power dissipation, since resistivity has already been measured. Comparison of the three values on the table 5.2 with the experimental results shows that power dissipation can not be used directly as current limitation for the PCD measurements. However the Eq.5.5 may be used as current limitation for the PCD measurements. The limitation suggested by the standards can only be applicable when the largest sample size was used since the measured τ_f will nearly be equal to τ_B, and Eq.5.5 almost fits to experimentally determined critical electric field.

C.T.	ρ (Ω-cm)	R_0 (Ω)	$i_0 = \sqrt{\frac{5mW}{R_0}}$ i_0, (mA)	E_0 (V/cm)	$E_0 = \frac{300}{\sqrt{\mu\tau_f}}$ (V/cm)	$E_0 = \frac{kT/e}{\sqrt{D\tau_B}}$ (V/cm)	$E_{0(measured)}$ (V/cm)
N	483.40	2832	1.33	1.30	0.45	0.21	0.21
N	355.14	1029	2.20	0.77	0.27	0.21	0.21
N	321.60	2826	1.33	1.30	0.40	0.10	0.21
N	357.00	5500	0.95	1.83	0.43	0.22	0.21
N	11.69	144	5.90	0.21	0.43	0.14	0.21
P	483.40	7527	0.82	1.89	1.55	0.15	0.12
P	7102.80	99777	0.22	7.44	0.89	0.40	0.14
P	355.14	836	2.45	0.72	0.36	0.13	0.14
P	1109.80	18610	0.52	2.96	1.07	0.45	0.12

Table 5.2 Critical electric field without distortion of excess carriers calculated from different equations.

5.2.4 Other Limitations

The effect of light turn-off time, pulse length, series resistance, specimen end contacts will be discussed shortly.

A- Light Turn-off Time

The photoconductive-decay method permits a resolution of the lifetime limited by the sharpness of the turn-off time of the light source. Fig.5.4-a and -b shows the output of pulse generator and light pulse used for PCD measurements. The turn-off time of the light source used was 20 μsec.

In practice, the most frequently used light sources are spark gap, a flask tube, constant light (i.e. carbon arc) in connection with a rotating mirror, and a Kerr cell, together with a constant light source. Of these light sources, the spark gap and Kerr cell reaches the limit of 0.1 μsec (35) . Measurement of lifetime by PCD method of the order of 10^{-8} sec has been adapted by Wertheim and Augustniak (38) by the use of a pulsed electron beam from a Van de Graff accelerator.

B- Pulse Length

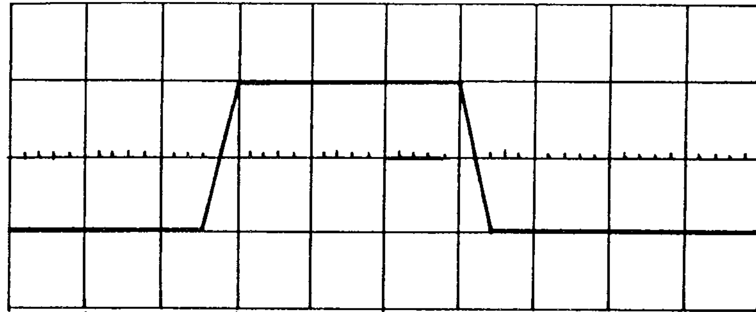
The pulse length of light source was variable from a few microseconds to a second. If the light is applied to the filament for a time equivalent to many times of bulk lifetime, a steady-state excess carrier distribution is established. This does not occur under very short pulsed light excitation.

C- Series Resistance

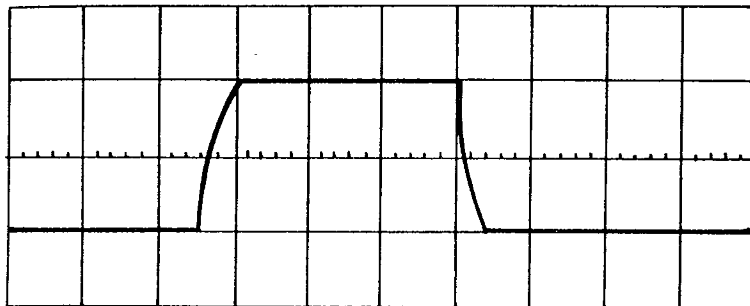
The present standards (10,11) suggested that the constant voltage supply should be in series with a resistance R_L which is at least twenty times the specimen resistance R_0. Experiments showed that almost no effect on τ_f for $R_L/R_0 \geqslant 1$ was observed.

D- Specimen End Contacts

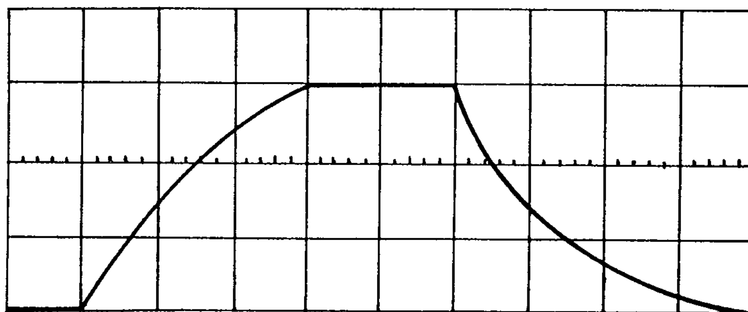
When two subtances are brought into contact, a redistribution of charge occurs;finally a new equilibrium condition is reached in which the Fermi levels of the two subtances are at equal heights (70) . Owing to the redistribution of charge, a dipole layer will be formed



(a)



(b)



(c)

Fig.5.4. The output of a) pulse generator applied to the light source,

b) light pulse used for PCD measurements,

c) the change of PCD signal amplitude with time on a silicon sample.

a, b, c have the same time base (50 µsec/div)

at the contact. There is a simple rule for determining whether a metal-semiconductor contact is an ohmic contact or a rectifying contact. The contact is ohmic if $\Phi_m < \Phi_s$, and rectifying if $\Phi_m > \Phi_s$ for n-type semiconductors. The reverse situation occurs for p-type semiconductors. Where Φ_m is the work function of the metal, Φ_s is the work function of the semiconductor.

During the experiments, two end faces of the filaments were lapped and electrical ohmic contacts were performed by the electroless nickel plating. The contacts covered the entire ends of samples to produce uniform electric field throughout the filament. A uniform electric field is required for theoretical analysis of the experimental results. The quality of end contacts was tested by observing the voltage across the sample corresponding to each polarity of the constant current source, since the specimen voltages for the two polarities agreed well (less than two percent), the contacts were considered as ohmic (non-rectifying). Rectifying contact barriers are usually characterized by photocurrent noise, and the presence of a photovoltaic effect. Since the middle of the sample was illuminated, and good ohmic contacts were performed, essentially no surface photovoltaic effects were observed, when the d.c. voltage across the sample was set at zero. The present standards suggest that the amplitude of any surface photovoltaic signal should be less than 1% of the maximum PCD signal for the lifetime measurement.

5.2.5 Determination of Bulk Lifetime, τ_B from Measured Filament Lifetime τ_f

Table 5.3 outlines the measured decay times of filaments with different conductivity type and resistivity silicon single crystals as a function of sample geometry and type of surface preparation. It is not a straightforward process to deduce constant filament lifetimes from the PCD measurements, since for a given material the filament lifetime depends on a number of quantities and conditions. In order to relate bulk lifetime, τ_B, to the measured value of filament lifetime, τ_f, the following conditions are satisfied during the experiment:

i- Resistivity of a specimen should be uniform.

ii- End contacts should be ohmic.

iii- E_0 (applied electric field) should lie in the linear part of ΔV-E_0 curve.

iv- It should be avoided from diffusion and drift effects. This requires $L_C \gg L_D$ and $L_C \approx 4d$
Where L_C is the distance between the illumination boundary and the nearest end contact. d is the drift length and L_D is the diffusion length given by

$$d = \mu E T_B \ , \ L_D = \sqrt{D T_B}$$

v- The relative excess carrier density ($\frac{\Delta n}{n_0}$ or $\frac{\Delta p}{p_0}$) must be less than 10^{-2}.

vi- The surface recombination rate, τ_s should be three times larger than the filament lifetime, τ_f.

Table 5.3 Decay times of specimens cut from different conductivity types and resistivities of silicon crystals as a function of specimen size and type of surface preparation.

Conductivity type	Resistivity (Ω-cm)	Sample size 2A×2B×2C (cm×cm×cm)	Type of surface preparation	Calculated τ_s (μsec)	Measured τ_f (μsec)	Bulk lifetime τ_B (μsec)
N	321.60	2.90×0.70×0.47	Lapped	438	216	426
			Etched	1330	426	627
	483.40	2.90×1.50×0.33	Etched	1280	326	437
	355.14	2.95×1.85×0.55	Etched	1960	938	1780
	357.00	2.85×0.50×0.37	Etched	1020	354	542
	11.69	4.00×1.30×0.25	Etched	1030	499	968
P	483.40	3.27×1.05×0.20	Lapped	317	281	2474
			Etched	830	78	86
	7102.80	2.95×1.05×0.20	Lapped	317	86	119
			Etched	830	237	332
	355.14	2.85×1.15×1.05	Lapped	4610	1344	1897
			Etched	2640	1464	3287
	1109.80	3.27×0.65×0.30	Lapped	607	184	264
			Etched	1010	164	196

CHAPTER 6

CONCLUSIONS

The optimum experimental conditions for the measurement of minority carrier lifetime in homogeneous silicon single crystals have been examined by the photoconductive decay (PCD) method.

a) The measurements of minority carrier lifetime between 68 μsec and 1464 μsec have been performed, where the smallest measurable lifetime was limited by the turn-off time of the light source (20 μsec), and taking $\tau_f = 4\tau_s = 4(1464)$ μsec, maximum sample dimensions which the present set-up could measure were found as 2.5 x 2.425 x 2.425 cm for n-type silicon and 2.5 x 1.265 x 1.265 cm for p-type silicon samples.

b) Although the PCD signal amplitude could be increased by

i- increasing the relative excess carrier density,

ii- increasing the applied electric field across the sample, or

iii- reducing the sample cross sections.

All of these put some limitations on measured values of lifetime.

c) For the measurement of minority carrier lifetime by the PCD method:

i- The relative excess carrier density must be less than 10^{-2}.

ii- The maximum applied electric field across the sample must satisfy $E_0 \leqslant (kT/e)/\sqrt{D_{n,p}\ \tau_B}$.

iii- Calculated surface recombination lifetime must be at least three times the measured filament lifetime ($\tau_s \geqslant 3\tau_f$).

iv- The early portion of PCD signal, where surface recombination dominates, must be neglected until it becomes exponential.

v- Diffusion and drift terms of excess carriers to the ohmic contacts were eliminated since the distance between illumination boundary and contacts was many times the measured diffusion length of excess carriers in the bulk of the filament (sample).

vi- Almost no effect on measured filament lifetime, τ_f was observed for $R_L/R_0 \geqslant 1$ where R_L is the series resistor and R_0 is the sample (dark) resistance.

SUGGESTIONS FOR FUTURE WORK

1) In order to make ohmic contacts to the thin samples, an electrolysis apparatus should be constructed.

2) A technology may be developed to improve the minority carrier lifetime by eliminating or reducing the density of recombination centers.

3) Changing the penetration depth of secondary light and superimposing this on the main light, the effect of trapping levels should be investigated.

4) Heat treatment effects on minority carrier lifetime measurements should be investigated.

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