MINORITY CARRIER LIFETIMES IN GERMANIUM AND SILICON

by

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ABSTRACT

An investigation of minority carrier lifetimes in germanium and silicon semiconducting material has been undertaken. A comparison of optical and electrical injection methods, as reported in the literature is given. An optical arrangement, including a coaxiallized spark gap system, is described.

Sample preparation is discussed with respect to surface treatments. A well etched surface (CP4 etched) reduces the surface effect to negligible proportions compared to the volume effect. However, a ground or sandblasted surface caused the surface term to be dominant.

The effects of constant current, photovoltaic effect at contacts, response time, and electrical field sweep-out of carriers are discussed.

A brief description of a suitable electrical injection circuit is given. Measured values of lifetime using this method are in good agreement with the optical measurements.

The volume lifetimes of n-type germanium were obtained for resistivities of 0.01, 5, 19, and 50 $\Omega$-cm material. The lifetimes found at room temperature were $<2\mu$s, 45 $\mu$s,
200 $\mu$s, and 175 $\mu$s respectively.

Both a 130 $\Omega$-cm p-type silicon sample and an 8.2 $\Omega$-cm n-type silicon sample displayed trapping effects at room temperature. A direct current light source, providing ambient background illumination, was found to eliminate the long decay component ($>10^{-3}$ sec) for the p-type silicon only.

Germanium at 78°K showed a trapping effect similar to the silicon at room temperature.

A diffusion constant of 50 cm$^2$/sec for holes in n-type material was used to establish a value for the surface recombination velocity of $2 \times 10^4$ cm/sec for a ground surface.
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CHAPTER I

INTRODUCTION

Section 1.1 - Intrinsic and Extrinsic Semiconductors

The energies of electrons associated with atoms of a crystal must take on values within certain "allowed" bands of energy. The full band of lowest binding energy is termed the valence band. The band adjacent in energy to the valence band which contains no electrons, or is only partially filled, is called the conduction band. A full band implies that the electrons are not available for conduction and the material will be an insulator at the absolute zero of temperature. At temperatures other than zero, some electrons from the valence band will be excited into the conduction band provided the "forbidden gap" between the two bands is small enough to allow some thermal excitation. A gap of several electron volts will produce insulator properties. For a gap of the order of one electron volt or less, however, a considerable number of thermally excited electrons appear in the conduction band at room temperature.
and the material is classified as a semiconductor.

The process of excitation of an electron to the conduction band leaves a vacancy or hole in the valence band. A hole can also contribute to conduction, and behaves like a particle with positive charge. For an "intrinsic" semiconductor, the number of electrons is equal to the number of holes in the valence band because the free carriers have all been produced by exciting electrons across the gap. Thus electrical conductivity is evident in intrinsic semiconducting materials.

Most semiconductors are not intrinsic but owe part of their conductivity to donor or acceptor impurities. The donor impurity levels \((N_d \text{ cm}^{-3})\) lie near the conduction band and donate to this band electrons which contribute to the conductivity. The acceptor levels \((N_a \text{ cm}^{-3})\) lie near the valence band and accept electrons from this band, producing additional holes to contribute to the hole conductivity. When the density of electrons or holes from these levels is much greater than the intrinsic concentration, the semiconductor is referred to as "extrinsic".

If complete ionization of the impurity levels is assumed, and electrical neutrality holds so that the total positive charge equals the total negative charge, it is found that \(np = n_1^2\), where \(n_1^2\) is independent of the individual impurity concentration. The distribution functions for the electrons
and holes are taken to be classical. Here $n$ denotes the electron concentration in the conduction band and $p$ denotes the hole concentration in the valence band. The situation is usually represented by an energy level diagram such as Figure (1).

![Energy Level Diagram](image)

Forbidden Gap Energy = $E_C - E_V$

Short lines at $E_d$ or $E_a$ represent ionized levels; a dot or circle at one of these lines represents a bound electron or hole respectively.

**Fig. 1. Energy Level Scheme for Donors and Acceptors.**

**Section 1.2a - Equilibrium Conductivity ($\sigma_0$) and Deviations from $\sigma_0$**

Thermal effects produce a random motion of free electrons and holes through the crystal. The net charge transport along any crystal direction averages to zero. Under the influence of an electric field, the free charge carriers in isotropic materials acquire a net drift parallel to the direction of the field. Due to collision processes, a steady
state carrier drift is reached, setting up an equilibrium conductivity. If \( n_0 \) and \( p_0 \) represent equilibrium carrier densities per unit volume, the equilibrium conductivity is given by

\[
\sigma_0 = e(n_0/\mu_n + p_0/\mu_p)
\]

Here \( \mu_n \) and \( \mu_p \) represent the electron and hole mobilities respectively \((1, 2)\) and \( e \) is the magnitude of the electronic charge.

If \( \Delta n \) and \( \Delta p \) are the excess numbers of electrons and holes per unit volume produced by some disturbance to this equilibrium, then the conductivity becomes

\[
\sigma = e(n_0 + \Delta n)/\mu_n + e(p_0 + \Delta p)/\mu_p
\]

Only changes in the number of charge carriers are considered here. Changes from \( \sigma_0 \) could arise if the mobilities were changed, for example.

Section 1.2b - Disturbances Causing Deviations from \( \sigma_0 \)

The concentrations can be upset in a number of ways, all of which involve freeing carriers bound to lattice sites. Thus radiation of the correct energy can inject electrons into the conduction band. For this treatment, impurity photoconductivity is not discussed. The equilibrium can also be disturbed by a pulse of minority carriers injected
electrically into a sample. Majority carriers are then drawn into the sample from an external source to preserve space-charge neutrality. The resultant effect is an excess density of both charge carriers. It will be shown later that it is only possible to inject carriers of the minority type.

Section 1.3 - Recombination Processes to Restore Equilibrium

Once the disturbing influence is removed, the excess electrons and holes must recombine to produce equilibrium again. The mechanisms for recombination can be grouped into three categories: (a) direct recombination (band-to-band transitions), (b) recombination through localized levels in the forbidden gap, (c) surface recombination. These will be discussed in section (2.1).

Section 1.4 - Information to be Gained by Studies of Recombination

Lifetime measurements are found useful for determining the presence of special types of crystal imperfections, which are usually present in such small amounts that they cannot be detected by Hall or resistivity measurements. Indeed, to make crystals more nearly "perfect", it has become common to characterize the degree of perfection in terms of the maximum value of volume lifetime available. It has been
stated (6) that "of all the volume properties of semiconductors, this (i.e. lifetime) seems to be the one that places the most stringent requirements on purity and crystal perfection".

Various workers have noted some of the factors which affect crystal perfection and hence, lifetime. N.B. Hannay et al (34) found that if the crystal was rotated during growth, there were two orders of magnitude more recombination centres than in similar crystals grown without rotation. J.A. Burton et al (35) found that lifetimes were reduced by the addition of chemical impurities. G.L. Pearson et al (36) found lifetimes reduced in samples with many dislocations.

Lifetime studies allow determination of surface recombination velocities (11,12), under certain conditions. Lifewise, diffusion constants can also be found. Studies of recombination have been used to determine the number of traps and depth of traps in silicon (15,16).

Section 1.5 - Purpose of this Investigation

It is the purpose of this investigation to study and verify some of the factors affecting the recombination processes and, in particular, to separate the volume from the surface effects. It was hoped to estimate the purity of the crystals which have been grown in this laboratory.
CHAPTER 2

THEORY OF RECOMBINATION

Section 2.1 - Recombination - General Processes

The three main processes by which a disturbed system returns to equilibrium were outlined in section (1.3) and these will now be treated qualitatively. Later, the mathematical derivations of the important cases will be discussed.

(a) Band-to-Band Transitions. In this process, electrons and holes recombine through the direct transition of an electron from a state in the conduction band to an empty state in the valence band. An amount of energy in excess of $E_G = E_C - E_V$ must be given up. The simplest process is radiative emission which can take the following forms (3): (i) excitation of lattice vibrations (phonon emission) (ii) transfer to another free electron or hole (Auger process) (iii) radiation of photons.

Processes (i) and (ii) have been shown to be very improbable (2,3). Process (iii) is the most probable and
has been studied theoretically and experimentally (3,9). Values of the associated lifetimes are \( >0.1 \) sec (section 2.3). These values are much longer than any lifetimes observed so far, so that the band-to-band radiative process must play only a negligible role compared to other recombination processes.

(b) **Recombination through Localized Levels**

(i) **Lattice Imperfections.** W. Shockley and W. T. Read (4) develop this case thoroughly. Generally, carrier lifetime is found to be an extremely structure sensitive quantity (3). For example, in different samples of the same material, variations in lifetime (of several orders of magnitude) may be found, with but minor differences in other electrical properties such as carrier concentration or mobility. In germanium, lifetimes can range from \( 10^{-8} \) sec to \( 10^{-2} \) sec, depending on the growth conditions and subsequent crystal treatment. Crystal imperfections of some sort must then play the dominant role in recombination, even in the most perfect germanium and silicon.

(ii) **Donors or Acceptors.** The electron can combine via localized donor or acceptor levels but this mechanism is believed to be relatively unimportant in germanium and silicon (6).

(c) **Surface Recombination.** In addition to combining in the volume, the electrons and holes may diffuse to the surface (3,6,8) and recombine there. This process may, in some cases,
be more important than the bulk recombination rate. "Surface states" can arise from impurities or imperfections at the semiconductor surface (8). They are also due to the termination of the periodic lattice regardless of surface conditions. The parameter for specifying the surface recombination rate is the surface recombination velocity, $s$, which is discussed in section (2.5). The values of $s$ range from less than $100 \text{ cm/sec}$ for a surface polished by etching to greater than $10^4 \text{ cm/sec}$ for a ground or sandblasted surface. The above four cases are shown in Figure (2).

Fig. 2. Possible Mechanisms for Recombinations of Electrons and Holes.
Section 2.2 - Definition of Lifetime

Free excess carriers must disappear in pairs across the gap or they may fall into localized levels (in the forbidden gap) and recombine. If the net rates of capture by localized levels are equal, the excess concentrations of free holes \((\Delta p = p - p_0)\) and free electrons \((\Delta n = n - n_0)\) are equal at any time. More commonly, the net rates of capture are not equal. This gives inequality in the concentrations of \(\Delta n\) and \(\Delta p\). In this case, some of the carriers of one type have been "trapped". However, such effects are observable only if the trapped number is comparable with or larger than the number of excess carriers of the same type. The term "trapping" will apply to this latter case. The condition of "non-trapping" implies that during the whole process \(\Delta n \approx \Delta p\).

The rate of change of the number of excess electrons per \(\text{cm}^3\), \(-U\), is equal to the rate of production of excess electrons per \(\text{cm}^3\), \(G\), minus the rate of depletion of excess electrons per \(\text{cm}^3\), \(R\). The rate of depletion of excess electrons is equal to the number of free electrons in the conduction band times the probability per unit time, \(\lambda_n\), for the recombination of an electron-hole pair. Associated with this recombination probability is a lifetime, \(\tau_n\), defined by the relationship,

\[
\tau_n = \frac{1}{\lambda_n}
\]

Hence

\[
-U = \frac{d}{dt} (\Delta n)
\]
and

\[ R = n \lambda_n = \frac{n}{\tau_n} \]

Thus the continuity equation is given by

\[ -U = G - R \]

or

\[ \frac{d}{dt} (\Delta n) = G - \frac{n}{\tau_n} \]

In equilibrium, \(-U = 0\), \(n = n_o\), \(\tau_n = \tau_{no}\) and \(G = G_o\), so that

\[ G_o = \frac{n_o}{\tau_{no}} \]

But \(\tau_n\) does not depend appreciably on concentration so that \(\tau_n \approx \tau_{no}\). Then the continuity equation gives

\[ \frac{d}{dt} (\Delta n) = \frac{n_o}{\tau_{no}} - \frac{n}{\tau_n} \approx \frac{\Delta n}{\tau_n} \]

where the value of \(G\) is assumed to remain constant and equal to \(G_o\).

When \(n \gg p\), \(p\) is the minority carrier concentration and \(|\Delta n| = |\Delta p| < p\). However, \(\tau_p\) does not depend appreciably on \(n\), so that

\[ G_o = \frac{P_o}{\tau_{po}} \approx \frac{P_o}{\tau_p} \]

A continuity equation for holes is therefore
\[
\frac{d}{dt} (\Delta p) = - \frac{\Delta p}{\tau_p}.
\]

If \((\Delta n)_{t=0}\) and \((\Delta p)_{t=0}\) are the values of \(\Delta n\) and \(\Delta p\) at \(t = 0\), the solutions of the equations of continuity are

\[
\Delta n = (\Delta n)_{t=0} \exp \left( - \frac{t}{\tau_n} \right)
\]

and

\[
\Delta p = (\Delta p)_{t=0} \exp \left( - \frac{t}{\tau_p} \right).
\]

Since \(|\Delta n| = |\Delta p|\), these equations show that \(\tau_p = \tau_n\), which states that the minority carrier lifetime equals the majority carrier lifetime.

For convenience of later developments, note that if \(\tau_p = \tau_n = \tau\), the above equations give

\[
\frac{1}{\tau} = - \frac{1}{\Delta p} \frac{d}{dt} (\Delta p) = \frac{U}{\Delta p} = - \frac{1}{\Delta n} \frac{d}{dt} (\Delta n)
\]

where \(U\) is the net rate of recombination per unit volume.

**Section 2.3 - Band-to-Band Recombination**

Let \(A\) be the capture cross section for band-to-band transitions and \(v\) be the thermal velocity. Then the average probability per hole of an electron combining with a hole can be expressed as the product \(vA\). Therefore, the rate of recombination for a density of \(n\) electrons and \(p\) holes is
In equilibrium, $U = 0$, thus giving

$$G_0 = R_o = Av_n p_o.$$  

If $G$ is assumed constant once again and equal to the value of $G_0$, when the system is perturbed, $U = R - G_0$ gives

$$U = vA(n_p - n_o p_o).$$

Substituting $n = n_o + \Delta n$ and $p = p_o + \Delta p$, and assuming charge neutrality, and $\Delta n = \Delta p$, gives

$$U = vA(p_o + n_o + \Delta p) \Delta p.$$  

Thus the associated lifetime, $\tau$, for this process, is given by

$$\tau = \frac{1}{vA(p_o + n_o + \Delta p)}.$$  

For low excitation intensity, $\Delta p \ll p_o + n_o$, which serves to define $\tau_o$, the "low-level" lifetime, as

$$\tau_o = \frac{1}{vA(p_o + n_o)}.$$  

For high intensity excitation, $\tau$ is a function of $\Delta p$. The transient case will be exponential only when $\Delta p \ll n_o + p_o$. For an intrinsic sample, $n_o = p_o = n_i$ and $R = vA n_i^2$. In this case, $\tau_o$ has a maximum value, $\tau_i$, given by
\[ \tau_i = \frac{1}{2vAn_i} = \frac{n_i}{2R} \]

When the value of \( R = 1.57 \times 10^{13} \text{ cm}^{-3} \text{ sec}^{-1} \) for \( T = 300 \degree \text{K} \) (9) is used, \( \tau_i = 0.75 \text{ sec} \). This value is much larger than anything observed and indicates the very low probability for this mode of decay.

Section 2.4 - Band-to-Localized Level Recombination

In this section, non-trapping means that \( \Delta n \approx \Delta p \). The trapping case (\( \Delta n \approx \Delta p \)) implies that some carriers have been removed from the conduction process by capture at localized levels. But they do not recombine at these levels. They must be thermally re-excited back into the conduction stream before the recombination can occur. The localized levels, through which recombination takes place, are not considered as traps for the following derivation.

(a) Lattice Imperfections. Suppose that the density of localized levels which contribute to recombination is \( N_t \) per unit volume and that these levels are situated in the forbidden gap at an energy \( E_t \). Each level can capture one electron when vacant and one hole when occupied by an electron. Figure (3) illustrates the situation. The rates of electron capture and emission are \( R_e \) and \( G_e \) respectively and \( R_h \) and \( G_h \) respectively for holes. Let \( f_t \) be the fraction of
localized levels occupied by electrons. Then $R_e$ is proportional to $n$ and $(1 - f_t)$ and is given by

$$R_e = C_n (1 - f_t)n$$  \hspace{1cm} (2.1)

where $C_n$ is the capture cross section per electron. $C_n$ is proportional to $N_t$. The rate of emission is proportional to $f_t$ so that

$$G_e = C_n' f_t$$ \hspace{1cm} (2.2)

![Diagram of electron energy levels and transitions](image)

**Fig. 3. Transitions between Bands and Localized Levels**

(a) Electron Capture (b) Electron Emission
(c) Hole Capture (d) Hole Emission

In equilibrium, $R_e = G_e$, so that

$$C_n' = \frac{C_n n_0 (1 - f_{to})}{f_{to}}$$ \hspace{1cm} (2.3)
Here, \( n_0 \) and \( f_{t_0} \) are the equilibrium values of \( n \) and \( f_t \). See equation (15), Appendix I, for the development which gives for \( \tau_0 \), the low-level lifetime, a value

\[
\tau_0 \approx \frac{C_p^{-1}(n_0 + n_1) + C_n^{-1}(p_0 + p_1)}{n_0 + p_0} \quad (2.4)
\]

When \( n_0 \gg p_0 \), equation (2.4) gives

\[
\tau_0 \approx \frac{C_p^{-1}(n_0)}{n_0} = C_p^{-1} = \tau_{p_0} \quad (2.5)
\]

When \( p_0 \gg n_0 \), equation (2.4) gives

\[
\tau_0 \approx \frac{C_n^{-1}(p_0)}{p_0} = C_n^{-1} = \tau_{n_0} \quad (2.6)
\]

Then equation (2.4) becomes

\[
\tau_0 \approx \frac{\tau_{p_0}(n_0 + n_1) + \tau_{n_0}(p_0 + p_1)}{n_0 + p_0} \quad (2.7)
\]

For extrinsic material, where the approximations for equations (2.5) and (2.6) hold, it is seen that \( \tau_{p_0} \) and \( \tau_{n_0} \) are constants. Note the difference here in comparing with band-to-band transitions which displayed an inverse proportionality to the concentration (section 2.3).
Figure (4) shows the variation of lifetime as a function of concentration when $\Delta p$ is small. This is a plot of equation (2.7). The plot in Figure (4) is for arbitrary values of the parameters $\tau_{po}$, $\tau_{no}$, and $E_t$. The quantities $\tau_{po}$ and $\tau_{no}$ are easily found, being the values of lifetime in strongly n-type and p-type samples respectively. However, some ambiguity exists in determining $E_t$. Two values of $E_t$, one above $E_i$ and one below, can equally well fit the curve. This can be seen, for instance, in the simple case where $\tau_{po} = \tau_{no}$. From equation (2.7), the maximum occurs when $n_o = p_o = n_i$ so that $\tau_o (\text{max})$ is given by
\[ \mathcal{V}_o \left( \text{max} \right) = \mathcal{V}_{po} \left[ 1 + \frac{n_1 + p_1}{2n_i} \right] = \mathcal{V}_{po} \left[ 1 + \cosh \left( \frac{E_t - E_i}{kT} \right) \right] \]

where use is made of the definitions of \( n_1 \) and \( p_1 \) (Appendix I). \( E_i \) is the Fermi energy for a pure sample at the temperature being used. In this special case, a symmetric curve results which is satisfied by energies of \( |E_t - E_i| \) below and above \( E_i \). The general case of \( \mathcal{V}_{no} \neq \mathcal{V}_{po} \) is assumed in order to plot Figure (4) and the exact position of the maximum will depend on the ratio \( \mathcal{V}_{po}/\mathcal{V}_{no} \). Unless this ratio differs by more than one or two orders of magnitude from unity, the maximum of \( \mathcal{V}_o \) will occur very close to \( E_i \).

When the number of localized levels, \( N_t \), is not small compared to \( n_o \) or \( p_o \), it cannot be assumed that \( \Delta n = \Delta p \). This more complex case is considered elsewhere by R.A. Smith (2).

(b) **Recombination via Donors or Acceptors.** This process has little importance at room temperature in germanium or silicon. However, it can play some role at low temperatures. Consider an n-type sample. The number of holes at low temperature is negligible and the dominant process is the decay of excited electrons to donors. Assume that the recombination centres are the donors themselves and that \( p_o \) and \( p_1 \) are negligible. Then

\[ n = (1 - f_t) N_d . \]
If $U_e$ is the net rate of recombination (Appendix I), $U_e$ is given by

$$U_e = C_n \left[ (1 - f_t)n - n_1 f_t \right].$$

Assume $N_d \gg n$, $C_n \propto N_t = N_d$, which gives

$$U_e = B(n^2 - n_o^2)$$

where $B$ is a constant and $n_o$ is once again the equilibrium concentration. Then, for $\tau_n$, the equation gives

$$\frac{1}{\tau_n} = \frac{U_e}{\Delta n} = B(2n_o + \Delta n).$$

At low temperature, $n_o$ is small so that for appreciable increase in carrier concentration, $\tau_n^{-1} \propto \Delta n$ and $U_e \propto (\Delta n)^2$ and not to $\Delta n$.

Then

$$\frac{d(\Delta n)}{dt} = -B(\Delta n)^2.$$

If at $t = 0$, $\Delta n$ becomes $(\Delta n)_{t=0}$, the solution of the above equation gives

$$\Delta n = \frac{(\Delta n)_{t=0}}{1 + (\Delta n)_{t=0}Bt}.$$

This shows that excess carriers decay by a hyperbolic law at low temperature.
Section 2.5 - Surface Recombination

Under equilibrium conditions for an n-type sample, the number of holes diffusing to the surface is equal to the number diffusing away.

Let \( r \) be the average probability of reflection of a hole striking the surface. The rate at which holes diffuse to the surface is equal to \( C v_p \), where \( v \) is the average thermal velocity, and \( C \) is a constant. If \( S \) is the rate of recombination of holes per unit area, the rate of holes diffusing from the surface is \( C v_p + S \). In equilibrium, these rates are equal and \( S = S_0, \) \( p = p_0 \), so that

\[
C v_p = C v_p + S_0.
\]

Hence,

\[
S_0 = C v_p (1 - r).
\]

In the perturbed case, the net rate of recombination of excess holes at the surface is \( S_a \), where \( S_a \) is given by

\[
S_a = C (1 - r) v (p - p_0) = C (1 - r) v (\Delta p).
\]

A surface recombination velocity, \( s \), is defined such that

\[
S_a = s \Delta p.
\]

Thus

\[
s = C (1 - r) v.
\]
It is seen that $s$ has the expected dimension of velocity.

Section 2.6 - Shockley's Theory of Filament Lifetime

This theory is given by W. Shockley (1) and others (11,12). The derivation that follows deals with holes injected into n-type material in small densities. These holes will set up a small electric field which will draw in electrons quickly to neutralize the charge of the holes. However, the electron density is so much larger than the hole density that the required field alters the electron distribution only very slightly. The electrons therefore move almost as if no holes were present at all and to a first approximation, the holes can be considered to move in the same field as would exist if no holes were present.

Suppose that the distribution along the filament is uniform (e.g. illuminating the filament by a flash of light). It will be shown that the hole density decays as $\exp\left(-\frac{t}{\tau_{p1}}\right)$, where $\tau_{p1}$ is the lifetime of holes in the filament.

The filament for the analysis is assumed to be as shown in Figure (5) with the field applied along the $x$-axis and the sample boundaries at $x = \pm A$, $y = \pm B$, $z = \pm C$.

Consider solutions for the continuity equation (3),
Appendix II. The hole current has components

\[ I_x = e \mu_p p E_x - e D_p \frac{\partial p}{\partial x} \]  \hspace{1cm} (2.8)

\[ I_y = -e D_p \frac{\partial p}{\partial y} \]  \hspace{1cm} (2.9)

\[ I_z = -e D_p \frac{\partial p}{\partial z} \]  \hspace{1cm} (2.10)

These components of current must satisfy the continuity equation (10), Appendix II. If \( g = \frac{P_0}{\xi_p} \), which is the case in equilibrium with no holes injected, this equation gives

\[ \frac{\partial p}{\partial t} = \frac{P_0 - P}{\xi_p} - \mu_p E_x \frac{\partial p}{\partial x} + D_p \left[ \frac{\partial^2 p}{\partial x^2} + \frac{\partial^2 p}{\partial y^2} + \frac{\partial^2 p}{\partial z^2} \right] \] \hspace{1cm} (2.11)

If the notation \( \Delta p = p - P_0 \) is used, equation (2.11) is a homogeneous partial differential equation which is linear in \( \Delta p \). It is separable and has solutions that can be written as products of separate functions of \( t, x, y, z \). One such solution is

\[ \Delta p = \exp \left[ -\gamma t - ax \right] \cos by \cos cz \] \hspace{1cm} (2.12)
where \(a, b, c\), and \(\gamma\) are constants. The relation between these constants is found by substituting equation (2.12) into (2.11) to get

\[
\gamma - \frac{1}{E_p} + \kappa_p E_x a + D_p (a^2 - b^2 - c^2) = 0 \tag{2.13}
\]

The most general solution of equation (2.11) corresponding to arbitrary initial conditions at \(t = 0\) can be expressed as the sum of a series of terms similar in form to equation (2.12) which includes sine and cosine terms of \(y\) and \(z\) and complex and imaginary values for \(a\).

If the filament is illuminated equally on all sides, so that the value of \(\Delta p\) is a constant at these sides, only the symmetric cosine terms will be needed. A number of terms are needed however so that the series sum at \(t = 0\) will represent the hole density. Each term will thereafter decay with its own characteristic lifetime so that the decay of the total number of holes in the filament will not be represented by a simple exponential decay but by a sum of decaying terms having different lifetimes.

One of the solutions of the form of equation (2.12) has a lifetime much longer than the others. This will persist long after the others have decayed to negligible proportions. These other terms can be considered to be initial transients which die away quickly leaving only the slowest decay, or the
filament lifetime, to be observed.

At the boundaries \( y = \pm B \), suppose that the excess of recombination over generation is directly proportional to \( \Delta p \), with a proportionality constant \( s \), the surface recombination velocity. The current towards the surface must satisfy

\[
\frac{1}{e} I_y = \pm s \Delta p \quad \text{at} \quad y = \pm B \quad (2.14)
\]

\[
\frac{1}{e} I_z = \pm s \Delta p \quad \text{at} \quad z = \pm C \quad (2.15)
\]

The boundary conditions for \( y = +B \) and \( y = -B \) are equivalent when \( \Delta p \) is given by equation (2.12). Therefore, using \( I_y \) from equation (2.9), and substituting in equation (2.14), the following condition arises,

\[
bB \tan (bB) = \frac{sb}{Dp} = \eta \tan \eta \quad (2.16)
\]

Similarly for \( z = \pm C \),

\[
cC \tan (cC) = \frac{sc}{Dp} = \frac{\eta}{2} \tan \frac{\eta}{2} \quad (2.17)
\]

The abbreviations \( \eta = bB \) and \( \frac{\eta}{2} = cC \) have been used. For every value of \( \frac{sb}{Dp} \), there is one solution of \( \eta \) in the range \( 0 \leq \eta \leq \pi/2 \) and also one solution in every interval \( n\pi \) to
The same is true for \( \mathcal{F} \). The term having the longest lifetime will be the one corresponding to \( \eta_0 \) and \( \mathcal{F}_0 \) which are defined to be the smallest solutions of equations (2.16) and (2.17). In terms of \( \eta_0 \) and \( \mathcal{F}_0 \), the values of \( b \) and \( c \) become \( \frac{\eta_0}{B} \) and \( \frac{\mathcal{F}_0}{C} \) respectively. Equation (2.13) then can be considered as an equation in the two parameters, \( a \) and \( \mathcal{F} \), giving when grouped

\[
\mathcal{F} + D_p a^2 + \lambda_p E_x a = \frac{1}{\mathcal{T}_p} + D_p \left[ \frac{\eta_0^2}{B^2} + \frac{\mathcal{F}_0^2}{C^2} \right] \equiv \mathcal{F}_f \quad (2.18)
\]

The terms on the right of the first equals sign are determined by the constants of the filament \( \mathcal{T}_p, B, C, \) and \( s \). It will be shown below that \( \mathcal{F}_f \) is the decay constant of the filament and is equal to \( \frac{1}{\mathcal{T}_p} \). Consider the case where the density is independent of \( x \), so that \( a = 0 \). In this case, equation (2.18) gives \( \mathcal{F} = \mathcal{F}_f \), which does not depend on the value of \( E_x \). The solution \( \Delta p \) can be written as

\[
\Delta p = e^{-\mathcal{F}_f t} \cos by \cos cz \quad (2.19)
\]

so that the hole density decays exponentially with a decay constant, \( \mathcal{F}_f \), equal to \( \frac{1}{\mathcal{T}_p} \), in accordance with

\[
\frac{1}{\mathcal{T}_p} = \mathcal{F}_f = \frac{1}{\mathcal{T}_p} + D_p \left[ \frac{\eta_0^2}{B^2} + \frac{\mathcal{F}_0^2}{C^2} \right] \quad (2.20)
\]

Equation (2.20) shows that \( \mathcal{F}_f \) for the material is the sum
of the "bulk material" decay constant, \( \frac{1}{\tau_p} \), plus a surface decay constant, \( \gamma_s \).

It is now apparent why terms involving \( \eta_n \) and \( \xi_n \) for \( n \) greater than zero can be disregarded for many purposes. For these terms, the values of \( \eta_n^2 \) and \( \xi_n^2 \) will at least be four times larger than \( \eta_0^2 \) and \( \xi_0^2 \). Consequently, such terms will decay rapidly compared to \( \eta_0 \) and \( \xi_0 \) and can be neglected.

Certain simplifications become useful. For example, as \( s \to \infty \), both \( \eta_0 \) and \( \xi_0 \) become \( \pi/2 \) and \( \gamma_s \) becomes

\[
\gamma_s = \frac{\pi^2 D_p}{4} \left[ \frac{1}{B^2} + \frac{1}{C^2} \right] \tag{2.21}
\]

On the other hand, as \( s \to 0 \), \( \eta_0 \tan \eta_0 \to \eta_0^2 \), so that

\[
\gamma_s = s \left[ \frac{1}{B} + \frac{1}{C} \right] \tag{2.22}
\]
CHAPTER 3

THEORY OF INJECTION AND ASSOCIATED EFFECTS

Section 3.1 - Response Time for Photoinjection

When a constant illumination is instantaneously applied to a sample, the photocurrent in the sample, responding to the illumination, increases to some equilibrium value. The response time is a measure of this "lag". It is defined to be the time for the photocurrent to attain the fraction \((1 - \frac{1}{e})\) of its maximum. Consider a semiconductor with \(M\) acceptor centres per unit volume. Suppose that some kind of radiation injects \(Q\) photoelectrons per unit volume per unit time into the conduction band from the valence band. Let \(G\) be the thermal excitation rate per unit volume per unit time for electrons. Then, if \(n'\) of the acceptor levels are occupied originally, leaving \(n'\) holes in the valence band, and if the only electrons in the conduction band are \(n_o\) per unit volume due to thermal excitation, the equation of continuity is
\[ \frac{dn}{dt} = Q + G - n B_1 (n + n' + M - n') \]

\[ = Q + G - n B_1 (n + M) \quad (3.1) \]

The same recombination coefficient, \( B_1 \), has been taken for both holes in the valence band and holes in the acceptor levels.

In equilibrium, \( \frac{dn}{dt} = 0 \). When \( Q = 0 \), \( G \) can be found from equation (3.1). Hence, in this case, \( n = n_o \) and

\[ G = n_o B_1 (n_o + M) \quad (3.2) \]

Putting \( \Delta n = n - n_o \) in equation (3.1) gives

\[ \frac{d(\Delta n)}{dt} = Q - B_1 \Delta n(\Delta n + X) \quad (3.3) \]

where \( X = M + 2n_o \). If \( n_m \) is the density of electrons in the conduction band when final equilibrium is reached during illumination, equation (3.3) can be integrated (integral No. 89, Handbook of Physics and Chemistry, 1954) to give

\[ \frac{\Delta n_m - \Delta n}{\Delta n_m + \Delta n + X} = \frac{\Delta n_m}{\Delta n_m + X} \exp \left[ -B_1 (X + 2 \Delta n_m) t \right] \quad (3.4) \]

In equation (3.4), \( \Delta n_m = n_m - n_o \). For small signals, \( \Delta n \ll X \) and \( \Delta n_m \ll X \), so that equation (3.4) gives
\[ \Delta n_m - \Delta n \simeq \Delta n_m \exp(-B_1 X_t) \]  

(3.5)

The ratio of \( \Delta n \) to the maximum value, \( \Delta n_m \), is

\[ \frac{\Delta n}{\Delta n_m} = 1 - \exp(-B_1 X_t) \]  

(3.6)

The response time from equation (3.6) is

\[ \tau = \frac{1}{B_1 X} = \frac{1}{B_1 (M + 2n_o)} \]  

(3.7)

T. S. Moss (13) states that equation (3.7) is equally well applied to the case where the photoelectrons originate at donor impurity levels. The above development has been simplified by assuming that the same recombination coefficient, \( B_1 \), applies to the two kinds of electron recombination with holes at impurity levels and with holes in the valence band. The derivation is considerably more complicated if this is not assumed to be the case. The formula for response time will be referred to in Chapter (5) in connection with the analysis of the experimental results.

Section 3.2 - P-N Junction Theory

(a) Theory. The equations describing the behaviour of p-n junctions lead to the photovoltage equation for metal-
to-semiconductor contacts. The general energy level scheme for a p-n junction is shown in Figure (6). The transition

![Diagram of p-n junction](image)

Fig. 6. P-N Junction Representation

region between the n- and p-type regions is sharp. In equilibrium, a potential $\Phi$ will exist across the junction as shown, so that the net current flowing is zero. The Fermi level must be the same for n and p regions in the equilibrium state. The formula for the current across a p-n junction is given by

$$I = I_1 e^{-\frac{\Phi}{kT}} \left[ 1 - e^{-\frac{-eV}{kT}} \right] + I_2 e^{-\frac{\Phi}{kT}} \left[ 1 - e^{-\frac{-eV}{kT}} \right]$$

(3.8)

In equation (3.8), $V$ is the potential applied across the junction, and $I_1$ and $I_2$ represent the electron and hole contributions to the current flow.
(b) **Photovoltaic Effect at Junction.** Suppose that the junction is now illuminated so that $Q$ photoelectrons and holes are produced per unit volume per unit time. Then the concentrations of electrons and holes change in the manner represented by equations (3.1) and (3.2). In this case

$$G = B' n_0 (n_0 + M)$$

and

$$Q + G = B'n(n + M) = Q + B'n_0(n_0 + M) \quad (3.9)$$

If $(\Delta n)^2$ is neglected, the ratio $\frac{\Delta n}{n}$ is given by

$$\frac{\Delta n}{n} = \frac{Q}{B'n(2n + M)} \quad (3.10)$$

Thus, for holes, a photosensitivity, $S_h$, is defined as

$$S_h = \frac{\Delta p}{Qp} = \frac{1}{B'p(2p + N_d)} \quad (3.11)$$

where $N_d$ is used as the number of recombination centres for holes. A similar relation holds for electrons for which the photosensitivity, $S_e$, is given by

$$S_e = \frac{\Delta n}{Qn} = \frac{1}{B'n(2n + N_a)} \quad (3.12)$$

In the p-region, shown on the left side of Figure (6), $N_d = 0$. In this case equation (3.11) reduces to
where it is assumed that the impurity centres are fully ionized. Also in the p-region, \( n \ll N_a \), so that equation (3.12) gives

\[
S(p)_h = \frac{1}{2B'p^2} = \frac{1}{2B'N_a^2}
\]  

(3.13)

where use has been made of \( np = n_i^2 \).

Now \( N_a \gg n_i \) usually, so that \( S(p)_e \gg S(p)_h \). This indicates that the density of minority carriers is the most important factor in the operation of a p-n junction. A similar result occurs for the n-region. If changes in majority carrier densities are then ignored, the current relation of equation (3.8) will be modified, under illumination, to give

\[
I_L = I_1 e^{-\phi/kT} \left[ 1 + QS(p)_e - e^{-eV/kT} \right] + I_2 e^{-\phi/kT} \left[ 1 + QS(n)_h - e^{-eV/kT} \right]
\]

(3.15)

When equilibrium is reached, \( I_L = 0 \), and the resultant voltage is the photovoltage, \( V = V_p \), which is

\[
V_p = -\left( \frac{kT}{e} \right) \log (1 + SQ)
\]

(3.16)
In equation (3.16), $S$ is given by

$$S = \frac{I_1 S(p)_e + I_2 S(n)_h}{I_1 + I_2} \quad (3.17)$$

Investigation of equation (3.16) indicates that for small intensities $V_p$ is proportional to $Q$. But for higher intensities, $V_p$ becomes proportional to $\log Q$. This has been found to hold experimentally.

Section 3.3 - Optical Effects

(a) Metal-Semiconductor Contacts. Such contacts are discussed elsewhere (1,13,14). Only a brief account will be given here. When a metal and semiconductor come into contact, an electric field will be set up due to the difference in contact potential. The induced charge on the semiconductor surface arises largely from a change in the number of electrons in the surface states. The effect of surface states extends only a distance of 2 or 3 atomic diameters into the sample. Figure (7) shows the equilibrium adjustment so that the Fermi level is the same on both sides of the contact.

(b) Photovoltaic Effect at Such Contacts. Assuming the transition region between the semiconductor and metal to be thin enough to allow electron penetration by the quantum mechanical tunnel effect, the current is given by an expression similar to equation (3.8) for the p-n junction case.
The current across the contact is

\[ I = I_o e^{-\frac{e\phi}{kT}} \left[ 1 - e^{-\frac{eV}{kT}} \right] \]  

(3.18)

where \( V \) is the applied voltage. The photovoltage, \( V_p \), will be given by an expression similar to equation (3.16) such that

\[ V_p = -\left(\frac{kT}{e}\right) \log (1 + S'Q) \]  

(3.19)

The conditions for \( V_p \) as a function of \( Q \) also hold.

---

Section 3.4 - Electrical Injection of Minority Carriers

W. Shockley (1) discusses the case of minority carrier injection in semiconductors. Figure (8) indicates the
Experimental arrangement which can be used to study electrical injection. The voltage observed on an oscilloscope is shown in Figure (9) for one cycle of S closing and opening. When S is closed, electrons in the germanium are conducted to the metal. The conduction in germanium may be due either to holes or electrons. This is shown in Figure (10). At first it might appear that the difference between these two processes is unimportant since the net result is a transfer of electrons from germanium to the metal point. The difference, however, is important because, in the hole process, an electron is transferred from the valence band structure to the metal. After this the hole moves deeper into the germanium. As a result, the electronic structure of germanium is modified in the neighbourhood of this point by the presence of injected holes. Under the electric field, these holes drift with velocity $\frac{L}{\mu pE}$ and cover the distance L (Figure 8) in a time $\frac{L}{\mu pE}$. They arrive at the collector at time $t_2$ to produce the noted increase in reverse current.

The difference between the signals at times $t_1$ and $t_2$ can be explained. The signal at $t_1$ would be produced if no hole injection occurred. This is the normal IR drop produced when the total current is changed by closing S. The withdrawal of a few electrons produces a local positive charge which sets up a weak electric field. Adjacent electrons move in to neutralize this and so on. The result is that
Fig. 8. Experimental Arrangement for Electrical Injection.

(1) S closes (holes injected)
(2) Holes arrive at collector
(3) S opens
(4) Holes depart from collector

Fig. 9. CRO Signal Showing Hole Arrival at Time $t_2$.

Fig. 10. Electron Flow and Hole Flow from a Point Contact.
the impulse is transferred swiftly but the charge carriers have moved only very little.

In a sample having carriers of one type, say electrons, it is impossible to alter the concentration of carriers by trying to inject or extract carriers of the same type. The reason is that such changes would produce an unbalanced space-charge in the sample. Such a process is self-annihilating and does not occur. When holes are injected, however, they also set up a space-charge. But this space-charge can be neutralized by electron flow from an external source. The net result is an increase in the total number of electrons and holes in the sample.

This will be applicable later in regard to the electrical injection experiments which depend on the phenomena discussed above.

Section 3.5 - Electrical Field Sweep-Out of Carriers

In order to measure lifetimes, an electric field must be applied across the sample. If the field is too large, carriers will be swept out of the sample before the recombination can occur. However, if the electric field is kept sufficiently small, the current will be primarily due to diffusion.

If variations are considered only in the x-direction, equation (2.11) gives
For a steady state, in which \( \frac{\partial}{\partial t} \Delta p = 0 \), equation (3.20) becomes

\[
\frac{\partial^2 (\Delta p)}{\partial x^2} + D_p \frac{\partial^2 (\Delta p)}{\partial x^2} = 0
\]

Assume that holes are generated at \( x = 0 \) at a sufficient rate to maintain a steady state such that \( \Delta p = \Delta p_0 \) at \( x = 0 \). Assume also that the sample is a semi-infinite bar of material extending from \( x = 0 \) to \( x = \infty \). Defining a diffusion length for holes, \( L_p \), such that \( (L_p)^2 = D_p \tau_p \) gives a solution of equation (3.21) as

\[
\Delta p = \Delta p_0 e^{-\frac{x}{L_p}}
\]

The hole current required to maintain this steady state condition is given by \( I_{p_0} \) at \( x = 0 \) (see equation (3), Appendix II) and is

\[
I_{p_0} = -e D_p \left[ \frac{\partial (\Delta p)}{\partial x} \right]_{x=0} = \frac{e D_p \Delta p_0}{L_p}
\]

where use has been made of equation (3.22).

The hole current due to the electric field is equal to \( e(p + \Delta p) \frac{\mu_{th}}{E_x} \). It is seen from equation (3.23) that this
will be small compared to the diffusion current at \( x = 0 \), provided

\[
E_x \mu \thicksim \frac{D_p}{L_p}.
\]

This condition may be obtained in a slightly different way (11), where it is found that

\[
\mu_p E_x \thicksim \frac{2D_p}{L_p}.
\]

This gives

\[
(\mu_p E_x)^2 \thicksim \frac{4D_p^2}{L_p^2} = \frac{4D_p}{L_p} \tau_p.
\]  \( (3.24) \)

An estimate of the approximate reduction of lifetime due to the sweep-out of carriers has been made (12). For a field along the \( x \)-axis as before, the number of carriers left in the sample at time \( t \) will be proportional to

\[
(2A - v_x t) e^{-\frac{t}{\tau_0}}
\]  \( (3.25) \)

Here, \( 2A \) is the length of the sample parallel to the \( x \)-direction, \( \tau_0 \) is the observed lifetime under the \( E_x = 0 \) approximation, and \( v_x \) is the drift velocity under the action of \( E_x \). However, \( v_x \) can be expressed in terms of \( \mu \) and \( V_0 \),
the applied voltage, as

$$v_x = \nabla E_x = \frac{\mu V_0}{2A}$$  \hspace{1cm} (3.26)

The quantity \((2A - v_x t)\) may be approximated by an exponential in the following manner:

$$2A \left[ 1 - \frac{v_x t}{2A} \right] \simeq 2A \left[ e^{-\frac{v_x t}{2A}} \right] \quad \text{for} \quad \frac{v_x t}{2A} \ll 1 \quad . \hspace{1cm} (3.27)$$

Thus, using equations (3.26) and (3.27), one obtains for the number of carriers left in the sample at time \(t\),

$$2A \left[ -e^{-\frac{\mu V_0 t}{(2A)^2}} \right] e^{-\frac{t}{\tau_0}} = 2A \left[ e^{-\frac{t}{\tau_1}} \right] \quad \hspace{1cm} (3.28)$$

From equation (3.28), if \(t = \tau_1\), the number of carriers has decayed to \(\frac{1}{e}\) of the original value, so that

$$\frac{1}{\tau_1} = \frac{1}{\tau_0} + \frac{\mu V_0}{(2A)^2} \quad \hspace{1cm} (3.29)$$

Equation (3.29) relates the value of \(\tau_1\), which allows for sweep-out, to \(\tau_0\), the zero field case, when no sweep-out occurs.
CHAPTER 4

EXPERIMENTAL ARRANGEMENT

Section 4.1 - Comparison of Experimental Methods

Table I shows some of the methods which may be employed to measure minority carrier lifetimes.

In this laboratory, it is generally necessary to make non-injecting electrical connections to the semi-conducting samples to be investigated. Consequently, the technique of J. R. Haynes and J. A. Hornbeck (15,16) and D. T. Stevenson and R. J. Keyes (11) was chosen to study the decay of injected minority carriers.

The R-C comparison methods (24,25) only apply for decays which are exponentials. This is not always the case. Also, there is difficulty in cancelling out the photoconductivity decay with a generated exponential which has to be adjusted to have the same amplitude.

The steady state methods usually apply to crystals of special geometry (28) and, in all cases, extra contacts are required to the sample (26,27,28).
# TABLE I

## COMPARISON OF EXPERIMENTAL METHODS

### Optical Injection (Transient Methods)

<table>
<thead>
<tr>
<th>Means of Detection</th>
<th>Material</th>
<th>Comments</th>
<th>Ref.</th>
</tr>
</thead>
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<td>Decay of Photoconductivity</td>
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<td>Trapping Effects Evident</td>
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</tr>
<tr>
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<td>&quot; &quot; &quot;</td>
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<tr>
<td>&quot; &quot; &quot;</td>
<td>Ge and Si</td>
<td>&quot; &quot; &quot;</td>
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<td>&quot; &quot; &quot;</td>
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<td>&quot; &quot; &quot;</td>
<td>Ge and Si</td>
<td>&quot; &quot; &quot;</td>
<td>21</td>
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### Optical Injection (Steady State Methods)

<table>
<thead>
<tr>
<th></th>
<th>Material</th>
<th>Comments</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Flying Light Spot Method</td>
<td>Ge</td>
<td>Gives $\tau$ and $\lambda$ simultaneously</td>
<td>26</td>
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<tr>
<td>d.c. Photoconductivity Method in filaments</td>
<td>Si</td>
<td>$\tau$ (with expt'l precaution)</td>
<td>27</td>
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<tr>
<td>Focused Light Spot on</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Semi-infinite Crystal</td>
<td>Ge</td>
<td>Only applies for this special geometry</td>
<td>28</td>
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### Electrical Injection

<table>
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<th></th>
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<th>Comments</th>
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<td>$\tau$ as a function of s</td>
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<td>&quot;</td>
<td>$\tau$ at a low temp, shows trapping</td>
<td>18</td>
</tr>
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<td>&quot; &quot; &quot;</td>
<td>&quot;</td>
<td>&quot; &quot; &quot;</td>
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<tr>
<td>&quot; &quot; &quot;</td>
<td>&quot;</td>
<td>$\tau$ as a function of s</td>
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<tr>
<td>Bridge Method using R.C. Network</td>
<td>Ge and Si</td>
<td>Demonstrates Bridge Method for Measuring $\tau$</td>
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<tr>
<td>p-n Junction</td>
<td>p-n junct. only</td>
<td>$\tau$ as a function of s</td>
<td>23</td>
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</table>
Fig. 11. Block Diagram of Apparatus
For electrical injection studies, the method utilizing large area soldered contacts (17) seems to be most widely used (12,18,19,20). The disadvantage of this method is the fact that for very few experiments does one require an injecting contact for subsequent work, after the lifetime has been measured. However, as a check on the photoconductivity decay method, it was desirable to try this method.

The bridge method (22), once again, requires an R-C setting.

Section 4.2 - Optical Arrangement

Figure (11) shows a block diagram of the apparatus used. The components of Figure (11) are numbered A to H. These are discussed below in order.

A: The 300 v d.c. regulated power supply is the source of power for C. The degree of regulation of the 300 volts is not critical since this voltage is only used to charge a condenser. The 6.3 v a.c. outlet supplies 0.6 ampere to the 2D21 filaments.

B: The Tektronix waveform generator (type No. 162) and pulse generator (type No. 163) plus its power supply (type No. 160A) is used for two purposes: (1) To provide the trigger pulse to the 2D21 which can be made to run continually or on a "one-shot" process. The amplitude is variable from 0 to 25 volts. (2) To apply a 50 v positive pulse to the
oscilloscope to trigger the base line. This baseline is necessary for the subsequent analysis of the photographs. The waveform generator is the source of a 50 v positive pulse and a negative sawtooth pulse. The former triggers the oscilloscope. The pulse generator triggers itself from the negative sawtooth pulse at any point along this waveform. This means that the output pulse to the 2D21 can be delayed up to a whole period after the 50 v pulse has been applied to the oscilloscope and triggered the baseline.

C: The 2D21 thyratron supplies a fast rising 300 v pulse to reliably trigger the next stage, the 5C22 thyratron. The circuit is given in Figure (12). The 300 volt supply charges the condenser C to 300 volts. The 2D21 will not conduct until the potential of the grid is raised to about -4 volts. Since the grid of the 2D21 is maintained at -10 v by a bias battery, at least a +6 volt pulse is necessary to trigger this tube. Effective triggering is obtained by using a +15 volt pulse from the pulse generator.

The width of this pulse applied to the grid must be greater than 1-2 $\mu$s for reliable triggering. In this work, a width of 5 $\mu$s was used.

When the thyratron begins conduction, the 300 volts across the condenser C immediately appear across $R_L$. The resulting 300 volt pulse is used to trigger the 5C22. The time required to charge condenser C is determined by both $R$
Fig. 12. Circuit Diagram of the 2D21 Trigger Unit.

Fig. 13. Circuit Diagram for 5C22 and Spark Gap System.
and C. Allowing a time of 5 time constants for the recharging of condenser C limits the frequency of operation of this unit to about 25 pps.

D: The 5C22 is necessary to hold off the high voltages necessary to fire a spark gap. Some of the 5C22 characteristics are listed below (see Ref. 29):

1. 16 Kv peak voltage rating
2. Heater power - 65 watts (6.3 volts)
3. 150 volt trigger pulse (minimum) is required
4. Tube life at maximum ratings is 500 hours
5. Ionization time is $0.07\mu s$
6. Continuous conduction if anode reaches 100-200 volts before de-ionization.
7. De-ionization time: grid-anode region about $5\mu s$
grid-cathode region much longer than this, say $50\mu s$.

It is found that a time constant $RC > 5ms$ will keep the anode voltage lower than 200 volts for $50\mu s$, when the high voltage supply is at 20 KV (see (6) and (7) above).

The high voltage lead from the power supply was bound securely to the framework to prevent strain on the 5C22 anode. Screening was placed around the tube and grounded to the chassis to help shield the other circuitry from the radiation due to the thyratron firing. Figure (13) shows the circuit for the 5C22 with the associated spark gap (to be described in part F).
E: The high voltage required to produce breakdown of the air spark gap was obtained from a commercial R.F. supply. By measuring the current flow through a 400 megohm resistor, the supply was found to have a range of 8-24 KV.

F: The design of spark gap systems has been discussed in detail elsewhere (30), as well as the associated electronic techniques (31). The system is shown to the right of dotted line in Figure (13). The system can be made into the very convenient coaxial unit shown below in Figure (14).

An Amphenol connector (UG 59 A/U) and panel jack (UG 61 A/U), rated at 30 Kv, are used as an electrode holder. A steel bolt is drilled to 3/16" diameter and fitted into the connector as shown. A 3/16" bakelite rod, with a 0.040" hole
drilled centrally, houses a 0.040" tungsten wire. One end of this wire is fitted with a tapered brass connector which fits into a tapered receptacle. The 100 KΩ resistor shown in the schematic (Figure 13) is comprised of 10 resistors (each 1 megohm) connected in parallel and spaced evenly around the rim of the panel jack (grounded end). These are insulated from ground at the other end by tape where they join with the central conductor and condenser C'. The other end of condenser C' is connected to the inner conductor of the RG 58U cable. The braided shield of this cable is attached to an outer brass cylinder which houses the whole system and is at ground potential. Thus, the bolt is at ground potential, as shown (Figure 13).

With this arrangement, it is possible to develop high voltage pulses of amplitude up to twice the initial charging potential. C' and RL' in series with the cable represent an infinite termination impedance for the transmission line. The value of C' can be varied from 0.005 μf to 0.0005 μf (30) without appreciable effect. When the 5C22 thyatron begins conduction, it short circuits the input end of the cable, bringing the voltage down to zero. Since the cable originally has been charged to a potential E, this short circuiting action is equivalent to applying a voltage pulse of amplitude -E to the cable. When it reaches the discontinuity at the other end, it is reflected back out of phase with the incident
pulse. As a result, the voltage at the end of the cable changes by an amount which is equal to 2E. Since the voltage across C remains unchanged, the voltage across R_L' is 2E. This voltage is applied to the gap. If 2E is greater than the sparking potential of the gap in air, the gap will break down. A series of reflections occur on the transmission line, all of which are of little importance because the gap breaks down before the first of these reflected waves reaches R_L'.

The time constant R'C' is 50 ms (assuming the cable capacitance is negligible compared to the capacitance of C'). This is greater than the time required for the 5C22 to de-ionize (part D).

Such a system should give a well defined flash of light, with a minimum of interference due to electrical or magnetic pickup. To test the system a photomultiplier tube (RCA No. 931) was used and the wave form of the current pulse produced by the incident light was observed (Figure 15). The pulse appears to be well defined and is approximately 1/\mu s in length with only a slight uncertainty in length (shown by dotted lines). For comparison purposes, a quartz enclosed spark gap was used and the light output was observed

Fig. 15. Photomultiplier Recording of Spark Source Output.
to have a long decay which persisted out to 10 μs. This trace was not nearly as well defined as the coaxial system spark and would probably be representative of most gaps which are not coaxial.

G: The sample, a 9v battery, a switch, and a variable resistor are enclosed in a metal box (electrical shielding) lined with mu-metal (magnetic shielding). The lid of this box swings out to allow easy replacement of another sample holder. The sample holder is positioned so that the sample is in line with the spark source (outside the box) and the entrance slit. The distance of the sample from the slit can also be varied. A d.c. light source is also mounted inside the box. The intensity of this source can be varied. The presence of the d.c. background illumination assists in the study of trapping effects. The arrangement used is shown in Figure (16). S1 connects the bias battery into the circuit to provide a field across the sample. R_s limits the currents through the sample to the constant current range. S2 provides a reversing switch for passing current through the sample in two directions.
S_3 provides the steady ambient light and R_L allows the intensity to be changed.

**H:** A high gain Tektronix preamplifier (type 53/54 D) and a Tektronix oscilloscope (type 545) were used to detect the photoconductivity signal. A polaroid camera (Type 2614 and 2620-Dumont) capable of handling 3000 ASA speed film was used to photograph the oscilloscope traces.

**Section 4.3 - Sample Preparation for Optical Work**

(a) **Resistivities.** Samples of rectangular geometry were used in this investigation. These filaments were cut from discs of semiconductor material whose resistivity had been measured previously. The resistivities were measured on a Baird-Atomic four-point-probe machine (Model JN) as instructed in the operating manual. Care was taken to apply any corrections necessary to account for the finite disc thickness. In this way, the samples of n-type germanium used in this experiment were found to be of resistivities 0.01, 5, 19, 50 Ω-cm. Silicon resistivities given by the manufacturer were n-type (8.2 Ω-cm) and p-type (130 Ω-cm).

(b) **Preliminary Cleaning.** The black wax, which is used to hold the discs during dicing, can be removed by toluene. The pieces are then throughly degreased by boiling for approximately 5 minutes in a 15% H_2O_2 solution.

(c) **Lead Attachment.** (i) Germanium - The germanium
filaments are etched in slow CP4 for 1 or 2 minutes. Then gold leads are alloyed on to the ends, particular care being taken to have the handling instruments scrupulously clean. A liberal flow of nitrogen is required around the sample during the actual alloying process to prevent oxides from forming when the sample is heated. A light etch (15 seconds of slow CP4) should follow the alloying process to remove any gold which may have adhered to the end or side and is not attached to the main lead. For lower resistivities, n-type gold wire (doped with 0.6% Sb) is used. When the intrinsic region is approached, Woods metal soldered contacts or pure gold wire are found best.

(ii) Silicon - The silicon filaments should have the ends roughed by course (F-RA) carborundum. This provides a rough surface on which a eutectic of gold and silicon can more easily be obtained. The end of the filament is cleaned in a saturated solution of KOH. Then, the end of the filament is immediately placed in a warm gold plating solution. This must be done quickly to prevent the formation of SiO$_2$. A plating current of 15 ma/cm$^2$ is found satisfactory. The gold plate forms a eutectic with the silicon when the filament is heated, and the alloying of gold leads proceeds as for germanium.

(d) Lead Protection. If the sample is to be etched, the gold leads must be protected. One or two etchings, as described above, will undermine the contact. Epoxy resin or nail polish can be applied to the ends of the filament for
protection. Epoxy resin gives a very sturdy bond and good support mechanically. It was used throughout, whenever required.

(e) Low $s$ Treatment. It was assumed that the lowest surface recombination velocity could be obtained when the sample had been etched (12). However, obtaining a good etched surface usually requires agitation of the sample in the etch. This is necessary to prevent local heating due to the vigorous manner in which the etch attacks the semiconductor material. The rate of etching will increase in a heated region, producing more heat and an uneven surface.

Etches usually have an "induction period" before they affect the sample. Also, the etching process usually starts at a small surface imperfection.

Low surface recombination velocity may also be obtained by boiling filaments in a 15% $\text{H}_2\text{O}_2$ solution. This is not as convenient as CP4 because the etching time required is much longer. Other treatments are to be found in the literature (12).

(f) High $s$ Treatment. The rougher and more irregular a surface becomes, the higher $s$ will be, due to the many recombination centres which a rough surface presents. Thus, high $s$ values can most easily be produced by grinding or sand-blasting. The latter method involves rigidly fixing the sample to some support and treating each side individually. Usually the rectangular shape of the filaments cannot be preserved due
to a rounding off of the edges. Hence, grinding with carborundum abrasive was used.

(g) **Sample Dimensions.** The sample dimensions were always measured after the lifetime measurement had been performed. This avoided the possibility of surface contamination before a lifetime measurement. A precision micrometer, calibrated to 0.001 inches was used for this purpose.

**Section 4.4 - V-I Linearity of Contacts**

(a) **Ohmic Contacts.** The samples are placed in a box to keep light and draughts away from them. The current, I, through the sample, was measured as a function of the voltage, V, across the sample. This was done for both directions of I. The voltage was measured by a precision Fluke null meter (Model No. 801) and the current by an avometer (Model No. 8). A linear plot should result in the two directions for ohmic contacts.

(b) **Heating Effects.** Since no provision was made for removing heat from the sample other than conduction down the leads, or radiation from the surface, deviations from a straight line were observed for the higher values of current. These deviations are in the direction of increasing resistance. They can be explained by the fact that the mobility decreases as the temperature rises. Thus, the conductivity decreases also, so that resistivity and resistance increase.
Cooling the sample, by blowing air on it, for example, will cause a decrease in the voltage reading. For the purpose of making lifetime measurements, the field across the sample was restricted to the linear region of the V-I curve.

(c) **Injecting Contacts**. The effect of an injecting contact should always show up as a decrease in resistance due to the extra carriers present in the sample. A very poor contact which is rectifying will show vastly different resistances for the two directions of current.

**Section 4.5 - Mounting Samples for Optical Work**

(a) **Holder**. Four specially designed holders are used to facilitate easy sample changing. Sample leads are clamped down to the terminals of the holder. The samples rest on a lucite base which can have three positions for proper positioning of the samples with respect to the slit.

(b) **Shielding of Sample Ends from Light**. It is necessary to reduce the effects of photovoltage which occur when light falls on a metal-semiconductor contact (section 3.3). The following methods are successful in doing this: (i) **Epoxy plus Black Pigment** - Since epoxy resin was found useful for etch protection, it was thought that black pigment mixed with the resin would provide the necessary shielding. Effective optical shielding could not be achieved in this way without sacrificing the mechanical strength of the epoxy required to
withstand etching. (ii) **Black Tape** - This was found to be the most convenient method for shielding. However, some reflected light was incident on the contacts due to the fact that the tape did not make contact with the specimen at all points. If too much of the sample was covered, carriers would not be created uniformly along the length of the specimen. Therefore, only a small part of the sample was covered near the leads.

(c) **Distance of Sample from Slit.** The receptacle for the sample holder can be placed in a number of positions, which vary its distance from the entrance slit. The spark source outside the box can be placed at any distance from the slit. Hence, the distance between sample and light source can be made any desired value.

From tests with a carbon resistor replacing the specimen, the amount of electromagnetic pickup was found to be a minimum for a particular distance from the slit.

(d) **Slit Adjustment.** Brass plates with mu-metal backing form the slit sides which are held in position by black tape. They should be wide enough to allow uniform illumination of the sample, and narrow enough to limit scattered radiation.

**Section 4.6 - Detection of Resulting \( \Delta R \)**

(a) **Sample Bias.** For constant current through the sample, the change in resistance, \( \Delta R \), due to photoinjection, must be
proportional to the change in voltage, $\Delta V$, across the specimen. The current, $I$, is determined by completing the circuit with an avometer at $S_1$ (see Figure 16). For example, the conditions pertaining to one of the experiments are $I = 250 \times 10^{-6}$ amp, $R = 400 \ \Omega$, $\Delta V = 3 \times 10^{-3}$ volt (from oscilloscope). This gives

$$R_s + R = \frac{9}{250 \times 10^{-6}} = 36,000 \ \Omega$$

so that $R_s = 35,600 \ \Omega$. The change in $R$ due to the burst of light is

$$\Delta R \simeq \frac{\Delta V}{I} = \frac{3 \times 10^{-3}}{250 \times 10^{-6}} = 12 \ \Omega$$

Thus only a change of $12 \ \Omega$ has occurred in $36,000 \ \Omega$. For all practical purposes, $I$ remains constant.

(b) **Field Sweep-Out Effect.** For the sample of the preceding section (4.6a), equation (3.24) may be used to estimate the effect of carrier sweep-out. The measured value of $\tau_p$ for the volume was found to be about $45 \times 10^{-6}$ second (this is the value with a well etched CP4 surface which gives a low surface recombination velocity). If $E_c$ is defined such that

$$\left(\kappa_p \frac{E_c}{\tau_p}\right)^2 = \frac{4D_p}{\tau_p}$$

the required value of $E_x$ should be $< \frac{E_c}{10}$, say. F. J. Morin
(32) gives the value of $\mu_p = 1820 \text{ cm}^2/\text{volt-sec}$ and
$D_p = 44 \text{ cm}^2/\text{sec}$ (12). The value of $E_c$ with these values is
1.1 volts/cm. Thus, $E_x < 0.11 \text{ volt/cm}$. The sample was about
1 cm in length. Hence, $E_x = \frac{VI}{l} \frac{\text{volt}}{\text{cm}} = 0.10 \text{ volt/cm}$, which
satisfies the condition above.

The expected reduction in lifetime (due to carrier sweep-out) is predicted by equation (3.29) and has been observed.
The lifetime of sample RB 1/6/3 was measured for the zero field
case and for a voltage of 1.64 volts across the sample. The
volume lifetime for the zero field case was found to be
$\tau_0 = 31.5 \times 10^{-6} \text{ sec}$. When $2A = 0.95 \text{ cm}$, $\mu_p = 1820 \text{ cm}^2/\text{volt-sec}$, $V_0 = IR = 1.64 \text{ volts}$, $\tau_1$ is given by

$$\frac{1}{\tau_1} = \frac{1}{31.5 \times 10^{-6}} + \frac{1820 \times 1.64}{(0.95)^2}$$

yielding $\tau_1 = 28.5 \times 10^{-6} \text{ sec}$. The measured value was
$29 \times 10^{-6} \text{ sec}$, so that the calculated value is within the
experimental error. It was observed that fields greater than
about 0.8 volt/cm applied to 5 $\Omega$-cm germanium would cause
a decrease in the value of the lifetime with respect to the
zero field approximation.

(c) Oscilloscope Triggering. The +50 v pulse (see
section 4.2) to trigger the baseline was found to do so satis­
factorily when the trigger mode control was set to
"EXTERNAL + ve". The change in the resistance, due to
illumination, produces a negative pulse which is applied to the oscilloscope preamplifier. The baseline has been completed when this latter pulse arrives. The breakdown of the spark gap was controlled manually at the pulse generator. The light intensity of the spark varied slightly from one discharge to another. This caused variations in the amplitude of the initial sample voltage signal observed on the oscilloscope. However, this does not affect the rate of decay of the voltage pulse.

(d) **Picture Techniques and Film.** A polaroid camera (Type 2614 and 2620-Dumont) is used to photograph the oscilloscope trace. High speed polaroid film (ASA No. 3000) produces the best photographs for analysis. The correct aperture for a particular sweep speed must be determined empirically.

The graticule is exposed by means of a separate illumination of the scale. All of the exposures are made with the shutter on "BULB". This holds the shutter open as long as the plunger is depressed.

The amount of electromagnetic pickup is noted by illuminating the sample with no current through it. This pickup is usually less than 3 $\mu$s in duration. Analysis of the decays should be commenced after this length of time has expired.

(e) **Analysis of Photographs.** The "negatives" of the actual prints were analysed using a Bausch and Lomb optical magnifier with a linear scale calibrated in 0.1 mm divisions. Usually, the vertical readings were taken at 1 cm intervals
along the time base. This gives the amplitude of the decay as a function of time along the graticule.

Section 4.7 - Electrical Injection Arrangement

(a) P-N Junction Method of Lederhandler and Giacoletto.
This method was first tried for the special case of the p-n junction. The measuring circuit is shown in Figure (17). The voltage developed across the junction due to carrier injection exhibits a long decay towards the equilibrium voltage. This decay begins when the injecting pulse is removed and D1 open circuits the system. A p-n junction develops its own voltage when carriers are injected and no external field is necessary (section 3.2a).

(b) Electrical Injection Method from End Contacts.
Figure (18) shows the circuit which was finally used to measure the lifetime of carriers injected electrically. Once carriers are injected and diffused uniformly throughout the sample, the situation for recombination is similar to the optical case. An electric field applied across the sample is necessary to measure the recombination process. The voltage across R is divided by D2 and R2. It is arranged to have D2 open circuited when the injecting pulse is being applied to the sample so that most of the d.c. voltage across R appears across D2. When the pulse terminates, D2 conducts and the voltage across R2 becomes equal to the voltage across R. The
1/2 6AL5 Diode

Fig. 17. Circuit of Lederhandler and Giacoletto for P-N Junction Measurement.

Fig. 18. Electrical Injection Apparatus.
characteristic decay to equilibrium should be observed. The value of $R_1$ is set so that a constant current flows through $R$, as in the optical case.

**Section 4.8 - Sample Preparation for Electrical Injection**

(a) **Injecting Contacts.** (i) **Alloyed:** An injecting contact should theoretically result when p-type gold wire (0.5% Ga doped) is alloyed to n-type germanium. The back to forward resistances were in the ratio of 3:1. However, no decay could be observed using these contacts. The samples behaved no differently from a resistor. (ii) **Plated:** Success was obtained with a sample which had been plated on one end with copper. When the positive injecting pulse was applied to this plated end, injection occurred and the decay of excess carriers was observed. D. Navon et al (17) have reported good injection from large area soldered contacts. J. P. McKelvey and R. L. Longini (12) report that metal plated n-type contacts, and bare metal-semiconductor p-type contacts, give the best injection.

(b) **Surface Treatments.** Once the injecting contacts have been applied, the various surface treatments are obtained as for the optical case.
CHAPTER 5

RESULTS

Section 5.1 - Preliminary Results for Germanium

(a) Etch Times. In obtaining a low surface recombination velocity (section 4.3e), it is necessary to etch off about 0.003" from the dimensions of the sample. The value of lifetime was measured after etching intervals of 1 min. 30 secs. in slow CP4. Usually 2 or 3 such treatments increased the lifetime up to some constant value. Since there is an initiation period before the etch takes effect, the same result could be achieved by a single etch of shorter duration. However, the etching is performed in steps to avoid etching away excessive amounts of the sample. Use of medium or fast CP4 would speed up the process of etching. However, this often leads to considerable departure from the required rectangular geometry of the specimen.

(b) V-I Linearity. The careful alloying of leads to n-type germanium gives a linear V-I characteristic past the point where heating starts. This was the case for the 0.01, 5,
and 19 \( \Omega \)-cm samples. A 50 \( \Omega \)-cm sample, with pure gold leads alloyed on, gave a linear region only for small values of current. However, only very small values of current are required to establish the measuring field for high resistivity samples.

(c) **Response Times.** The value of response time (section 3.1) under constant illumination is given by equation (3.7) and is

\[
\tau = \frac{1}{B_1(M + 2n_0)}
\]

where \( n_0 \) is the number of electrons in the conduction band in the dark, \( M \) is the number of impurities, and \( B_1 \) is the recombination coefficient. At room temperature, assume \( n_0 = M = N_d \). T. S. Moss (13) gives values of \( B_1 \) from \( 10^{-10} \) to \( 10^{-14} \) cm\(^3\)/sec.

If \( B_1 = 10^{-10} \) cm\(^3\)/sec and \( n_0 = 3.5 \times 10^{14} \) cm\(^{-3}\) for 5 \( \Omega \)-cm material, \( \tau \) becomes

\[
\tau = \frac{1}{3B_1n_0} = 9.5 \times 10^{-6} \text{ sec}
\]

If light was on the sample long enough, the trace would rise to \( (1 - \frac{1}{e}) \) of maximum in about 9.5 \( \mu \)s. The response time in germanium at room temperature has been measured to be < 12 \( \mu \)s (13). Thus the calculated value is the right order of magnitude.

The oscilloscope traces observed for the various samples
Sample RB 1/6/5
5 Ω-cm, n-type Ge

Time bases:
(a) 10 μs/cm
(b) 2 μs/cm

Sample No.47(1)
130 Ω-cm, p-type Si

Time base:
20 μs/cm for
(c)(d)(e)

Germanium with
Injecting Contacts
(Copper Plated)

Time base:
10 μs/cm for (f)

Fig. 19. Photographs of Decays.
could be seen to rise for about 1.5 μs. This is just about the time interval of the burst of light from the spark gap according to the photomultiplier recording of Figure (15).

(d) **Photovoltaic Effect.** The analyses, with no black epoxy or tape covering the ends of the samples, usually showed traces which were non-exponential. These traces dropped faster than an exponential near the beginning of the decay. A plot, on semi-log graph paper, of relative magnitude versus time would show most points lying on a straight line. But a few of the initial points would be above this line. The black epoxy or tape covering the ends was found to eliminate this effect and the decay became exponential.

**Section 5.2 - Analysis of Decay Curves for Germanium**

(a) **Ground and Etched Surfaces.** It was always found that when a good "low s" surface treatment was obtained, the value of lifetime was nearly constant and independent of the sample dimensions. On the other hand, lifetime for a high s surface treatment varied as a function of the cross sectional area, becoming smaller as the cross section became smaller. Typical data showing these two effects are given below in Table II. The values of lifetime are obtained by measuring decay curves similar to Figure (19a,b). Figure (19a) is a photograph of RB 1/6/5 on a sweep speed of 10 μs/cm. Figure (19b) is on a sweep of 2 μs/cm and shows a response time of about 2 μs in duration.
TABLE II

DATA FOR ETCHED AND GROUND SURFACES ON GERMANIUM

<table>
<thead>
<tr>
<th>Resistivity and Type</th>
<th>Sample Number</th>
<th>Dimensions 2Ax2Bx2C cm$^3$</th>
<th>Surface Treatment</th>
<th>Lifetime ($\mu$sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 $\Omega$-cm n-type</td>
<td>RB 2/2/1</td>
<td>2.1 x 1.37 x 1.22</td>
<td>*</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>5 $\Omega$-cm n-type</td>
<td>RB 1/4/4</td>
<td>1.5 x 1.63 x 0.63, 1.5 x 0.97 x 0.61, 1.5 x 0.97 x 0.41, 1.5 x 0.97 x 0.023</td>
<td>Ground</td>
<td>5, 4, 2.6, 1.1</td>
</tr>
<tr>
<td>5 $\Omega$-cm n-type</td>
<td>RB 1/6/1</td>
<td>0.95 x 0.81 x 0.58, 0.95 x 0.76 x 0.41, 0.95 x 0.76 x 0.23</td>
<td>Ground</td>
<td>3.3, 1.8, 0.87</td>
</tr>
<tr>
<td>5 $\Omega$-cm n-type</td>
<td>RB 1/6/3</td>
<td>0.95 x 1.27 x 0.64, 0.95 x 1.09 x 0.45, 0.95 x 0.94 x 0.33</td>
<td>Ground</td>
<td>4.9, 3.2, 2.1</td>
</tr>
<tr>
<td>5 $\Omega$-cm n-type</td>
<td>RB 1/6/5</td>
<td>0.95 x 1.83 x 0.86, 0.95 x 1.78 x 0.84, 0.95 x 1.73 x 0.81, 0.95 x 1.62 x 0.66</td>
<td>*</td>
<td>20, 43, 48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>**</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>***</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ground</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>*</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>**</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>***</td>
<td>50</td>
</tr>
<tr>
<td>19 $\Omega$-cm n-type</td>
<td>19/1</td>
<td>0.95 x 1.04 x 0.76, 0.95 x 0.99 x 0.74, 0.95 x 0.94 x 0.71</td>
<td>*</td>
<td>150, 225, 200</td>
</tr>
<tr>
<td>19 $\Omega$-cm n-type</td>
<td>19/2</td>
<td>0.85 x 1.04 x 0.84, 0.85 x 1.01 x 0.79, 0.85 x 0.99 x 0.76</td>
<td>*</td>
<td>160, 195, 210</td>
</tr>
<tr>
<td>50 $\Omega$-cm Intrinsic</td>
<td>L.H. Intrinsic</td>
<td>1.15 x 0.66 x 0.89</td>
<td>*</td>
<td>175</td>
</tr>
</tbody>
</table>

* CP4 Etched after Lead Attachment
** Another 1 min 30 secs slow CP4 etch
*** An additional 1 min 30 secs slow CP4 etch
(b) **Lifetime for Germanium at Low Temperatures.** A cursory investigation of the lifetime of minority carriers in germanium at 78°K was made. The decay curve showed an initial rapid decrease in the number of excess minority carriers. The rate of decay then lessened and only gradually approached equilibrium conditions. Similar effects were observed in silicon at room temperature (Table III). Analysis of such traces indicates the hyperbolic form which such a decay is expected to have (section 2.4b).

Section 5.3 - Preliminary Results for Silicon (as in section 5.1)

(a) **Etch Times.** The same effects as section (5.1a) were observed.

(b) **V-I Linearity.** It is more difficult to make non-injecting contacts to silicon. However, a linear region of the V-I characteristic was found to exist. The 130 Ω-cm p-type silicon indicated the same resistances in forward and reverse directions for currents up to 40 x 10\(^{-6}\) ampere. The 8.2 Ω-cm n-type silicon showed linear regions out to 1 x 10\(^{-3}\) ampere.

(c) **Response Times.** The response time which is about 3 μs is not as fast-rising as for germanium. The fact that it is longer than the width of the light pulse is probably due to the poorer contacts made to the silicon.
(d) **Photovoltaic Effect.** A large photovoltaic effect exists with silicon due to poorer contacts. In some cases, this is almost the same magnitude as the expected decay. It is eliminated by covering the leads as described earlier.

**Section 5.4 - Analysis of Decay Curves for Silicon**

The silicon samples displayed trapping effects at room temperature which could be eliminated in p-type samples by ambient light, but could not be eliminated in n-type silicon. Table III below gives some of the data for silicon.

**TABLE III**

**DATA FOR ETCHED SILICON WITH AMBIENT LIGHT**

<table>
<thead>
<tr>
<th>Resistivity and Type</th>
<th>Sample Number</th>
<th>Dimensions 2Ax2Bx2C(cm³)</th>
<th>Surface Treatment and Ambient Light Conditions</th>
<th>Lifetime(sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>130 Ω-cm p-type</td>
<td>47(1)</td>
<td>1.5x.10x.104</td>
<td>All Etched Surfaces</td>
<td>&gt;10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No Ambient Light</td>
<td>11.5x10⁻⁶</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Small &quot;</td>
<td>120x10⁻⁶</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Moderate &quot;</td>
<td>12.5x10⁻⁶</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Full &quot;</td>
<td>50x10⁻⁶</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15x10⁻⁶</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18x10⁻⁶</td>
</tr>
<tr>
<td>8.2 Ω-cm n-type</td>
<td>N-type Si</td>
<td>1.15x.104x.089</td>
<td>Etched Surface</td>
<td>27x10⁻⁶</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No Ambient Light</td>
<td>7x10⁻⁶</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Full &quot;</td>
<td>No change</td>
</tr>
</tbody>
</table>
Thus ambient light is seen to eliminate the long decay in p-type silicon at room temperature. Figure (19c,d,e) shows the effect of ambient light on the decay of No. 47(1) as indicated in Table III.

Section 5.5 - Typical Calculations for Germanium at Room Temperature

For the 5 Ω-cm sample, RB 1/6/3, the pertinent data is given in Table II. It is desired to investigate equation (2.20) where

\[
\frac{1}{\tau_{p1}} = \frac{1}{\tau_p} + 4D_p \left[ \frac{(\eta_0)^2}{(2B)^2} + \frac{(\gamma_0)^2}{(2C)^2} \right].
\]

Recall that \( \eta_0 \) is the smallest solution of

\[
\eta_0 \tan \eta_0 = \left[ \frac{s}{2D_p} \right], \quad 2B = K
\]

in the interval \( 0 \leq \eta \leq \pi/2 \). Similarly, for \( \gamma_0 \),

\[
\gamma_0 \tan \gamma_0 = \left[ \frac{s}{2D_p} \right], \quad 2C = K' \quad ;
\]

However, the value of \( \frac{s}{2D_p} \) is needed to calculate \( \eta_0 \) and \( \gamma_0 \). J. P. McKelvey and R. L. Longini (12) give \( D_p = 44 \text{ cm}^2/\text{sec} \). D. Navon et al. (17) find \( D_p = 55 \text{ cm}^2/\text{sec} \). A value of \( D_p \) can be found from equation (2.21) when the measured value.
Fig. 20. Log-Log Plot of $\eta$ versus $\tan \eta$.
is almost entirely due to surface effects. Taking the dimensions of 2Bx2C as the smallest value, (which makes the approximation even more correct), and \( \frac{1}{\nu_{p1}} \approx \nu_s \approx \frac{1}{2.1 \times 10^{-6}} \) sec\(^{-1}\), equation (2.21) gives

\[
\frac{1}{2.1 \times 10^{-6}} = \pi^2 D_p \left[ \frac{1}{(0.094)^2} + \frac{1}{(0.033)^2} \right].
\]

Solving gives \( D_p = 47 \) cm\(^2\)/sec. Similar calculations show \( D_p \) values up to 56 cm\(^2\)/sec. Thus, choose \( D_p = 50 \) cm\(^2\)/sec for convenience. Then it is proposed to find the value of \( \frac{s}{2D_p} \) which satisfies equation (2.20) when \( \frac{1}{\nu_{p1}} \) is plotted against

\[
\left( \frac{\nu_0}{2B} \right)^2 + \left( \frac{\nu_0}{2C} \right)^2.
\]

The slope of this curve is equal to \( 4D_p \) and the intercept is equal to \( \frac{1}{\nu_p} \). It is desired to find the value of \( s \) which gives a slope of \( 4D_p = 200 \) cm\(^2\)/sec. The following table (Table IV) gives values for \( \frac{s}{2D_p} = 150 \) cm\(^{-1}\), 200 cm\(^{-1}\), 250 cm\(^{-1}\).

The method of solution of \( \eta \tan \eta = K \) is given in the following paragraph.

To solve \( \eta \tan \eta = K \), take logarithms of both sides to get

\[
\log \eta = \log K - \log (\tan \eta) \tag{5.1}
\]

Then, if \( \log \eta \) is plotted against \( \log (\tan \eta) \), a straight line of slope \(-1\) results. The intercept along the line \( \eta = 1 \)
### TABLE IV

Calculated values of $\frac{1}{t_{p1}}$ and $\left(\frac{\mu_0}{2B}\right)^2 + \left(\frac{\mu_0}{2C}\right)^2$ as functions of $\frac{S}{2D_p}$

<table>
<thead>
<tr>
<th>$2B \times 2C$ ($cm^2$)</th>
<th>$t_{p1}$ (sec)</th>
<th>$\frac{1}{t_{p1}}$ (sec$^{-1}$)</th>
<th>$K=150(2B)$</th>
<th>$\eta_0$</th>
<th>$K'=150(2C)$</th>
<th>$j_0$</th>
<th>$\left[\left(\frac{\mu_0}{2B}\right)^2 + \left(\frac{\mu_0}{2C}\right)^2\right]_{cm^{-2}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.127 \times 0.064$</td>
<td>$4.88 \times 10^{-6}$</td>
<td>$205 \times 10^3$</td>
<td>19.1</td>
<td>1.50</td>
<td>9.6</td>
<td>1.42</td>
<td>632</td>
</tr>
<tr>
<td>$0.109 \times 0.045$</td>
<td>$3.20 \times 10^{-6}$</td>
<td>$312 \times 10^3$</td>
<td>16.4</td>
<td>1.49</td>
<td>6.7</td>
<td>1.37</td>
<td>1112</td>
</tr>
<tr>
<td>$0.094 \times 0.033$</td>
<td>$2.14 \times 10^{-6}$</td>
<td>$467 \times 10^3$</td>
<td>14.1</td>
<td>1.47</td>
<td>4.9</td>
<td>1.31</td>
<td>1824</td>
</tr>
<tr>
<td>$0.118 \times 0.063$</td>
<td></td>
<td></td>
<td>K=200(2B)</td>
<td></td>
<td>K'=200(2C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25.4</td>
<td>1.52</td>
<td>12.8</td>
<td>1.46</td>
<td>663</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>21.8</td>
<td>1.51</td>
<td>9.0</td>
<td>1.41</td>
<td>1177</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18.8</td>
<td>1.50</td>
<td>6.6</td>
<td>1.37</td>
<td>1975</td>
</tr>
<tr>
<td>$0.131 \times 0.071$</td>
<td></td>
<td></td>
<td>K=250(2B)</td>
<td></td>
<td>K'=250(2C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>31.7</td>
<td>1.53</td>
<td>16.0</td>
<td>1.48</td>
<td>680</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>27.2</td>
<td>1.52</td>
<td>11.2</td>
<td>1.44</td>
<td>1214</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23.5</td>
<td>1.51</td>
<td>8.3</td>
<td>1.40</td>
<td>2058</td>
</tr>
</tbody>
</table>
(i.e. \( \log \eta = 0 \)) is \( K = \tan \eta \). If \( \eta \) vs. \( \tan \eta \) is plotted on log-log graph paper, the value of \( \eta_0 \) is given by the point where the straight line of equation (5.1) intersects this latter curve. Figure (20) shows \( \eta \) versus \( \tan \eta \) on log-log graph paper and a few lines with slope \(-1\) and \( K \) as a parameter. Note the intersections along the line \( \eta = 1 \) where \( K = \tan \eta \).

For \( K = 0.4 \), the value of \( \eta_0 \) is 0.59, as shown, and similarly for the others. It has been reported (7) that the roots of \( \eta \tan \eta \) are to be found in "Conduction of Heat in Solids" by H. S. Carslaw and J. C. Jaeger (Oxford U. Press, 1947).

When the values calculated in Table IV are plotted, different slopes result (Figure 21). In this case, a slope of \( 4D_p = 200 \text{ cm}^2/\text{sec} \) occurs when \( \frac{s}{2D_p} = 200 \text{ cm}^{-1} \) exactly. This gives a value for \( s \) of \( 2 \times 10^4 \text{ cm/sec} \). The lines on either side give values of \( D_p = 56 \) and \( D_p = 47 \text{ cm}^2/\text{sec} \).

The intercept on the \( \frac{1}{\tau_{p_1}} \) axis is about \( 75 \times 10^3 \text{ sec}^{-1} \). This implies that \( \tau_{p_1} = 13 \mu s \) which is smaller than the expected volume lifetime of \( >40 \mu s \). However, other such analyses show values of \( \tau_{p_1} \) which are closer to the expected value.

Section 5.6 - Results for Electrical Injection Method

Only two samples with copper plated ends have been used. These give the expected decays which are in good agreement with the optical method.
Fig. 21. Plot of \( \frac{1}{\tau p_1} \) vs \[ \left( \frac{\eta_0}{2B} \right)^2 + \left( \frac{3\eta}{2C} \right)^2 \]

Sample RB 1/6/3
(Ground Surface)

Key

1. \( \frac{s}{2D_p} = 150 \text{ cm}^{-1} \); \( D_p = 56 \text{ cm}^2/\text{sec} \) (from slope)

2. \( \frac{s}{2D_p} = 200 \text{ cm}^{-1} \); \( D_p = 50 \text{ cm}^2/\text{sec} \) ("")

3. \( \frac{s}{2D_p} = 250 \text{ cm}^{-1} \); \( D_p = 47 \text{ cm}^2/\text{sec} \) ("")

\[ \left[ \left( \frac{\eta_0}{2B} \right)^2 + \left( \frac{3\eta}{2C} \right)^2 \right] \text{ cm}^{-2} \]
One important result here is that injection from an alloyed p-type gold contact to an n-type sample is too small to be observed.

Figure (19f) shows a decay from carriers injected electrically.
CHAPTER 6

CONCLUSIONS

A number of effects associated with photoconductivity have been observed during the course of this study. Firstly, the response time of the photocurrent can be observed. This effect is seen to be of the correct order of magnitude predicted by equation (3.7). Photographs, such as Figure (19b), show this effect. This agrees with the photomultiplier recording of Figure (15).

Another effect observed is the photovoltaic effect. This is rather small in germanium because good contacts can usually be applied to these filaments. It does show up when the decays are analysed by plotting relative amplitude against time on semi-log graph paper. The photovoltaic effect is very large with silicon samples, however. This is due to the difficulty in making good contacts to these filaments. For both germanium and silicon, the photovoltaic effect was greatly reduced by shielding the ends from incident light.

The main result from the photoconductivity experiments,
however, was the observance of the change in conductivity when samples are illuminated by a flash of light. This was observed to be a very sensitive method for measuring the combined surface and volume effects. The volume effect was found to be dominant when the surface recombination velocity was made as low as possible. This verified equation (2.20) where the surface effect is negligible. The measured lifetimes for samples with well etched surfaces were found to be constant, independent of the sample dimensions. The surface term became effective when the surface recombination velocity was made large. In the extreme case where \( s = \infty \), equation (2.21) affords a method of determining diffusion constants. These varied from 46 cm\(^2\)/sec to 56 cm\(^2\)/sec for observations on the 5 \( \Omega \)-cm n-type germanium. The condition of the surface can be estimated by measuring the lifetime. For example, contaminations of the surface reduce the value of lifetime, since the surface recombination velocity increases with the addition of foreign material. The volume lifetimes were found, for n-type samples of germanium, to be less than 2 \( \mu \)s for 0.01 \( \Omega \)-cm material, and 45 \( \mu \)s, 200 \( \mu \)s, 175 \( \mu \)s for 5 \( \Omega \)-cm, 19 \( \Omega \)-cm, and 50 \( \Omega \)-cm material respectively. From the theoretical curve (Figure 4), the maximum lifetime is expected to occur for the purer samples, where \( E_F \approx E_i \). The maximum lifetimes measured were for the purest samples, namely, 19 \( \Omega \)-cm and 50 \( \Omega \)-cm germanium. This is in qualitative agreement with
the theoretical predictions.

Trapping effects (Δn ↔ Δp) were observed in silicon at room temperature. Ambient light from a direct current source was found to eliminate the long decay due to traps for p-type silicon only (Figure 19c,d,e). This is in agreement with similar findings reported in the literature (15). The ambient light did not eliminate the long decay in n-type silicon, however. Whereas trapping effects in silicon are evident at room temperature, they are not observed in germanium until the temperature is reduced. Such effects were observed at 78°K (section 5.2b). This substantiates evidence from the literature (18,19,20).

The electrical injection experiments were in good agreement with the optical results. This method is not as useful as the optical method because of the fact that the samples require injecting contacts. A p-type gold wire alloyed to an n-type sample did not give sufficient injection to measure lifetimes.

In both of these methods, the effect of the electric field sweep-out of carriers was observed, as predicted by equations (3.24) and (3.29).

Although CP4 etching gives a low surface recombination velocity, other etches are found to be more consistent, giving even lower values for the surface recombination velocity (12). For example, the Westinghouse silver etch (12) gives values of
15 < s < 77 cm/sec, while the CP4 etch gives 50 < s < 220 cm/sec for n-type samples. In addition to the lower surface recombination velocity produced, the observed scatter is less. The superoxol etch (12) also gives low s values on the average.

The lifetime of the 0.01 \( \Omega \)-cm germanium sample was not observed. It is presumed that this decay is shorter than the time during which electromagnetic pickup occurs. A spark gap of different design (30) might reduce the pickup to a point where the lifetime is observable.
APPENDIX I

LOW-LEVEL LIFETIME FOR BAND-TO-LOCALIZED LEVEL TRANSITIONS

The low-level lifetime, $\tau_0$, for the transitions between bands and localized levels is obtained in the following derivation for a density of $N_t$ localized levels per unit volume situated at an energy, $E_t$, in the forbidden gap.

The rates for electron capture by the localized levels and emission from these levels are designated as $R_e$ and $G_e$ respectively (section 2.4a).

Since $R_e = G_e$, $n = n_o$, and $f_t = f_{to}$ in equilibrium, equation (2.3) becomes

$$C_n' = \frac{C_n (1 - f_{to}) n_o}{f_{to}}$$

(1)

From the definition of the Fermi function, $f_{to}$ is given by (neglecting spin),

$$\frac{1 - f_{to}}{f_{to}} = \exp \left[ \frac{E_t - E_F}{kT} \right]$$

(2)

The value of $n_o$ is given by W. Shockley (1). It is
\[ n_0 = N_c \exp \left( \frac{E_F - E_C}{kT} \right) \]  
(3)

for \( E_C - E_F \gg kT \). From equation (3), the value of \( \exp \left( \frac{-E_F}{kT} \right) \) is

\[ \exp \left( \frac{-E_F}{kT} \right) = \frac{N_C}{n_0} \exp \left( \frac{-E_C}{kT} \right) \]  
(4)

Substitution of equation (4) in equation (2) gives

\[ \frac{1 - f_{to}}{f_{to}} = \exp \left[ \frac{E_t - E_C}{kT} \right] \frac{N_C}{n_0} \]  
(5)

Substitution of equation (5) in equation (1) gives

\[ C_n' = C_n \exp \left[ \frac{E_t - E_C}{kT} \right] N_C = n_1 C_n \]  
(6)

where \( n_1 \) is the number of electrons in the conduction band when the Fermi level coincides with the localized levels.

The net recombination rate for electrons, \( U_e \), is given by

\[ U_e = R_e - G_e = C_n (1 - f_t)n - n_1 C_n f_t = C_n \left[ (1 - f_t)n - n_1 f_t \right] \]  
(7)

Similarly, for holes, the net rate of recombination, \( U_h \), gives

\[ U_h = R_h - G_h = C_p \left[ f_t p - p_l (1 - f_t) \right] \]  
(8)
where \( p_1 \) is given by
\[
p_1 = N_v \exp \left( \frac{E_v - E_t}{kT} \right)
\]  
(9)

If a disturbance creates \( U \) electron-hole pairs per unit time, then when steady conditions have been reached, the electrons and holes will be disappearing in equal numbers, since they recombine in pairs. The situation then is
\[ U_e = U_h = U \]  
(10)

This gives an equation from which \( f_t \) can be found. Hence, from \( U_e = U_h \),
\[
f_t = \frac{n \, C_n + p_1 \, C_p}{C_n(n+n_1) + C_p(p+p_1)}
\]  
(11)

Using the fact that \( n_1 p_1 = n_1^2 \) in equation (7) or (8) gives
\[
U = \frac{C_n C_p \, (p n - n_1^2)}{C_n(n+n_1) + C_p(p+p_1)}
\]  
(12)

Substituting \( n = n_o + \Delta n \) and \( p = \Delta p + p_o \) into equation (12) and assuming \( \Delta n = \Delta p \), gives
\[
U = \frac{n_o \, \Delta p + p_o \, \Delta p + \frac{\Delta p^2}{C_p - 1(n_1 + n_o + \Delta p) + C_n - 1(p_1 + p_o + \Delta p)}}
\]  
(13)

As before, define \( \tau = \frac{\Delta p}{U} \), so that \( \tau \) is given by
\[
\tau = \frac{C_p^{-1}(n_o + n_1 + \Delta p) + C_n^{-1}(p_o + p_1 + \Delta p)}{n_o + p_o + \Delta p}
\]  
(14)
When $\Delta p$ is small, $\tau = \tau_0$, the low-level lifetime, which is

$$\tau_0 = \frac{C_p^{-1}(n_o+n_1) + C_n^{-1}(p_o+p_1)}{n_o + p_o}$$  \hspace{1cm} (15)
APPENDIX II

THE EQUATIONS OF CONTINUITY

W. van Roosbroeck (10) has discussed the main equations of continuity for semiconductors. Some of the important results are given here.

For holes, the following equation applies:

\[ \frac{\partial p}{\partial t} = -\frac{1}{e} \text{div} \mathbf{I}_p - \left( \frac{p}{\tau_p} - g \right) \quad (1) \]

where \( \mathbf{I}_p \) is the current density due to holes and \( g \) is the rate of generation of carriers per unit volume. For electrons, a similar equation gives

\[ \frac{\partial n}{\partial t} = \frac{1}{e} \text{div} \mathbf{I}_n - \left( \frac{n}{\tau_n} - g \right) \quad (2) \]

where \( \mathbf{I}_n \) is the current density due to electrons. \( \mathbf{I}_p \) is given by

\[ \mathbf{I}_p = \sigma_p \mathbf{E} - e D_p \text{grad} p \quad (3) \]

and \( \mathbf{I}_n \) by

\[ \mathbf{I}_n = \sigma_n \mathbf{E} + e D_n \text{grad} n \quad (4) \]
The total current density, \( \vec{I} \), is given by \( \vec{I} = \vec{I}_p + \vec{I}_n \). The definitions of \( \sigma_p \) and \( \sigma_n \) have been given earlier and are \( e\mu_p p \) and \( e\mu_n n \) respectively. Thus, the total conductivity, \( \sigma \), is given by

\[
\sigma = \sigma_p + \sigma_n \tag{5}
\]

If \( p - p_o = \Delta p = \Delta n = n - n_o \), equations (5), (4), and (3) give

\[
\vec{E} = \frac{\vec{I}}{\sigma} - \frac{e}{\sigma} (D_n - D_p) \text{ grad } \Delta p \tag{6}
\]

Substituting equation (6) into (3) and (4) gives

\[
\vec{I}_p = \left( \frac{\sigma_p}{\sigma} \right) \vec{I} - e D \text{ grad } \Delta p \tag{7}
\]

\[
\vec{I}_n = \left( \frac{\sigma_n}{\sigma} \right) \vec{I} + e D \text{ grad } \Delta n \tag{8}
\]

which serves to define the ambipolar mobility, \( D \), as

\[
D = \frac{\sigma_n D_p + \sigma_p D_n}{\sigma} = \frac{n + p}{\frac{n}{D_p} + \frac{p}{D_n}} \tag{9}
\]

The second formulation of equation (9) comes from using the Einstein relationships for mobilities which are \( \mu_n = \left( \frac{e}{kT} \right) D_n \) and \( \mu_p = \left( \frac{e}{kT} \right) D_p \). More generally, equations (3) and (4) substituted into (1) and (2) give

\[
\frac{\partial p}{\partial t} = D_p \text{ div grad } p - \frac{1}{e} (\text{div } \sigma p) \cdot \vec{E} - \frac{1}{e} \sigma p (\text{div } \vec{E}) - \left( \frac{p}{t_p} - g \right) \tag{10}
\]
and

\[
\frac{\partial \mathbf{n}}{\partial t} = D_n \ \text{div} \ \text{grad} \ \mathbf{n} + \frac{1}{\varepsilon} (\text{div} \ \mathbf{E}) \cdot \mathbf{E} + \frac{1}{\varepsilon} \ \mathbf{E} \cdot (\text{div} \ \mathbf{E}) - \left( \frac{n}{\tau_n} - g \right)
\]

(11)
BIBLIOGRAPHY


