MEASUREMENT OF CARRIER LIFETIMES
IN SEMICONDUCTING DIAMOND

By

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CHAPTER I

INTRODUCTION

Generally there are three methods used for measuring carrier lifetimes in semiconducting materials. One method is called the intrinsic photoconductivity response which is sometimes referred to as the pulse response technique. In this method, direct observation is made of the photocurrent pulse produced by a very short intense spark of light. The lifetime is then determined by the calculation of the time required for the pulse to decay to 1/e of its maximum. A variation of this method (usually applied in the case of extrinsic semiconductors) is made when the rise time is used to calculate the lifetime. In this case the time difference between a photocell and the semiconductor's rise to (1 - 1/e) of the maximum is taken to be the lifetime. In another method of determining lifetime, the diffusion length experiment is used. This permits a calculation of lifetime by measuring the diffusion length of carriers when values of mobility are known. The third method of measuring lifetime stems from the photoelectromagnetic effect which is essentially a Hall effect produced by diffusion currents. A measurement of the ordinary photocurrent and the photoelectromagnetic current made simultaneously provides a means of calculating the lifetime.

I The Problem

It is the purpose of this study to attempt to determine the lifetime of the free carriers in a type II b semiconducting diamond.

The diamond used in this study has p type conductivity (1). The methods used to investigate the lifetimes will be the three methods already mentioned.

The problem of determining free carrier lifetimes used in the steady state photocurrent equation becomes one of determining the lifetime independent of shallow trapping centers. A semiconductor can be characterized by three lifetimes---the diffusion lifetime, the conductivity lifetime, and the photoconductivity response lifetime. This study will be concerned with all three of these lifetimes. A brief statement has already been made concerning the methods (diffusion length experiment and photoelectromagnetic effect) of obtaining the diffusion lifetime. The pulse response technique is used to obtain the conductivity lifetime and the photoconductivity response lifetime.

II Definitions of Terms Used

Trapping Centers. This term refers to bound states lying near the conduction band. Here the word near means that the energy separating the bound state from the conduction band is small so that an electron which might be trapped in this bound state could readily be thermally re-excited. This definition applies for the case of holes as well, with the words conduction band being replaced with the valence band. The lifetime of a free carrier is not terminated when caught in these shallow trapping centers.

Deathnium Centers or Ground State. The deathnium center is a bound state lying deep in the forbidden zone. When a carrier is captured by a ground state, its lifetime is ended since it would have to be photoionized to reach the conduction band (or valence band) again.

Electron-hole Pair Lifetime. This term refers to the average time that both carriers are simultaneously free. The lifetime of an electron-hole pair is ended when either carrier recombines with a ground state.

Diffusion Lifetime. This lifetime can be equal to the electron-hole pair lifetime but it is not limited to this definition since the term can be applied to the lifetime of holes or electrons independently.

Conductivity Lifetime. This lifetime is not ended until both carriers have recombined with ground states. The lifetime in this case lasts as long as either carrier remains free to contribute to current flow. It is however independent of shallow traps.

Photoconductivity Response Lifetime. This lifetime can be equal to the conductivity lifetime under certain conditions such as high light intensity etc. Usually this lifetime includes the time the carriers spend in shallow traps.

Majority Carrier. If the conductivity of a semiconductor is mainly due to holes, it is classified as p type and the majority carrier is the hole. The majority carrier in n type material is the electron.

Minority Carrier. The minority carrier in a p type material is the electron and in n type material the hole.

III General Information

When an electron-hole pair is created in a semiconductor by photo-ionization, various events take place which may be complex and varied. One or both of these carriers may be caught in shallow trapping centers or they may recombine with ground states. A carrier may be thermally re-excited from a shallow trap but excitation from a ground state requires energy equivalent to photo-ionization. When an electric field is placed on an illuminated photoconductor, a current flow will result, and one of the parameters, which determines the amount of photocurrent, is the conductivity lifetime.

In the case of the conductivity lifetime of an electron, only the time spent in the conduction band is counted as its lifetime; similarly for a hole, the time spent in the valence band determines its lifetime (2). If a carrier is trapped in a temporary trap from which it may be thermally re-excited, its lifetime is not ended since it may be freed again and contribute to current flow. On the other hand, a carrier which has recombined with a ground state has ended its lifetime because it would require photo-ionization to remove it from the deep lying ground state.

The lifetimes of electrons and holes need not be equal (3). The minority charge carriers may be temporarily captured and thermally freed a number of times before ultimate recombination with a ground state. This process applies not only to minority carriers but to the majority carriers as well since both may experience this temporary trapping.

The capture cross section of the trapping centers for minority and majority carriers determines the difference in behavior of trapping centers and recombination centers in semiconductors (3). Recombination centers may have a large capture cross section for both minority and majority carriers while the temporary trapping centers may have a large capture cross section for the minority carrier and a small capture cross section for the majority carrier. Shallow trapping states do not affect the steady state photocurrent; however, they do affect the time required to set up the steady photocurrent and the time of decay of the photocurrent when the excitation is removed. The rise time of the photocurrent is increased because the density of carriers caught in these shallow traps has to be increased in the same proportion in order to increase the density of the free carriers. The decay of the photocurrent is slowed down since it may take a very long time for all the shallow traps to empty, and, as long as these traps are being emptied, the photocurrent will persist (2).

A photoconductor's performance can be described if its free carrier lifetime can be obtained. The lifetime of a free carrier almost completely characterizes a photoconductor (2). This lifetime describes the essential performance and contains the essential physics of a photoconductor. The lifetime of a free carrier is determined by the rate of recombination of these carriers with their ground states. These ground states lie deep in the forbidden zone as contrasted to the shallow trapping states which lie very near the conduction or valence band. The ground states are composed of impurities, vacant lattice sites, interstitual atoms, and other crystal defects. From the physics of the ground states, it is evident that the recombination process may be highly complex and varied. The recombination lifetime is not a material constant; instead, it varies with the mode of preparation and impurity content of the material.

CHAPTER II

REVIEW OF THE LITERATURE

Much has been written concerning the importance of free carrier lifetimes in semiconducting materials and the methods of measuring the lifetimes; but only a brief summary of the work done on problems very closely related to the one at hand will be given here.

I. Literature Concerning the Pulse Response Method of Determining Lifetime

K.G. McKay (4,5), in an attempt to measure carrier lifetime in ordinary diamond, used a modified pulse response method. The diamond sample was placed in an evacuated chamber and positioned similar to the anode of a cathode ray tube. An electric field was applied to the sample lengthwise and then the diamond was pulsed with electrons emitted from the cathode. The lifetime of the carriers was determined by measuring the average range of the generated carriers. The value of electron lifetime obtained was approximately 2×10^{-8} sec.

A method which was essentially that of McKay was used by E.A. Pearlstein and R.B. Sutton (6) to make lifetime measurements in ordinary diamond. Instead of injecting electrons, the diamond was bombarded with alpha particles. They calculated the electron lifetime to be approximately 8×10^{-9} sec. The lifetime measured was of the order obtained by McKay.

D. Navon, R. Bray and H.Y. Fan (7) describe a method for the determination of the lifetime of injected carriers in a semiconductor. Their method of determining lifetime was by measuring the variation of the sample conductance after a voltage pulse had produced excess carriers. The decay of the conductivity was used as a means of calculating the lifetime of the excess carriers. Different size samples were used to check the effect of surface and volume recombination. The surfaces of the samples were treated to cut down surface recombination. The samples of germanium with ground surfaces (high surface recombination) had a lifetime which ranged for different size samples from 3 to 144 micro-sec. Etched surfaces on the samples cut down the variation of lifetime for these same samples; however, the lifetime became larger, from 235 to 280 micro-sec. These values for lifetime were of the order expected for germanium.

A variation of the pulse response technique is described by T.S. Moss (8). Moss used this method to confirm carrier lifetime obtained for lead sulphide crystals by other methods. A pulse of light from a spark gap is applied to the specimen and the rise time of the photocurrent is observed. The rise time of the spark is measured with a photocell. The signal waveform from the crystal is assumed exponential, and the lifetime is taken to be the difference of the times required for the signal to reach 1-1/e of the maximum for the crystal and the photocell. Carrier lifetime in lead sulphide crystals had been measured between 6×10^{-10} and 9×10^{-6} sec. These large values were confirmed by the pulse response measurements (9).

D. Redfield (10, after other methods of determining carrier lifetime in tellurium proved to be unsuccessful, resorted to the pulse response method. A study of the photocurrent pulse response had indicated a lifetime of less than 10^{-4} sec. He was successful using the pulse response method, and the value of lifetime ranged from 15 to 20 micro-sec. This value agreed with his calculated value for lifetime.

J.R. Haynes and J.A. Hornbeck (11) used a 0.2 micro-sec. spark of light on germanium and silicon to calculate lifetime. In an attempt to eliminate trapping, an ambient light was applied to the samples. The pulse decay was used to calculate the lifetimes. For germanium, the values for lifetimes agreed with other investigators' and appeared to be independent of the intensity of the ambient light. This led to the conclusion that trapping is not apparent in germanium at room temperature. For silicon, the decay time of the pulse decreased to a minimum value as the ambient light intensity was increased. When the intensity of the steady light was high, the values obtained for lifetime were of the right order. At lower light intensities the lifetime calculated was larger than expected. In this case shallow trapping seemed to cause the extended lifetime.

An investigation similar to Haynes and Hornbeck's was carried out by D.F. Stevenson and R.J. Keyes (12). The carrier lifetime again was determined by the decay of the photocurrent pulse. The results of their work were in good agreement with accepted values for carrier lifetimes in germanium. For silicon, a strong continuous light was applied to the sample to get rid of the long time constant or long exponential decay. Using the continuous light, the lifetime obtained for silicon was of the right order of magnitude.

E.O. Johnson (13) describes a modified pulse response experiment. The method takes advantage of the linear dependence of the surface photovoltage on the excess carrier density at low signal levels. The surface photovoltage is generated by a brief light flash and is picked up by a small electrode capacitively coupled to the surface of the specimen. The signal decay time constant is used to calculate the lifetime. The method achieves about the same results as other photoconductivity response methods, but it also has the limitations imposed by shallow trapping. Using this method to calculate lifetimes in germanium and silicon gave good results.

II. Literature on the Diffusion Length Experiment Method of Calculating Carrier Lifetime

L.B. Valdes (14) used a method developed by Morton and Haynes at the Bell Telephone Laboratories to calculate the minority carrier lifetime in germanium. Carriers are generated by light from an optically flat face of a crystal, and the concentration of the minority carriers is measured as a function of the distance from the point of liberation. Valdes gives a theoretical treatment of the method, and the relationship between the diffusion length and lifetime was used to calculate carrier lifetime. This method takes advantage of the linear relationship of the current through a reverse bias point contact to the minority carrier concentration (15). The values obtained for lifetimes were of the right order of magnitude.

A similar experiment was carried out by T.S. Moss (8) to check the results of other lifetime measurements made on lead sulphide. The carrier diffusion length was measured by observation of the photocurrent through a crystal-tungsten probe contact as a narrow line of light was traversed across the contact. The diffusion length was obtained from a plot of photocurrent versus distance from the light spot to the probe. The relationship between the lifetime and the diffusion length was then used to calculate the lifetime. The results of Moss's experiment were satisfactory since the lifetime obtained agreed with values obtained by other lifetime measurement methods.

Both of these investigations were carried out using single crystals. There has been much work done using the diffusion length as a means to calculate lifetime; however, a great deal of the literature is devoted to junction samples.

III. Literature on the Photoelectromagnetic Effect with Application to Lifetime Measurement

The open circuit voltage equations for the photoelectromagnetic effect have been derived by T.S. Moss, L. Pincherle, and A.M. Woodward (16). The short-circuit current (due to the diffusion process produced by the photoelectromagnetic effect) yields a useful relationship in regard to carrier lifetime. Moss (8), Pincherle (17), and others have derived the equations for this short-circuit current. Using the equation for the normal photocurrent and the equation for the PEM short circuit current, a simple equation is formed for carrier lifetime. The carrier lifetime is found to be proportional to the ratio of the semiconductor's photocurrent to the short circuit PEM current squared.

T.S. Moss (8, 18) has used the photoelectromagnetic effect for the calculation of carrier lifetime in lead sulphide and germanium. The results of this work have been in agreement with other investigators, and the values of lifetime obtained from other methods on the same crystals were of the right order of magnitude.

R.P. Chasmar (19), working with lead sulphide crystals, achieved good results using the PEM effect for calculating carrier lifetime.

The calculation of lifetime by the PEM effect is given a mathematical analysis by S.W. Kurnick and R.N. Zitter (20). Their analysis agreed with Moss's theoretical treatment and their work was successful in obtaining accepted values for carrier lifetimes in InSb. (indium antimonide).

H.P. Frederikse and R.F. Blunt (21), using the equations derived by Moss for the carrier lifetime (PEM effect), performed measurements on InSb. The values of carrier lifetime were from 10^{-7} sec. at room temperature to 10^{-6} sec. at 77° K. These values were of the order expected and they were confirmed by other methods of lifetime measurement.

CHAPTER III

MEASUREMENT OF MINORITY CARRIER LIFETIME BY THE DIFFUSION LENGTH EXPERIMENT

I. Discussion

One method of measuring minority carrier lifetimes in single crystals is derived from the diffusion length experiment. The diffusion length is obtained from data taken in the experiment, and the lifetime is then calculated using this relationship:

$$\tau_n = L_n^2/D_n$$

$\tau_n =$ lifetime for an electron in p type material

$L_n =$ diffusion length. This is defined as the average distance an electron will diffuse before recombining.

$D_n =$ diffusion constant. This comes from the Einstein relation, $D_n = kT\mu_n/q$ where k is Boltzman's constant, T is the absolute temperature, q is the charge of the electron, and μ_n is the electron mobility.

The method of measuring the diffusion length was developed by Morton and Haynes at the Bell Telephone Laboratories. The method consists of liberating electron-hole pairs by a light on the surface of a crystal and measuring the concentration of minority carriers as a function of the distance from the point where they were liberated (14).

The physical model for a single crystal is shown in Fig. 1. The surface is illuminated with a long narrow line of light. The point contact is located a distance r from the illumination. Assuming that the surface recombination is small or at least of negligible order, the flow will be outward from the line of light in radial lines. To keep the problem one of diffusion currents only, the electric field at the point contact must be kept small. The contact is located away from the edges

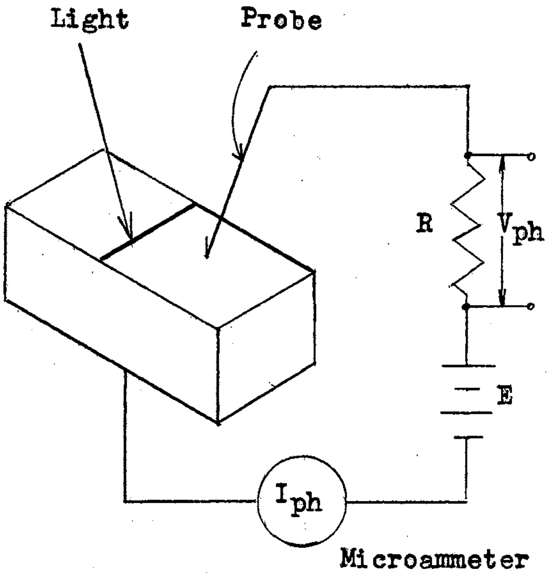

Fig. 1 Physical Model of the Single Crystal

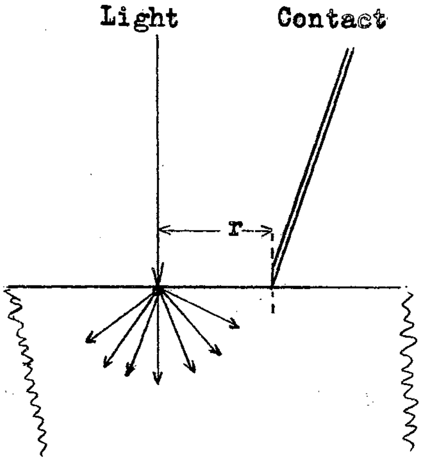

Fig. 2 Diffusion Current

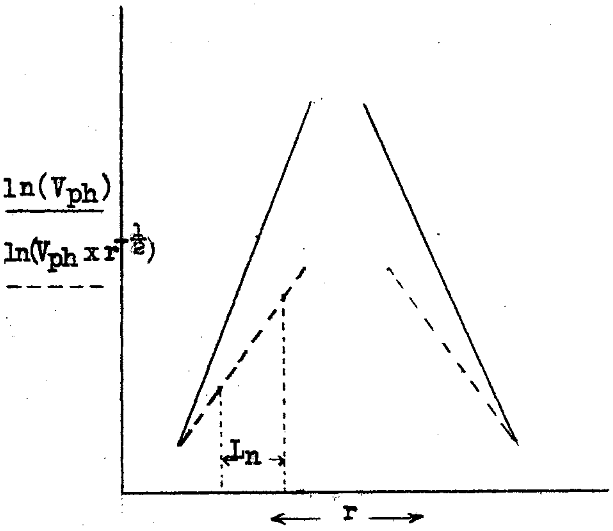

Fig. 3 Determination of the Diffusion Length

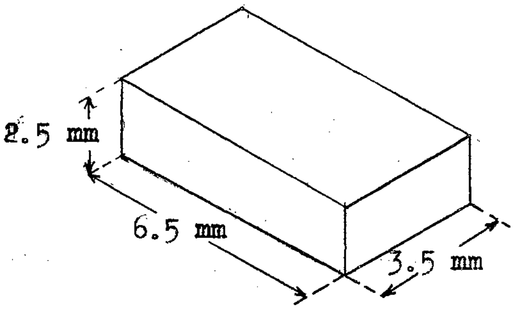

Fig. 4 Crystal Dimensions

of the crystal to prevent edge effects.

The mathematical approach to the problem is obtained (using Fig. 2) as follows:

The continuity equation for the flow of excess electrons in p type material is (22)

$$\frac{\partial n}{\partial t} = -\frac{n}{\tau_n} + \frac{1}{q} \nabla \cdot I \equiv 0 \qquad \text{at equilibrium} \quad (1)$$

I is given by

$$I_n = q \mu_n nE + q D_n \nabla n \qquad (2)$$

$$I_n = qD_n \nabla n \qquad \text{for zero applied field} \quad (3)$$

$$\nabla \cdot I_n = q D_n \nabla^2 n \qquad (4)$$

$$\frac{1}{q} (q D_n \nabla^2 n) - \frac{n}{\tau_n} = 0 \qquad \text{substituting equation (3) into equation (1) at equilibrium.}$$

$$\nabla^2 n - n/L_n^2 = 0 \qquad \text{since } L_n = (D_n \tau_n)^{\frac{1}{2}} \quad (5)$$

Equation (5) is the diffusion equation for electrons in p type material where n is the excess electron density and L_n is the diffusion length of the electrons.

Assuming an infinitely long, very narrow line of light with radial diffusion outward, the problem becomes a two dimensional one. For the case of a long line of light and a point contact collector, equation (5) can be expressed in terms of cylindrical coordinates (23), considering the z direction as infinitely long.

$$\frac{d^2 n}{dr^2} + \frac{1}{r} \frac{dn}{dr} - \frac{n}{L_n^2} = 0 \qquad \text{assuming n depends on r alone.} \quad (6)$$

The solution to equation (6) is a Bessel function but an approximate solution can be obtained by using a relationship given by T.S. Moss(8). $n = ar^{-\frac{1}{2}}$

Equation (6) becomes:

$$\frac{d^2a}{dr^2} - a\left[\frac{1}{L_n^2} - \frac{1}{4r^2}\right] = 0 \qquad (7)$$

For $r > L_n$ (which is the normal condition for the distances where the data is taken) the term $1/4r^2$ in equation (7) is neglected. The solution for equation (7) is $a \sim e^{-r/L_n}$ and $n \sim r^{-\frac{1}{2}} e^{-r/L_n}$. The boundary conditions for $r = 0$ and $r = \infty$ are satisfied by this solution as $\underline{r} \rightarrow 0$, n should become very large and as $\underline{r} \rightarrow \infty$, n should become zero.

The method of determining the minority carrier concentration at the probe may be explained in the following way. The light source is chopped at a low audio rate and the voltage V_{ph} developed across R (Fig. 1) is measured as the distance $\underline{r}$ is varied. A chopped light source permits the use of ac measurements, thereby separating the liberated minority carriers from steady state concentrations. But the experiment can be performed under dc conditions. Bardeen (15) has shown that the current through a reverse bias collector electrode is linearly related to the minority carrier density at the probe. The collector electrode in the experiment is operated under reverse bias conditions so that the current through R (and therefore V_{ph}) will be linearly related to the concentration of minority carriers at the probe. From the solution to the diffusion equation it is seen that the minority carrier concentration should decay exponentially as $\underline{r}$ is increased from $\underline{r} \sim 0$ (at the probe) because of the recombination of these carriers.

When plots of ln ($e^{-r/Ln}$) vs. r and ln ($r^{-\frac{1}{2}} e^{-r/Ln}$) vs. r are made, the distance $\underline{r}$ where the voltage decays to a value 1/e of its maximum (since $r = L_n$) is called the diffusion length. (see Fig. 3).

The diffusion length is used as explained earlier to determine the lifetime of the minority carriers using the equations:

$$\tau_n = L_n^2/D_n \quad ; \quad \tau_n = L_n^2\, q/kT \mu_n$$

$$\tau_n = 0.022\, L_n^2 \quad \text{using } \mu_n = 1800 \text{ cm}^2/\text{volt-sec (24) at } 300^\circ\text{K}$$

II. Limitations

The dimensions of the particular diamond used are shown in Fig. 4. One assumption made was that the probe or collector was far from the edges. Since the probe is located (as shown in Fig. 4) near the center of the crystal, the assumption would hold considering a maximum L_n of 0.0175 cm. The contact would then be at least 10 times L_n away from the edges. An upper limit of accurate measurement of carrier lifetime is imposed by the crystal dimensions; the limit would lie in the range of 6 micro-sec.

The assumption that the z direction is infinite would seem valid since this dimension is 20 times L_n maximum using the above assumption. The whole width of the crystal being illuminated would correspond to a long line of light.

The surface recombination would be most prominent when $\underline{r}$ became small. The electric field would also affect the data at the small $\underline{r}$ range. Data taken when the $\underline{r}$ values are small would deviate from theory. The surface recombination is considered low, so the cylindrical flow would not be distorted except at small values of $\underline{r}$. Surface recombination could cause a more rapid decay of the carrier concentration than predicted by the theory as the distance $\underline{r}$ is increased.

As far as the width of the line being narrow is concerned, this is taken care of by omitting the data taken at very small values of $\underline{r}$. These points would probably lie well off the curve.

III. Experimental Results

The data obtained from the diffusion length experiment is shown on the following pages. The graphs display a plot of photocurrent versus distance from the probe. A crystal holder was constructed and the holder was mounted on a micrometer head for measuring the distance between the point contact and the line of light. Two light sources were used in this experiment. A tungsten bulb for the visible range and a mercury arc source for the ultra violet range. The graphs are the results obtained using the Hg arc; however, the results from the tungsten bulb have essentially the same characteristics.

Figures 5, 6, and 7 show the results of the experiment performed using dc measurements. Using a chopped light source, no ac photocurrent was observed. The dc current did increase in a linear fashion as the distance from the probe to the light decreased.

The results from this experiment could be due to several factors. The carriers have to be produced at or very near the surface to cause the diffusion process necessary in this experiment. If carriers were produced throughout the bulk of the crystal, this would tend to reduce the diffusion current. Also, light sources are weak in the range required to excite carriers across the energy gap (5.5 ev), (1). When performing ac photoconductivity measurements under conditions of whole crystal illumination and broad end contacts, it was found that the ac

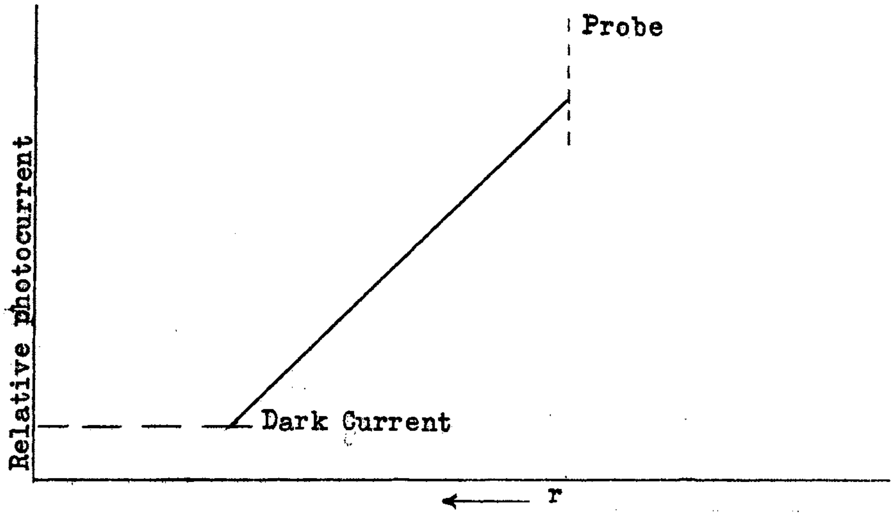

Fig. 5 DC Photocurrent vs. distance from the probe,using steady light

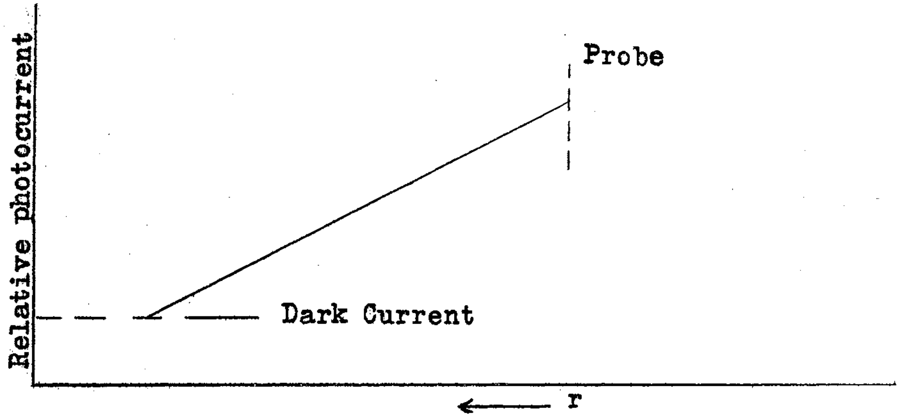

Fig. 6 DC Photocurrent vs. distance from the probe, using chopped light (run 1)

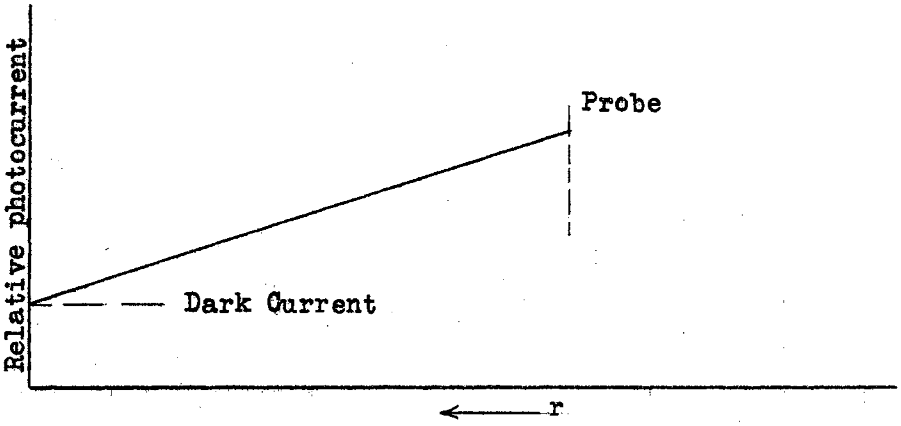

Fig. 7 DC Photocurrent vs. distance from the probe,using chopped light (run 2)

photocurrent was very small and not detectable except when using high amplification. It seems reasonable when illuminating only a narrow portion of the diamond that the ac photocurrent becomes even more difficult to measure. The noise present, due to the very high impedance of the point contact could overshadow any effect produced by the minority carrier diffusion when performing ac measurement.

Since the experiment is based on the diffusion of minority carriers, it is felt that the linear increase in current through the crystal is essentially due to holes being produced, and the results obtained are simply due to these excess holes producing an increase in the conductivity of the diamond.

CHAPTER IV

MEASUREMENT OF CARRIER LIFETIME BY THE RATIO OF THE PHOTOELECTROMAGNETIC CURRENT TO THE PHOTOCURRENT

The photoelectromagnetic effect was discovered by Kikoin and Noskov in 1934 (17). Although they were not aware of the existence of holes they did realize that the PEM effect was a Hall effect produced by diffusion currents. The PEM effect has become an effective method of measuring carrier lifetime when used in combination with the ordinary photocurrent produced in semiconductors.

I. Discussion

The photoelectromagnetic effect is produced as follows: a semiconductor is placed in a magnetic field and then illuminated on one of its surfaces normal to the direction of the magnetic field. This situation will cause an emf to appear in the third perpendicular direction. The situation is illustrated in Fig. 8.

The open circuit voltage equations have been derived by T.S. Moss, L. Pincherle, and A.M. Woodward (16). When crystals are used that have short diffusion lengths, and there is no control of the preparation of the samples, a simple theory of short-circuit currents has been found preferable (8). The expression for short-circuit currents replaces the more complex equations for the open-circuit voltage.

The sample (see Fig. 9) is considered to be a rectangular specimen of length d, thickness t and width w. The specimen is illuminated normal to its length and width so that Q excitations per second are produced in the material. The illumination produces photo-electrons

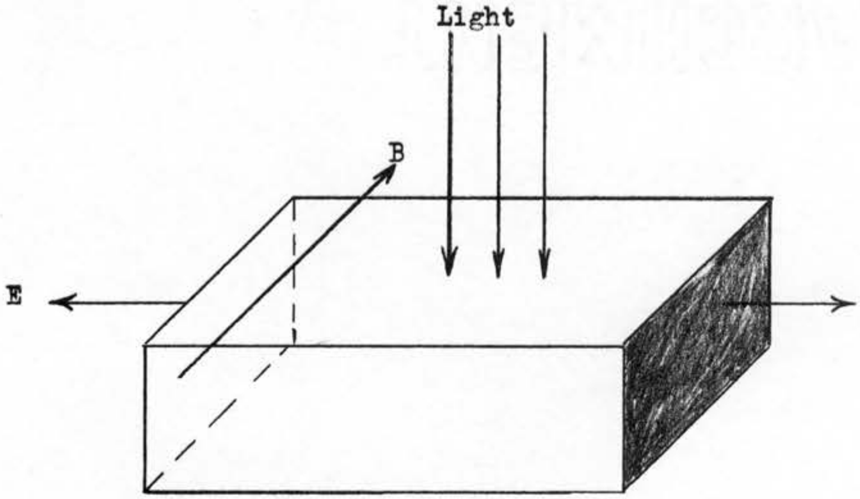

Fig. 8 Production of the PEM effect

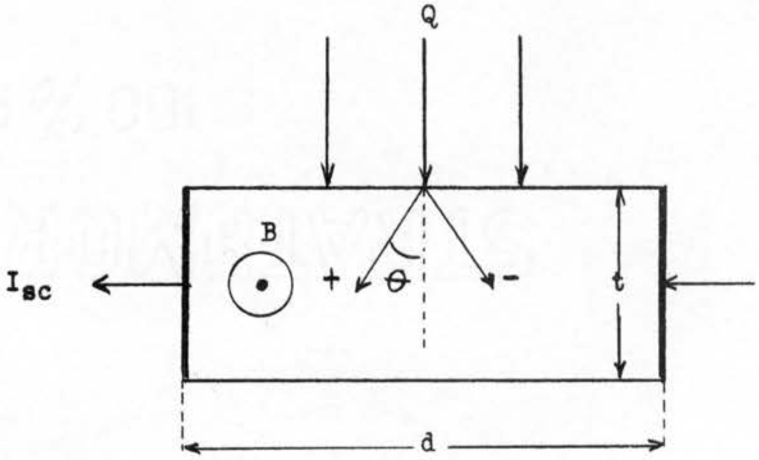

Fig. 9 Diffusion of carriers due to the PEM effect

and photo-holes. When the electron-hole pairs are generated near the surface, a concentration gradient will be set up and the carriers will diffuse down through the crystal. The magnetic field (transverse) will cause these two types of carriers to be deflected in opposite directions through the Hall angle $\theta = \tan^{-1} \mu B$ (18), where μ is the mobility in meters^2/volt-second and B is the magnetic induction in webers/meters^2 (25, 26).

Using the relationship $L = (D\tau)^{\frac{1}{2}}$, the diffusion length L_n travelled by an electron is given by $L_n = (D_n \tau_n)^{\frac{1}{2}}$ where D_n is the diffusion constant and τ_n is the electron lifetime. The assumption is valid provided there is no appreciable electric field in the direction of motion. This condition would be satisfied as long as the electric field building up in the direction of the thickness of the crystal is small compared to kT/q per diffusion length.

For small magnetic fields the carriers will move a distance $\mu B (D\tau)^{\frac{1}{2}}$ between electrodes. A charge $q\mu B(D\tau)^{\frac{1}{2}}/d$ will be given to the external circuit for each carrier (electrons and holes). For the case of the electron the charge will be $q\mu_n B(D_n \tau_n)^{\frac{1}{2}}/d$ and for the holes the contribution will be $q\mu_h B(D_h \tau_h)^{\frac{1}{2}}/d$. Using the relations for the total charge due to the electrons and holes, the net steady short-circuit current will be:

$$I_{sc} = \frac{QqB}{d}\left\{\mu_n(D_n \tau_n)^{\frac{1}{2}} + \mu_h(D_h \tau_h)^{\frac{1}{2}}\right\} \qquad (1)$$

where

D_n = diffusion constant for electrons
D_h = diffusion constant for holes
μ_n = mobility of electrons
μ_h = mobility of holes

The general equation characterizing steady state photoconductivity is (27):

$$W = Q\tau$$

W = total increase in free carriers in a given specimen
Q = total number of excitations per second occuring in the specimen
τ = lifetime of carriers in the free state

The combination of the general equation above with ohm's law, gives an expression for photocurrent in a given photoconductor as:

$$Iph = qQ\tau / Tr \text{ amperes}$$

Tr is the transit time of a carrier between electrodes and is defined as:

$$Tr = d/E\mu = d^2/V\mu$$

d = electrode spacing in meters
E = electric field in volts/meters
V = applied difference in potential in volts
μ = mobility of a free carrier

In the presence of an applied field, the distance travelled by an electron between electrodes is $\mu_n E \tau_n$ and similarly for holes the distance travelled between electrodes is $\mu_h E \tau_h$. The expression for the photocurrent in the specimen becomes:

$$Iph = Qq(\mu_n\tau_n + \mu_h \tau_h)E/d \qquad (2)$$

Where τ_n and τ_h are the carrier lifetimes of electrons and holes respectively.

Either of the equations (1), (2), could be used to obtain a value for the free carrier lifetime; however, both involve the factors of quantum efficiency and light source intensity which are difficult to determine experimentally. The ratio of steady state photocurrent to the PEM short circuit current will eliminate the term Q and this ratio becomes:

$$\frac{I_{ph}}{I_{sc}} = \frac{(\mu_n \tau_n + \mu_h \tau_h) E}{\left\{ \mu_n (D_n \tau_n)^{\frac{1}{2}} + \mu_h (D_h \tau_h)^{\frac{1}{2}} \right\} B}$$

This expression as it stands does not provide a very convenient relationship if it is to be used to measure free carrier lifetime because the two lifetimes can not be separated. But it can be changed to a much simpler form if certain characteristics of the semiconductor are known. These characteristics involve essentially the physics of the semiconductor. For example, if the ratio of the mobilities of the two types of carriers is almost one or at least close enough for the assumption to be made, the expression becomes:

$$\frac{I_{ph}}{I_{sc}} = \frac{(\tau_n + \tau_h) E}{D^{\frac{1}{2}} (\tau_n + \tau_h)^{\frac{1}{2}} B}$$

A similar relationship would be evolved if the ratio of mobilities had been very great and the lifetimes of the carriers approximately equal except that one type of carrier could be neglected altogether. In this expression the lifetime factor is due to one type of carrier only. This is usually the minority carrier in most of the semiconductors used for study.

$$\frac{I_{ph}}{I_{sc}} = \frac{\tau^{\frac{1}{2}} E}{D^{\frac{1}{2}} B}$$

The lifetime of one carrier may be a great deal longer than the other, and this condition also yields the above equation. The quantum efficiency of the semiconductor for generation of electrons may be different from that for holes in which case one type of carrier may be neglected. This leads to an expression for the lifetime involving quanities which are easily measured.

$$\tau = \frac{(\text{ph B})^2 \text{ D}}{(\text{Isc E})^2}$$

The above relationship is the one most used in semiconductor study. The assumption that it is valid is usually explained by one or more of the reasons just discussed. The lifetime obtained from this method is of course limited in accuracy by the uncertainty in the value of the diffusion constant.

II. Limitations

The theory discussed previsouly assumed ohmic contacts and infinite crystal dimensions. The dimensions have to be large compared to the diffusion length of the carriers. The comparison of crystal dimensions to the diffusion length has been discussed in Chapter III. This assumption seems to be avalid in the case of the particular diamond crystal used in this study.

The Hall angles have to be small to fit the theoretical treatment given to the problem. This condition requires that the angles $(\mu B)^2$ be much less than one. In the case of diamond with mobilities in the range of 1000 cm^2/volt-second to 2000 cm^2/volt-second (24) and the magnetic field B equal to 7000 gauss, this gives a maximum value of μB equal to 0.14. With μB equal to 0.14 the term $(\mu B)^2$ equals 0.0196 which is small enough to be neglected.

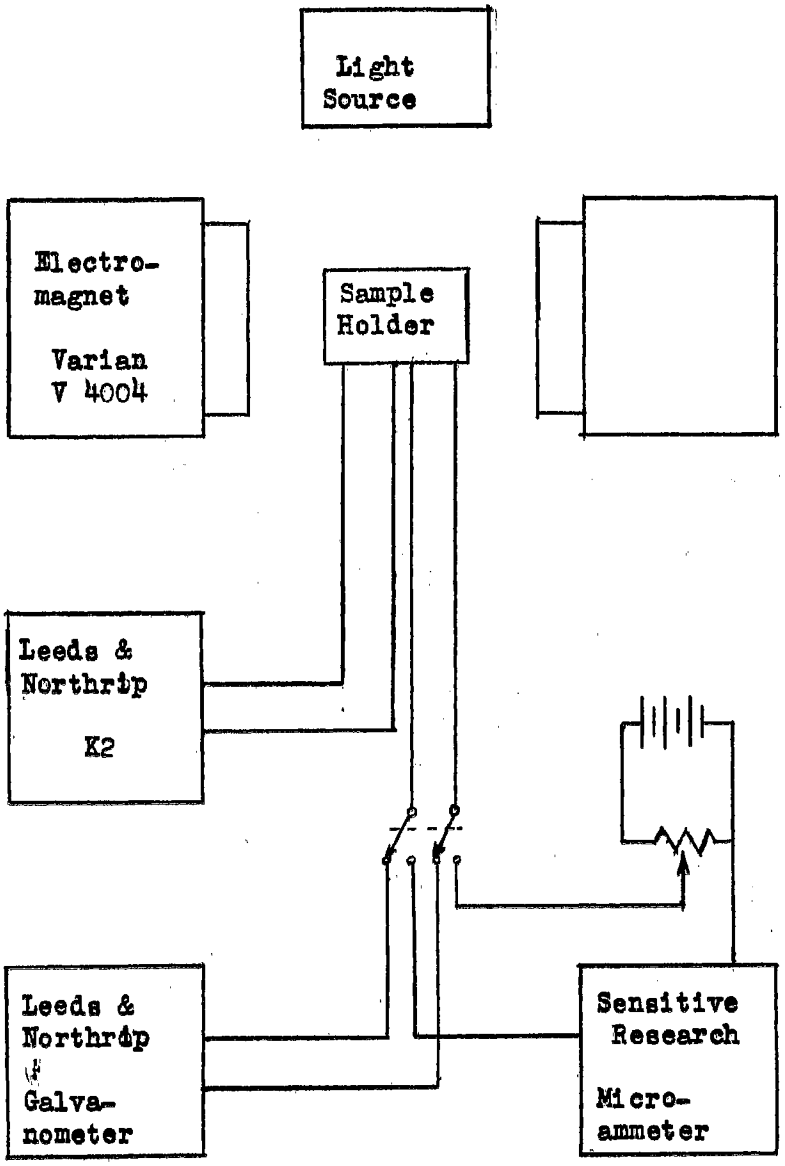

Fig. 10 Block diagram of equipment used for photoconductivity and PEM measurements

III. Experimental
Results

Mercury and hydrogen arcs and a tungsten bulb were used as the light sources in this experiment. The mercury and hydrogen arcs were used to provide the ultra-violet wavelengths and the tungsten bulb for the visible range. A very high photocurrent was produced using the mercury and hydrogen arcs, but no photoelectromagnetic effect was detected.

One might expect to observe the PEM effect in the visible region because the diamond crystal is photoconducting in this region (29,36). However, the diamond is very transparent to visible light and therefore, the carriers are probably generated throughout the bulk of the material, thus preventing the development of a concentration gradient of carriers which is necessary for the PEM effect.

In the uv, the absence of the PEM short-circuit current could be caused in part by the high resistance of the end contacts. Except at very low values of resistance it is evident that the diffusion current would be of extremely low value. In the case of germanium and silicon it is possible to get low resistance contacts which aid in obtaining a large short-circuit current. Also the thickness (d) of the crystal enters as a parameter in the short-circuit current. For germanium and silicon, (d) could be kept to a minimum value; however, this parameter could not be adjusted in the case of the diamond without destroying it. Furthermore, the lifetimes at the surface of the crystal may be considerably less than lifetimes in the bulk. Possibly some surface treatment of the diamond could remove recombination centers at the surface enabling a PEM effect to be obtained.

CHAPTER V

MEASUREMENT OF CARRIER LIFETIMES USING THE PULSE RESPONSE METHOD

I. Discussion

The electric current in semiconductors is carried by electrons in the conduction band and holes in the valence band. The equilibrium concentrations of holes in the valence band and electrons in the conduction band are not necessarily equal. When there is an excess of either the minority carrier or the majority carrier or both over the normal concentrations, there will be a net rate of recombination attempting to restore equilibrium to the crystal (7).

Excess carriers (electrons, holes, and electron-hole pairs) produced by a short pulse of light will build up in proportion to an exponential function during the period the light is on and then decay at an exponential rate after the light is extinguished. The photocurrent equations are:

$$\frac{dI}{dt} = Ip_s(1 - e^{-t/\tau_h}) + In_s(1 - e^{-t/\tau_n}) \qquad (1)$$

p_s = steady state value of excess holes
n_s = steady state value of excess electrons
τ_h = lifetime of holes
τ_n = lifetime of electrons
t = time

$$\frac{dI}{dt} = Ip_s e^{-t/\tau_h} + In_s e^{-t/\tau_n} \qquad (2)$$

Equation (1) represents the build up of the photocurrent pulse and equation (2) is the equation determining the decay of the photocurrent.

In most semiconductor studies, the main factor is the minority carrier and consequently one of the lifetimes is omitted. This omission yields for the build up of photocurrent a function $K(1-e^{-t/z'})$ and $Ke^{-t/z}$ for the decay of the photocurrent. The quanities z' and z are not necessarily the same but both are called lifetimes. Z' should be designated as the "response time," representing the time for a photocurrent signal to reach (1-1/e) of its final value. The photoconductivity response lifetime z is the time required for the excess carriers to decay to 1/e of the maximum value of excess carrier concentration after the illumination is removed. The "response time" can be misleading when used as a measure of carrier lifetime unless the pulse of light is long compared to the carrier lifetimes. Very commonly z' appears less than z because the semiconductor never reaches steady state conditions. Also this difference can be accounted for depending on the type of semiconductor studied since the neglection of one type of carrier may not be a correct assumption.

In the preceeding discussion, shallow trapping phenomena has been neglected. When shallow trapping predominates the recombination process--that is, shallow trapping is much greater than the direct recombination with ground states--the photoconductivity response lifetimes obtained from the pulse response technique are erroneous and generally several orders of magnitude too long. Rose (31) has shown that the lifetimes observed in the pulse response method under the assumption of high light intensity are valid, and that the decay time constant z can be equal to the true lifetime. This lifetime is the photoconductivity response lifetime and may be equal to the conductivity lifetime under the preceeding assumption. Since the photoconductivity can be due to the transport of either or both carriers, depending on the semiconductor under observation, the conductivity lifetime is a combination lifetime lasting as long as either carrier is free. In agreement with Rose, Bube (32) concludes that generally the decay of photocurrent consists of two parts, an initial rapid part corresponding to the direct recombination of free carriers, and a much slower portion corresponding to the recombination of carriers which have been freed from shallow traps. The time of decay of photocurrent in the usual case is assumed to be determined by the recombination with trapping centers and ground states (33). Clarke (34) has carried through a mathematical analysis of the decay of photocurrent based on a model containing recombination and trapping centers. His solution demonstrates the complexity of the problem.

Young (30) describes the diamond crystal used in this study as having p type conductivity, and from studies of photoconductivity behavior, the author classifies the photoconductivity in the diamond as being largely due to holes with the electrons playing a smaller part in the process. Based on the results obtained in the diffusion length experiment (Chapter III), it would seem that the photoconductivity produced by the mercury arc light was all due to the majority carrier; however, the spectrum of this light contains light of sufficiently short wavelengths to excite carriers across the energy gap. The electron may have a very short lifetime in the diamond but its presence must not be neglected in photocurrent since the conductivity lifetime is a summation of the lifetimes of both carriers. The decay of photocurrent after the light is removed from the sample will depend on the decay of both carriers.

II. Method

Measurement of the carrier lifetime involves the production and detection of the excess carrier concentration in the semiconductor. Excess holes are produced in the semiconductor by a very short, intense spark of light. The measurement of the change in sample conductance is accomplished by measuring the change in the voltage drop across a fixed resistor in series with the sample.

Figure 11 shows the circuit used in this experiment. The pulse generator consists of approximately 150 feet of RG-8U coaxial cable and a 5KV power supply. The pulse produced is 8 micro-seconds in duration with a rise time of about 0.2 micro-second and 0.2 to 0.4 micro-second fall time. When the relay is activated the delay line discharges into a 51 ohm load producing a very intense spark of light at the electrodes. The light illuminates the crystal producing the excess holes. The impedance of the diamond crystal used is approximately 1 meg-ohm; consequently a 1 meg-ohm load R_3 was used to measure the change in sample conductance as the crystal was illuminated. The crystal steady state electric field was provided by R_2. To prevent any polarization or residual effects between pulses, the sample was not pulsed continuously. A single pulse was applied to the crystal, and a photograph was taken of the response on a Tektronix 515 oscilloscope. The end contacts on the sample were covered to prevent any photo-voltaic effects.

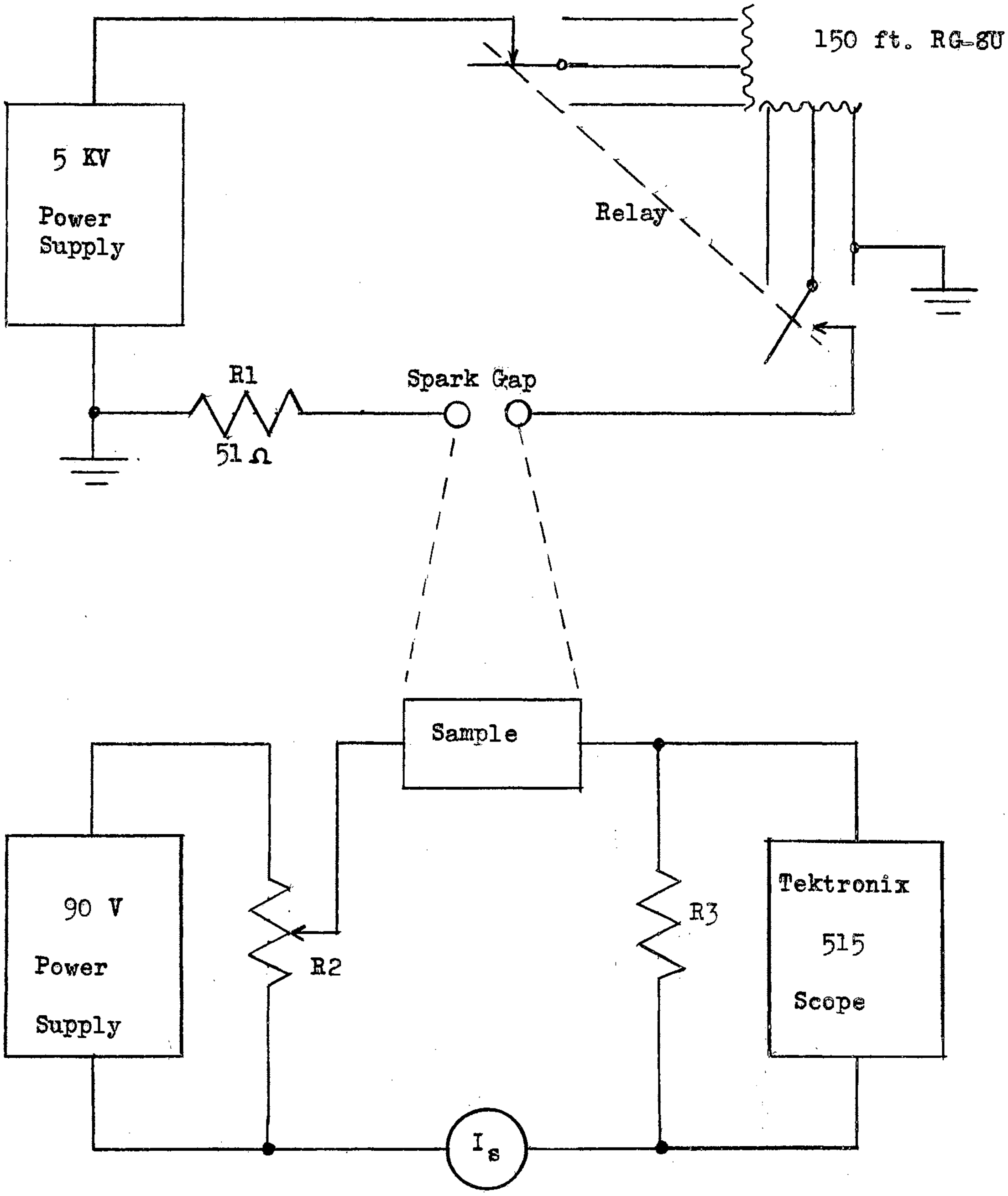

Fig. 11 Schematic Diagram for the measurement of the pulse response

III. Results

Referring to Fig. 12, the lifetime computed from these decay curves give a value of 0.25 seconds. The decay curves were taken at room temperature (300° K). The time constant of decay, assuming an equation of the form (35) $Ke^{-t/\tau}$ describes the decay of the photocurrent pulse, yields a value for lifetime that would imply a very long lifetime in the diamond. The value could hardly be taken as representing the free carrier lifetime since it is evidently several orders of magnitude shorter than this value. The very long time of this decay could not be attributed to the shallow trapping phenomena that is usually associated with the long tail that accompanies the decay of photocurrent measured on other types of semiconductors. These tails are associated with times ranging from 10^{-3} to 10^{-2} seconds. In the case of the diamond, the long decay is probably due to very slowly emptying traps which would be much deeper in the forbidden zone and require a much longer time to empty than the normal shallow traps encountered.

It was found that the slow decay could be made even slower by cooling the sample. The time constant of decay was increased to 0.4 seconds at a temperature of 260° K. The addition of a steady ambient tungsten light had no noticeable effect on the time of decay of the photocurrent pulse.

IV. Trapping

The results obtained in the pulse response experiment created a necessity for a study to be made on the trapping phenomena observed

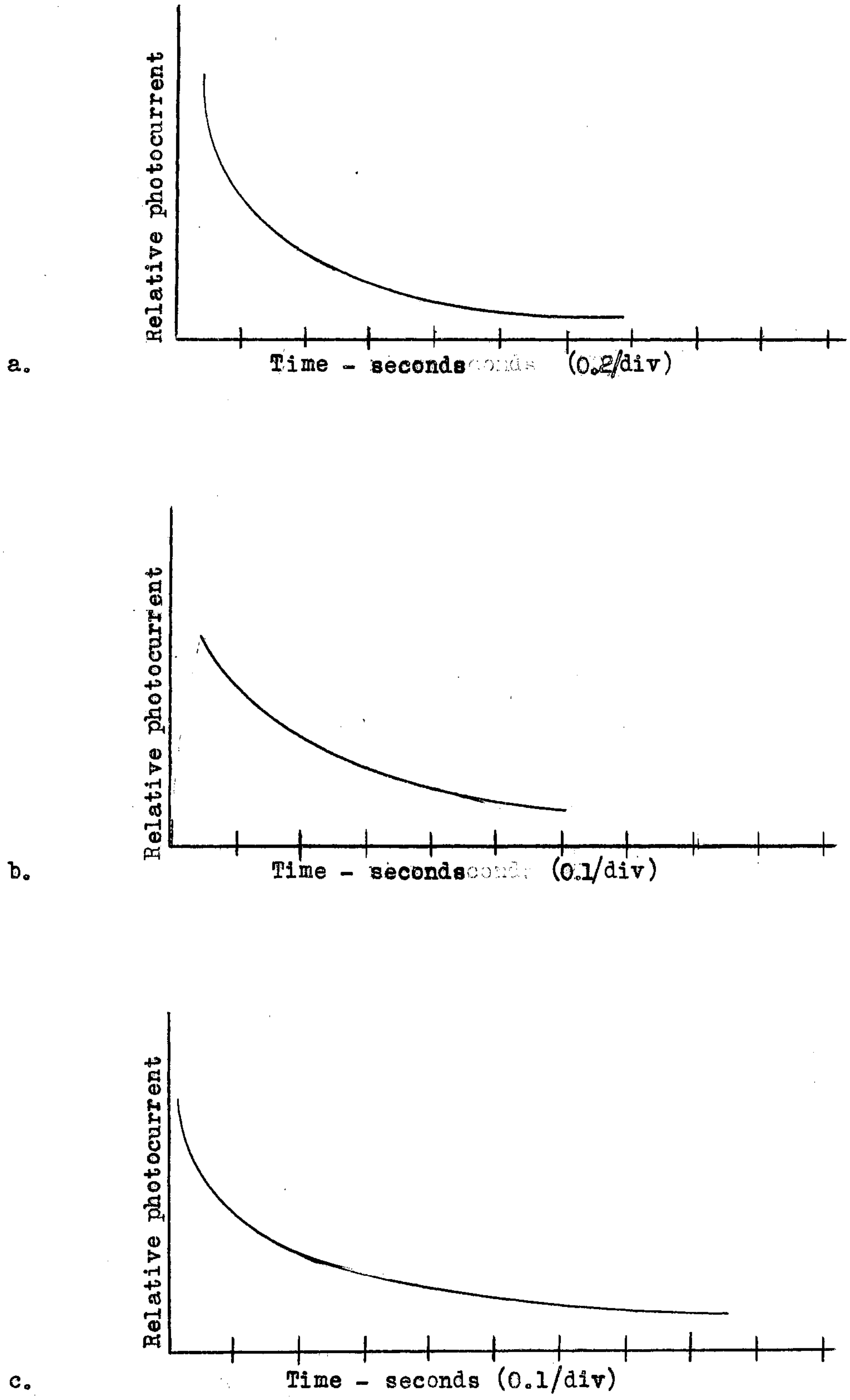

Fig. 12 Decay of photocurrent pulse

in the sample.

The first investigation made on the trapping centers was in the visible range of wavelengths. Using a camera shutter to obtain fast illumination and cut off, a plot of photocurrent was made using the whole visible spectrum from a tungsten bulb. The photocurrent was allowed to reach a steady value and then the light was removed from the crystal. The decay of the photocurrent was timed, and the results are shown in Fig. 13. The build up time required is shorter than the decay, but this can be caused by the traps having a different filling and emptying time. If it is assumed that the curve is exponential, the time of decay is in the range of 40 minutes. The curve is not an exponential; however, it is the sum of several exponential terms. There are two peaks in the photoconductivity vs. wavelength in the visible range (36), and the time constant of decay of these wavelengths were investigated. At 6300 Å the decay constant was of the order of 6 minutes, 8000 Å gave a time constant of less than a minute, while the 4400 Å took about 30 minutes to decay to 1/e of its maximum value. When a decay is assigned to the whole visible spectrum taken from photocurrent measurement, the measured quanity will be the longest decay that is contained in that range of wavelengths.

Figure 14 is a decay curve obtained from the spectrum of a mercury arc light. Although this curve is obviously not a true exponential, the constant of decay is in the range of 90 minutes. Again an investigation was made at the peaks of the photocurrent vs. wavelength which are at 2220 Å and 2280 Å. Both of these wavelengths yielded a value of decay in the range of 90 minutes. The traps filled

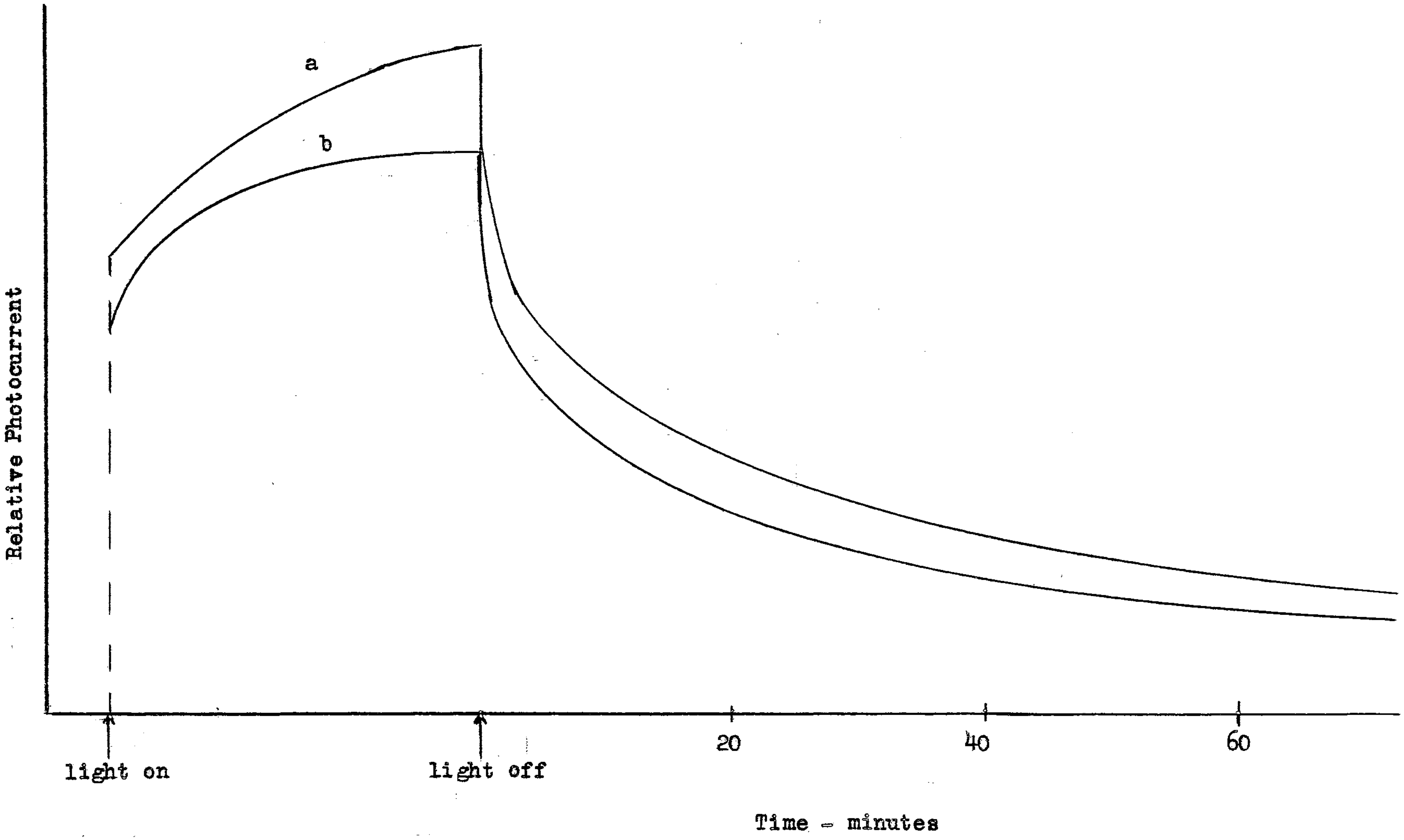

Fig. 13. Decay of DC Photocurrent in the Visible Range

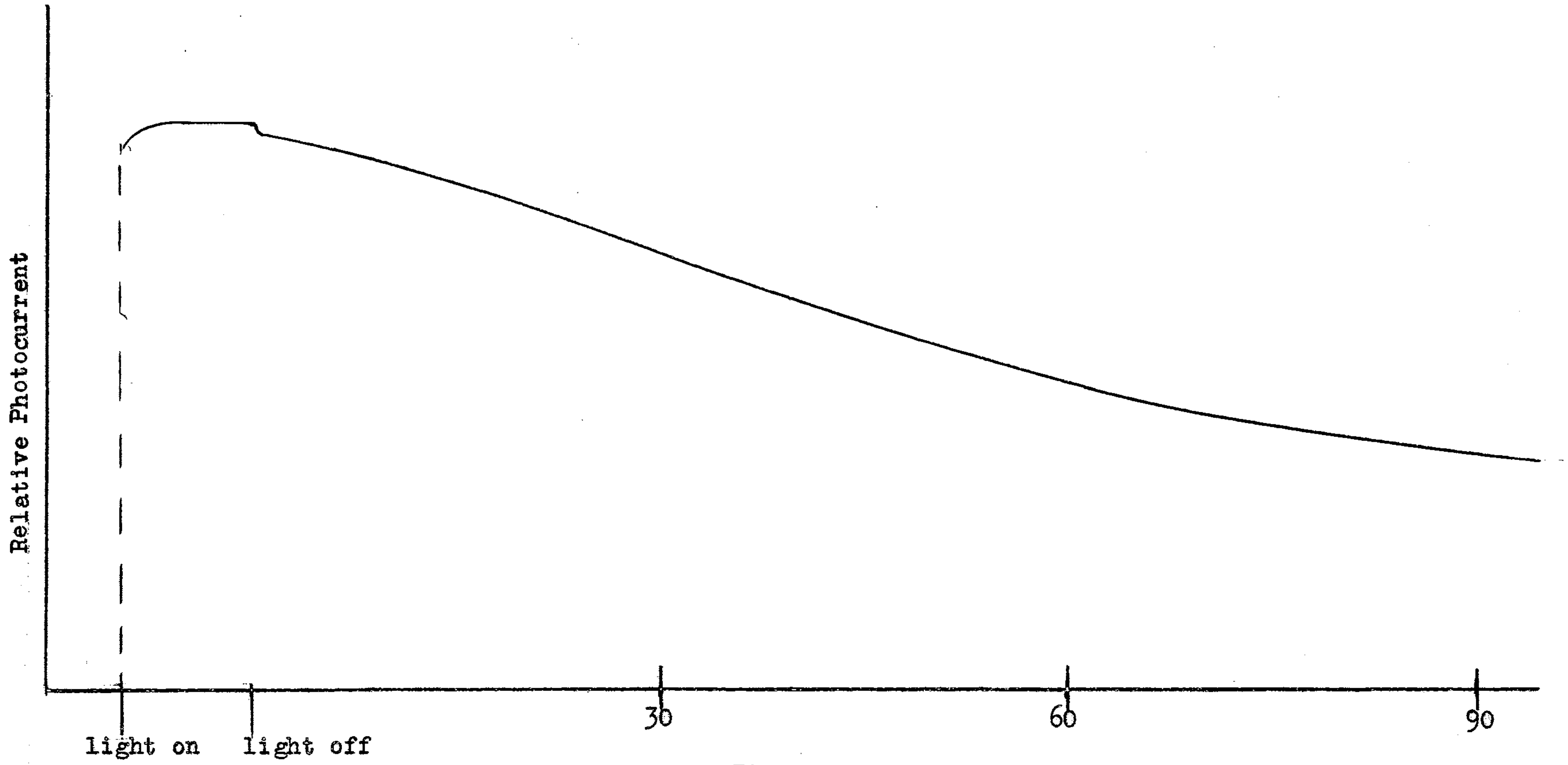

Fig. 14. Decay of DC Photocurrent using a Mercury Arc Light

by the uv light empty much slower than those associated with the visible region. The build up time of the photocurrent in both the visible and uv region is much faster than the decay. This can be explained by the fact that the filling and emptying of these traps does not necessarily require the same amount of time.

CHAPTER VI

CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDY

The general methods used in obtaining carrier lifetimes in semiconductors have been used in an attempt to measure lifetimes in the type IIb semiconducting diamond. The methods which have been used very successfully in most semiconductors do not seem to provide effective means for actual measurement of carrier lifetimes in the present study.

The diffusion length experiment met with several difficulties which are not present in the case of semiconductors, such as germanium and silicon. The diamond may have very high surface recombination rates, and since this experiment is based on surface phenomena creating a diffusion current, the effect could be undetectable. The effect would be small in any case, and this would necessitate ac measurements in order to provide the necessary amplification. In the case of other semiconductors such as germanium it is possible to remove surface recombination states by etching with acid. Possibly some technique could be devised to remove surface recombination states in diamond. Although the high impedance of the probe would not necessarily be detrimental to the diffusion effect, it does amplify the pick-up and can overshadow any effect produced at the point contact.

Much the same can be said about the PEM short-circuit current method of measuring lifetimes. The high surface recombination rate would render the effect practically impossible to measure. The contact resistance would affect the PEM short-circuit current to a lesser degree but could seriously cut down the short-circuit current, even to the extent that it would be impossible to measure.

Although all measurements of carrier lifetimes using the pulse response method on semiconductors are plagued with the trapping phenomena, the degree can be much less in the case of a small energy gap. Diamond with an energy gap of 5.5 ev can contain many multiple trapping levels with different times of emptying associated with each. From the investigations made in Chapter V, it would seem that the decay times vary with the depth of the traps. The trapping does not necessarily have to be a simple process; it can be highly complex and varied. The curves of the decay of the photocurrent show that the trapping is not a single exponential type, but it contains several terms which have to be studied independently. It was known that ac photoconductivity measurements could be made on this particular sample. The chopped light frequency of 480 cycles per second applied to the sample produced an ac photocurrent; this meant that there was at least a lifetime less than one millisecond or the diamond would not respond to this frequency.

Observations were made on the build up and decay of the photocurrent produced by a 480 cycle light chopper. The initial rise or fall of the photocurrent can provide a means of determining the conductivity lifetime. The photo-signal required 100 microseconds to build up to $(1 - 1/e)$ of its maximum. Since the light from the chopper is not on and off instantaneously, the lifetime determined from the curve will be an upper limit. It is concluded that the conductivity lifetime is less than 100 microseconds.

The author intends to make a further study of the lifetimes in the diamond with the accent on new methods and different approaches.

The use of a Kerr cell for fast illumination might provide a method of finding the very fast decay that must surely be contained in the diamond. Also the Van De Graff accelerator can be used to obtain a beam of high speed electrons which can be started and terminated quickly, enabling a determination of lifetimes from the initial decay portion of the curve.

The investigation made on the many trapping levels obtained from the study of photocurrent decay provide useful information which is necessary to predict the model to be associated with the diamond crystal. The trapping levels appear all the way from the visible wavelengths (including the near infra-red) to the far ultra-violet regions of wavelengths. The diamond with its wide energy gap provides a broad territory for the investigations of trapping with the emphasis on capture cross sections both for the minority carriers and the majority carriers.

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