

CHARACTERISTIC TIMES OF ELECTRONIC PROCESSES IN SEMICONDUCTORS

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1. INTRODUCTION

THE application of semiconductors has as its physical basis processes which are, thermodynamically, non-equilibrium ones, and which are caused by external influences (illumination, non-uniform heating, exposure to radioactivity, injection, etc.). To describe these processes the concept of minority carrier lifetime τ has been introduced as a fundamental characteristic.¹⁻³

The lifetime τ_e of a non-equilibrium electron is usually defined as the mean time, as determined by the recombination process, for which a free excess electron exists at a given point in a crystal. By the concentration of free excess (non-equilibrium) electrons n' is meant that part of the general conduction electron concentration n which is in excess of the concentration n_0 at thermodynamic equilibrium:

$$n' = n - n_0. \tag{1.1}$$

Thus, we arrive at the relationship:

$$\tau_e = \frac{n'}{R_e}, \tag{1.2}$$

where R_e is the recombination rate for electrons. Similarly, the lifetime of non-equilibrium holes is given by

$$\tau_h = \frac{p'}{R_h}. \tag{1.3}$$

Both theoretical considerations²⁻⁴ and the analysis of experimental data⁴⁻¹⁰ show that there is practically no electron-hole recombination (band-to-band electron transitions) in an ideal lattice, and that recombination occurs only at certain structural defects which act as recombination centers (Fig. 1). In this case the energy released in the act of electron-hole recombination is as a rule converted into energy of thermal oscillations (radiationless recombination).*

In references 6 - 10 it is shown that foreign atoms of a number of metals (copper, nickel, iron, cobalt, gold, etc.) form in semiconductors recombination and trapping centers for electrons and holes - such centers having levels in the forbidden band. The centers formed by these impurities are usually (depending on

*The probability of radiative recombination, according to calculations made in reference 11, corresponds to lifetimes in germanium of ≈ 1 sec, while the observed lifetimes do not exceed 10^{-2} sec. This type of recombination is involved in semiconductors with small forbidden energy gaps, for example, in InSb, where its contribution amounts to 20% of all recombinations.

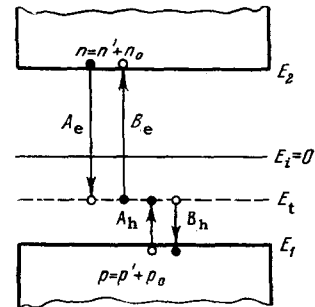


FIG. 1

the temperature) both trapping centers (the center interacting only with one carrier type) and recombination centers (interaction takes place with both carrier types). Usually at a given temperature only one of the levels in such centers is effective. As a rule the deepest level is recombinative. Besides impurities, dislocations and other mechanical imperfections of the crystalline lattice can be recombination centers.^{13,14}

We remark that, besides the radiationless transition mechanism discussed in references 16 and 17 (the energy given out in the recombination process being transformed into thermal energy of lattice vibrations), there are also other mechanisms in semiconductors.

Bonch-Bruевич¹⁸ has discussed the exciton mechanism of radiationless recombination. In addition, "impact" or three-body recombination^{19,20} takes place, where the energy released is given to a free electron or hole which is close to the defect. Finally, the energy can be given to the entire assembly of free carriers surrounding the defect²¹ (transformation into energy of plasma oscillations). The last two mechanisms play an important part at large free carrier concentrations.

It should be noted that, according to (1.2) and (1.3), the lifetime depends in the general case on the generation level [$\tau = f(n', p')$]. In the majority of cases the measured lifetime is constant, which corresponds to monomolecular recombination. However, in other recombination modes (for example, bimolecular) τ can depend on the concentration of non-equilibrium carriers.

It should also be noted that recombination centers can be provided not only by volume imperfections of the lattice, but also by defects and contamination at the semiconductor surface.^{22,23} If the surface is not treated carefully enough, surface recombination domi-

nates. The volume lifetimes are, therefore, upper limits of the possible lifetimes in a semiconductor in a given state, i.e., the limiting theoretical characteristics which can be obtained experimentally, with careful etching of the surface and with such dimensions of the specimen that surface effects can be neglected in comparison with volume effects.

The basic theoretical papers in which the kinetics of non-equilibrium electronic processes in semiconductors are treated are those of Shockley and Read² and Hoffman.³ Shockley and Read start by considering for electrons and holes* the separate acts of capture by and thermal escape from centers (Fig. 1). After averaging over all free carrier states (free carriers are taken to have a Boltzmann distribution, but carriers captured by centers are assumed to have a Fermi distribution), the authors arrive at a system of equations for the absolute capture rates for electrons (R_e) and holes (R_h), which are equal for stationary processes to the recombination rate R . These equations are written in the form:

$$\left. \begin{aligned} R_e = R &= A_e N_t f_{vt} n - A_e N_t f_t n_1, \\ R_h = R &= A_h N_t f_t p - A_h N_t f_{vt} p_1, \end{aligned} \right\} \quad (1.4)$$

where f_t and f_{vt} are, respectively, the fractions of filled and empty centers. The system (1.4) gives the recombination rate of non-equilibrium electron-hole pairs as

$$R = \frac{A_e A_h N_t (np - n_0 p_0)}{A_e (n + n_1) + A_h (p + p_1)}, \quad (1.5)$$

where N_t is the concentration of recombination centers, A_e and A_h are, respectively, the mean values of the capture coefficients for electrons and holes, and n_1 and p_1 are constants which have the dimensions of concentrations and are given by the equations:

$$\left. \begin{aligned} n_1 &= 2 \left(2\pi m_e \frac{kT}{\hbar^2} \right)^{\frac{3}{2}} \exp \left\{ -\frac{E_2 - E_t}{kT} \right\}, \\ p_1 &= 2 \left(2\pi m_h \frac{kT}{\hbar^2} \right)^{\frac{3}{2}} \exp \left\{ -\frac{E_t - E_1}{kT} \right\}. \end{aligned} \right\} \quad (1.6)$$

Here m_e and m_h are the effective masses of electrons and holes, E_2 is the lower edge of the conduction band, E_1 is the upper edge of the valence band, E_t is the energy level of the centers (see Fig. 1). We remark that the entire Shockley-Read treatment is carried out only for stationary processes occurring during uniform generation. By considering the electron processes for small recombination center concentrations, i.e., when the neutrality condition can be written in the form

$$p' = n', \quad n' \gg |n'_t|, \quad p' \gg |p'_t|,$$

and using the relationships (1.2) and (1.3) and assuming that $R_e = R_h = R = G$ for steady-state generation of non-equilibrium pairs, where G is the generation rate

*Shockley and Read assume that all the recombination centers are of one type, i.e., have a common energy level E_t and are described by the same capture coefficient A_e and the same A_h .

of non-equilibrium pairs, Shockley and Read obtain an expression for the lifetime in the form

$$\tau = \tau_{p_0} \frac{n_0 + n' + n_1}{p_0 + n_0 + n'} + \tau_{n_0} \frac{p_0 + p_1 + p'}{p_0 + n_0 + p'}. \quad (1.7)$$

For small concentrations n' the expression for τ takes the form

$$\tau_0 = \tau_{p_0} \frac{n_0 + n_1}{n_0 + p_0} + \tau_{n_0} \frac{p_0 + p_1}{n_0 + p_0}. \quad (1.8)$$

The other limiting case $n' \rightarrow \infty$ gives

$$\tau_\infty = \tau_{p_0} + \tau_{n_0}, \quad (1.9)$$

where

$$\tau_{p_0} = \frac{1}{A_h N_t}, \quad \tau_{n_0} = \frac{1}{A_e N_t}.$$

If the concentration of centers N_t is large, (1.7) does not apply and it is necessary to proceed from the expressions (1.4) for the recombination rates R_e and R_h .

By separating in (1.4) the concentrations of non-equilibrium carriers ($p = p_0 + p'$, $n = n_0 + n'$, $f_t = f_{t0} + \delta f_t$) and assuming that at any point in the semiconductor the neutrality condition is satisfied (uniform generation) and that the departure from thermodynamic equilibrium is small, we obtain a system of equations linear in n' and p' :

$$\left. \begin{aligned} R_e = R &= A_e N_t [(1 - f_{t0}) n' - (n_0 + n_1) \delta f_t], \\ R_h = R &= A_h N_t [f_{t0} p' + (p_0 + p_1) \delta f_t], \\ p' - n' &= n'_t = N_t \delta f_t. \end{aligned} \right\} \quad (1.10)$$

Here $n'_t = N_t \delta f_t$ is the concentration of non-equilibrium electrons captured by the centers.

By solving (1.10) using (1.2) and (1.3), we obtain the following expressions for the electron and hole lifetimes:

$$\tau_e^{st} = \frac{n'}{R_e} = \frac{\tau_{p_0} (n_0 + n_1) + \tau_{n_0} \left[p_0 + p_1 + N_t \left(1 + \frac{p_0}{p_1} \right)^{-1} \right]}{n_0 + p_0 + N_t \left[\left(1 + \frac{p_0}{p_1} \right)^{-1} \left(1 + \frac{p_1}{p_0} \right)^{-1} \right]}, \quad (1.11)$$

$$\tau_h^{st} = \frac{p'}{R_h} = \frac{\tau_{n_0} (p_0 + p_1) + \tau_{p_0} \left[n_0 + n_1 + N_t \left(1 + \frac{n_0}{n_1} \right)^{-1} \right]}{n_0 + p_0 + N_t \left[\left(1 + \frac{n_0}{n_1} \right)^{-1} \left(1 + \frac{n_1}{n_0} \right)^{-1} \right]}. \quad (1.12)$$

We note first of all that, because n' and p' are not equal to one another, the lifetimes for electrons (τ_e^{st}) and holes (τ_h^{st}) are different. But experimentally one lifetime is always observed. Shockley and Read therefore assume that the measured lifetime is that of the minority carriers and determines the recombination process. Consequently, the graph showing the variation of lifetime with the position of the Fermi level F in the forbidden gap (Fig. 2) will have a step at the point corresponding to intrinsic conductivity. In fact, we have two different graphs: $\tau_e^{st}(F)$ for the p-type and $\tau_h^{st}(F)$ for the n-type semiconductor, which join at the point corresponding to intrinsic conductivity. Leaving aside the fact that under the assumption stated the lifetime of the intrinsic semiconductor is not well

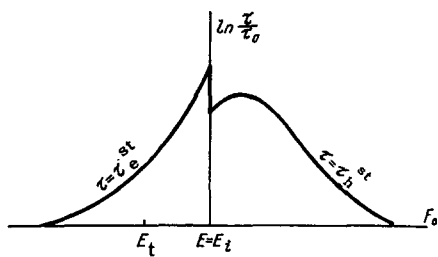


FIG. 2

defined, since the concept of minority carriers loses its meaning, it is not even clear whether the assumption that the measured lifetime is $\tau_{\text{min. c.}}^{\text{st}}$ (the minority carrier lifetime) will be true.

It should be noted that the agreement obtained in reference 6 between $\tau^{\text{st}}(F)$ and the measured lifetime proves nothing; because of the limited accuracy of the measurements it is impossible to determine whether, in fact, the experimental curve has the step mentioned (Fig. 3). Apart from this, it should be pointed out that in this work the lifetime was determined from diffusion length measurements, i.e.,

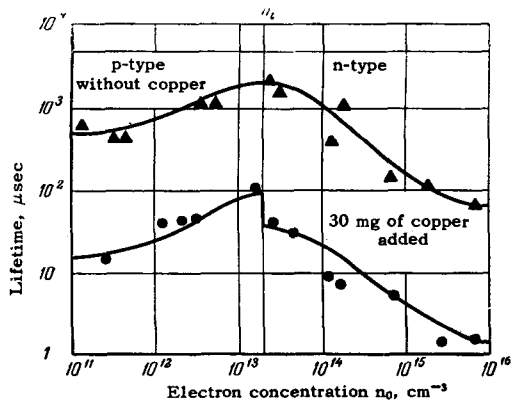


FIG. 3

under conditions of non-uniform generation [$G = f(x, y, z)$, but not $G = \text{const}$]. Therefore, the conditions under which the Shockley-Read relationships would be true (uniform generation) are not satisfied in the method of measurement, and, consequently, the measured values of the lifetime cannot be compared with the analogous quantities given by (1.11) and (1.12).

Thus, stationary electronic processes during uniform generation are described by two times: τ_e^{st} and τ_h^{st} . The inequality $\tau_e^{\text{st}} \neq \tau_h^{\text{st}}$ corresponds to the inequality $n' \neq p'$, i.e., it is due to the capture of carriers by the centers ($p' = n' + n_t' \neq n'$, $n_t' \neq 0$).

Hoffman³ has worked on these problems. Starting from the theory of chemical reaction kinetics proposed by Schottky,²⁴ he proceeds to a detailed analysis of the electronic processes in semiconductors both for direct recombination of free electrons and holes (band-to-band transitions) and for recombination occurring at centers (transitions through an intermediate level). He assumes that free electrons and holes have a Boltz-

mann distribution (nondegenerate semiconductors), and that the law of mass action is true; this leads to equations for the lifetime agreeing with the analogous formulae of Shockley and Read.

Schottky's basic idea is that the reaction parameters are both the concentrations of the separate components n_j and their rate of change \dot{n}_j . This viewpoint allows the "expectation times" of the separate components $\tau_j = n_j / |\dot{n}_j|$ to be introduced; for small departures from thermodynamic equilibrium these are constants for a given reaction. As Schottky remarks, these times do not coincide in most cases with the usually considered "lifetimes" in semiconductors, which are determined by the capture processes for non-equilibrium carriers or by diffusion. In the general case the lifetimes are functions of all the times τ_j , but are not equal to any of these times (they describe processes in which all carrier types participate and all the τ_j).

In view of the complexity of the problem, Schottky limits himself to a detailed consideration of the case when a single characteristic reaction time can be introduced. In fact he shows, like Shockley and Read, that this is possible if the processes at defects can be neglected, i.e., if the concentration of carriers in defects and their rate of change can be assumed small and if the space charge is also small. In the other cases Hoffman considers that only the separate $\tau_j = n_j / |\dot{n}_j|$ have meaning. Using these ideas, Hoffman discusses the kinetics of electronic processes. He divides all electronic processes in semiconductors into two classes: steady-state and non-steady-state.

Hoffman starts with the simplest case of the direct recombination of free electron-hole pairs. In this case the lifetime is given by the relationships

$$\tau = \frac{n'}{R} = \frac{1}{r(n_0 + p_0)}, \quad (1.13)$$

$$R = r(np - n_0 p_0) \approx r(n' p_0 + p' n_0) \approx r(n_0 + p_0) n', \quad (1.14)$$

where r is the recombination coefficient, which is the same for electrons and holes.

We first note that at small generation rates G [when the product $n'p'$ in the recombination equation (1.14) is small] the recombination process can be considered as the superposition of two parallel processes: the recombination of a non-equilibrium hole with an equilibrium electron ($p'n_0$) and of a non-equilibrium electron with an equilibrium hole ($n'p_0$).

Let us suppose that the majority carriers are electrons ($n_0 \gg p_0$). Then, according to (1.14), the recombination rate is determined by the most rapid process — the recombination of non-equilibrium holes with equilibrium electrons — since $n'p_0 \ll p'n_0$ ($n' = p'$, there are no trapping centers). In this case the minority carriers (holes) thus play a dominant part in the recombination process. Correspondingly, the lifetime will be determined by the lifetime of minority carriers. In fact, according to (1.13) and (1.14), τ

$\approx 1/rn_0$ i.e., the lifetime of a non-equilibrium hole. This comprises the physical meaning of the term "minority carrier lifetime". Consequently, for direct recombination the lifetime is always determined by the recombination of minority carriers ("minority-carrier lifetime").

We note that when recombination occurs at special centers there is no general recombination coefficient r , but capture coefficients A_e for electrons and A_h for holes. The lifetime is no longer determined by the recombination of minority carriers. In fact, following Hoffman and retaining (1.13) for lifetime, where now

$$\frac{1}{r} = \frac{1}{A_e N_t} (p_0 + p_1) + \frac{1}{A_h N_t} (n_0 + n_1),$$

we obtain, when $p_1 \gg n_0 \gg p_0 \gg n_1$

$$-\frac{1}{r} \approx \frac{1}{A_e N_t} p_1^*,$$

and, consequently,

$$\tau \approx \frac{p_1}{n_0 + p_0} \frac{1}{A_e N_t} \approx \frac{p_1}{n_0} \frac{1}{A_e N_t}. \quad (1.15)$$

The presence of the coefficient A_e shows that we are dealing with the recombination of electrons (majority carriers).

The analysis presented thus shows that it may be incorrect to assume that the lifetime is determined by the recombination of minority carriers in the case mentioned (transition through an intermediate level), and that an additional investigation is needed.

For steady-state processes Hoffman obtains for the lifetimes expressions that agree with τ_e^{st} and τ_h^{st} [formulae (1.11) and (1.12)], and he assumes, as did Shockley and Read, that the measured quantity is the lifetime of minority carriers. Hoffman therefore considers that the lifetime determined experimentally by measuring the diffusion length is also $\tau_{min. c.}^{st}$ — one of the times for stationary processes during uniform generation ($\nabla p = \nabla n = 0$) discussed by Shockley and Read, i.e., under conditions which exclude any carrier diffusion.

For non-steady-state processes Hoffman obtains two characteristic times, τ_1 and τ_2 , from the kinetic equations. Without giving accurate expressions for them, he shows that these times are functions of τ_e^{st} and τ_h^{st} . According to Hoffman, only in the case of extremely large center concentrations do we have

$$\tau_1 \approx \tau_{min.}^{st}, \quad \tau_2 \approx \tau_{max.}^{st}. \quad (1.16)$$

Independently of Hoffman, it has been shown in reference 25 that a semiconductor possesses not one characteristic time ($\tau_{min. c.}^{st}$), irrespective of the conditions that destroy thermodynamic equilibrium, but has several characteristic times, each of which becomes dominant under definite external conditions.

*This corresponds to the case when the recombination-center levels and the levels of the dominant impurity are in different halves of the forbidden gap.

So far we have considered semiconductors containing only recombination centers.^{2,3} But it has been shown^{26,27,28} that germanium and silicon also contain centers that interact only with one carrier type (trapping centers).

Experimental evidence of the existence of trapping centers was obtained in investigations of photoconductivity^{26,29} and carrier drift^{27,30} at low temperatures. The work of Fan and co-workers^{26,29} showed that in germanium at low temperatures ($T \sim 200^\circ K$) the photoconductivity has two components: a fast one (decay time $\sim 20 - 30 \mu\text{sec}$), which varied linearly with the illumination intensity, and a slow one (decay time $\sim 1000 \mu\text{sec}$), which saturated as the illumination intensity increased. With additional specimen illumination (artificial filling, which makes the centers ineffective) the slow component disappears. The slow component mentioned had an anomalous variation of time constant with temperature (it increased as the temperature was decreased).

Clearer evidence of the existence of trapping centers is provided by investigations of carrier drift at low temperatures in germanium²⁷ and at room temperatures in silicon.³⁰

Pulses of long duration (~ 0.1 sec for silicon at room temperature) were observed at the collector (Fig. 4) in reference 30, whereas the injecting pulses were short. In reference 27 the decay constant of non-equilibrium conductivity in germanium was determined by measuring the variation of collector

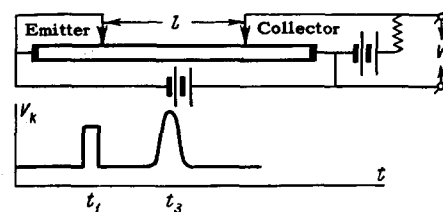


FIG. 4

signal amplitude with the field applied to the specimen. This constant was anomalously large ($\sim 1000 \mu\text{sec}$). The collector signals observed had an unusual shape: the front was comparatively sharp and the rear slowly declining. With additional illumination or at higher temperature, both the effects mentioned disappeared; the usual symmetrical pulse shape of injected non-equilibrium carriers, but distorted by diffusion, appeared, and the time constant agreed with the lifetime measured by other methods. Thus, the long-duration pulse of the collector was caused by the gradual release of carriers captured by centers. All this proves the existence of centers where carriers are captured.

The distinction between trapping and recombination centers can be based either on the rates of capture and thermal release of carriers³¹ or on the ratio of the capture cross sections for electrons and holes.^{30,32} If it is assumed that these cross sections are approxi-

mately equal for holes and electrons, then, following the first terminology, all centers with energy levels close to the band edges will be trapping centers (thermal release back into the band is more probable than capture of carriers of opposite sign), but centers with levels situated near the middle of the forbidden gap ("deep levels") will be recombination centers. However, if there is a marked difference in the capture cross sections for electrons and holes, then centers with "deep levels"^{30,32} can also be trapping centers.

In this review the classification of centers into trapping centers and recombination centers will be made on the basis of the ratio of cross sections only; a center is a recombination center if it interacts with both electrons and holes ($A_e A_h \neq 0$), irrespective of the position of the energy level in the forbidden gap, and, correspondingly, a center will be a trapping center if interaction takes place either only with holes or only with electrons ($A_e A_h = 0$).

We note that both the carrier capture cross sections and the parameters of thermal release [the constants n_1 and p_1 in (1.8)] depend on the temperature.³³ Therefore, the division of centers into trapping centers and recombination centers depends on the conditions. For example, it has been shown³⁴ that copper atoms introduced into germanium are recombination centers at room temperature and trapping centers for holes at low temperatures.

The basic work, in which the kinetics of carrier capture processes by trapping and recombination centers are discussed, is that of Fan and co-workers,^{29,35} devoted to trapping centers in germanium, and that of Haynes and Hornbeck,^{30,32} where this phenomenon is considered in silicon.

Fan considered the saturation of steady-state photoconductivity due to carriers captured by centers, as well as non-steady-state processes associated with carrier capture. By introducing a recombination time τ_R , determined by centers of other types, and by assuming that minority carriers are captured, Fan³⁵ obtains an expression for the non-equilibrium conductivity of n-type material

$$\Delta\sigma = q(\mu_e + \mu_h) G\tau_r + q\mu_h p'_t, \quad (1.17)$$

where, according to the Shockley-Read formulae,

$$p'_t = \frac{A_h n_{t0} p' - A_e p_{t0} n'}{A_e(n_0 + n_1) + A_h(p_0 + p_1) + A_h p' + A_e n'} \quad (1.18)$$

(n_{t0} and p_{t0} are, respectively, the equilibrium concentrations of full and empty centers).

Since $A_h \gg A_e$ (the centers trap only holes), $p'_t \approx n_{t0} \frac{p'}{p_0 + p_1 + p'}$ and $p' \approx G\tau_r$, so that we finally obtain

$$p'_t \approx n_{t0} \frac{1}{1 + \frac{p_0 + p_1}{G\tau_r}} \approx n_{t0}, \quad G\tau_r \gg p_0 + p_1.$$

Thus we do, in fact, have two components, one of which

tends to a constant value as the illumination intensity increases.

It is, however, impossible to agree with Fan that the saturation effect occurs only for trapping centers: a similar phenomenon also occurs at recombination centers. Indeed, the relationship (1.18) remains true in this case also, but the limiting occupation is now determined (see reference 36) by the expression

$$p'_t = \frac{A_h n_{t0} = A_e p_{t0}}{A_e + A_h},$$

since $p' \gg |p'_t|$ and $n' \gg |n'_t|$ as $G \rightarrow \infty$. Fan's mistake (the conclusion that capture at recombination centers does not give saturation) arises because he obtains the variation of non-equilibrium carrier concentration with illumination intensity valid for p' and $n' \ll n_0$, which he then substitutes in the expression for p'_t . Thus he does not obtain saturation, since his expression for p'_t becomes untrue for large G .

Fan also treats non-steady-state processes (the growth and decay of photoconductivity). By analyzing the solutions of the system of kinetic equations for the case in question:

$$\frac{dp'}{dt} = G - \frac{p'}{\tau_0} + \frac{dn'_t}{dt}; \quad -\frac{dn'_t}{dt} = \frac{p'}{\tau_r} + \frac{n'_t}{\tau_f},$$

he finds that the growth and decay curves for photoconductivity at small generation levels are determined by two exponential terms with exponents

$$\alpha_{1,2} = \frac{1}{2} \left[\frac{1}{\tau_r} + \frac{1}{\tau_f} + \frac{1}{\tau_t} \right] \pm \left[\frac{1}{4} \left(\frac{1}{\tau_r} + \frac{1}{\tau_f} + \frac{1}{\tau_t} \right)^2 - \frac{1}{\tau_f \tau_r} \right]^{\frac{1}{2}},$$

where

$$\tau_f = \frac{1}{A_e(n_0 + n_1) + A_h(p_0 + p_1)}$$

is the lifetime of a captured hole,

$$\tau_c = \frac{1}{A_e(n_0 + n_1)}$$

is the time required for recombination of a captured hole with a conduction electron,

$$\tau_t = \frac{1}{A_h n_{t0}} \approx \frac{1}{A_h N_t}$$

is the capture time of a free hole, and τ_R is the recombination time of non-equilibrium carriers determined by centers of a different type.

At low temperatures²⁹

$$\alpha_1 \gg \alpha_2$$

and

$$\alpha_1 \approx \left(\frac{1}{\tau_r} + \frac{1}{\tau_f} + \frac{1}{\tau_t} \right) \approx \frac{1}{\tau_t} + \frac{1}{\tau_r}, \quad \alpha_2 \approx \frac{1}{\tau_s} \approx \left(\frac{1}{\tau_r \tau_f} + \frac{1}{\tau_r \tau_t} \right) \frac{1}{\alpha_1}.$$

At the limit of very low temperatures

$$\tau_s \approx \frac{1}{\alpha_1} \approx \tau_c + \frac{1}{\frac{1}{\tau_r} + \frac{1}{\tau_f}} \approx \tau_c \approx \frac{1}{A_e n_0}. \quad (1.19)$$

For not too low temperatures ($A_h \gg A_e$, $A_h p_1 \gg A_e n_0$)

$$\tau_s \approx \tau_f \left(1 + \frac{\tau_r}{\tau_t} \right) = \frac{1}{A_h p_1} (1 + A_h N_t \tau_r). \quad (1.20)$$

Expressions (1.19) and (1.20) lead to a growth of τ_s with decreasing temperature (it is assumed⁵ that τ_r varies little with temperature), which is also proof of the existence of trapping centers (the diminishing rate of thermal release of carriers into band as the temperature is lowered). We note that the temperature variation of the recombination time τ_r does not give an increase at low temperatures.

Fan's assumption concerning the capture of minority carriers only was proved by the work of Haynes and Hornbeck,³⁰ who studied the decay of non-equilibrium photoconductivity with and without additional illumination. In fact, by comparing the non-equilibrium conductivity pulse amplitudes with additional illumination:

$$\Delta\sigma_1 \approx q(\mu_e + \mu_h) p' \quad (1.21)$$

and without it:

$$\Delta\sigma_2 = \begin{cases} q\mu_e n', & \text{if holes are captured} \\ q\mu_h p', & \text{if electrons are captured} \end{cases} \quad (1.22)$$

it is possible to be determined from the ratio $\Delta\sigma_1/\Delta\sigma_2$ which carrier type is captured.

Measurements made on p-type silicon³⁰ gave

$$\frac{\Delta\sigma_1}{\Delta\sigma_2} \approx 3 = \frac{\mu_e + \mu_h}{\mu_h}.$$

Such measurements, according to Haynes and Hornbeck, prove that in silicon always minority carriers are captured (electrons in p-type and holes in n-type material).

By studying the photoconductive decay in p- and n-type silicon, Haynes and Hornbeck discovered that both types have a whole system of centers with different levels. Thus, in p-type silicon non-exponential photoconductive decay was observed. Haynes and Hornbeck explain this non-exponential variation as due to repeated capture (carriers released from the center are captured again before they recombine; this occurs for $\tau_r \gg \tau_t$). This effect also explains the different minority carrier capture cross sections in p-type material ($S = 10^{-13} \text{ cm}^2$), where there is repeated capture, and in n-type material ($S = 10^{-18} \text{ cm}^2$), where there is not. By analyzing the temperature variation of the lifetime of captured carriers τ_f , they conclude that recombination as well as capture occurs at centers with "deep levels" (the temperature variation of $1/\tau_f$ shows a break and has two slopes). Therefore, in place of

$$\frac{1}{\tau_f} = A_h p_1 = S_h \cdot 2\pi m_h (kT)^2 h^{-3} \exp \left\{ -\frac{E_t - E_1}{kT} \right\}, \quad (1.23)$$

they introduce τ , defined by the expression

$$\frac{1}{\tau} \approx \frac{1}{\tau_j} + \frac{1}{\tau_0}.$$

The assertion of Haynes and Hornbeck, that the relationship (1.23), obtained from detailed-balance conditions, determines the lifetime of carriers in centers, is untrue. In fact, according to Fan,³⁵ the process of non-equilibrium conductivity decay which takes place is described, not by the equations of detailed balance, which are true at thermodynamic equilibrium, but by the corresponding kinetic equations. As Fan has shown,³⁵ this leads to a different expression for τ_f , and instead of (1.23) we obtain

$$\frac{1}{\tau_f} = A_h (p_0 + p_1).$$

For our case the Fermi level is close to the level of the centers ($F = 0.30 \text{ eV}$ from the valence band edge, $E_t - E_1 \sim 0.35 \text{ eV}$) i.e., $p_0 \sim p_1$, and, consequently, this effect makes a significant contribution, masking the recombination. Therefore, all the evidence of Haynes and Hornbeck relating to three-body (impact) recombination in silicon must be regarded as unreliable.

A detailed analysis of the electronic processes in semiconductors having a system of centers with different levels has been made by Kalashnikov.³⁷ By considering steady-state processes for the case when the concentration of only one type of center is large, he showed that when recombination centers with different energy levels are present, the recombination does not remain additive; in other words, the effective lifetime $\tau_{\text{min. c.}}^{\text{st}}$ of a steady-state process is given by the expression

$$\frac{1}{\tau} = \sum_j \frac{1}{\tau_j} + \xi_0,$$

where $1/\tau_j$ is the probability of recombination through centers with the j-th level and ξ_0 describes the effect on one another of centers of a different type. The author shows that when the concentration of centers is small ($n' \approx p'$), the recombination probability is always additive, i.e.,

$$\frac{1}{\tau} \approx \sum_j \frac{1}{\tau_j}$$

— carrier recombination through each type of center proceeding independently of the presence of the others. As is revealed by the treatment, the appearance of ξ_0 is caused by the fact that the fractional occupation of centers of a given type is changed by the presence of the other centers.

Expressions were obtained in reference 38 for the times τ_e^{st} and τ_h^{st} in the general case of a semiconductor having a system of centers of different types with different energy levels. If the semiconductor has a small concentration of recombination centers of one type [$n_t^{(1)}$, $p_t^{(1)}$] and a large concentration of trapping centers [e.g., for electrons $p_t^{(2)}$, $n_t^{(2)}$], then the expressions for τ_e^{st} and τ_h^{st} take the form:³⁸

$$\tau_e^{st} = \frac{1}{1 + \frac{n_0 p_0^{(2)}}{(n_0 + p_0)(n_0 + n_1^{(2)})}} \tau_0,$$

$$\tau_h^{st} = \tau_0 \frac{1 + \frac{p_0^{(2)}}{n_0 + n_1^{(2)}}}{1 + \frac{n_0 p_0^{(2)}}{(n_0 + p_0)(n_0 + n_1^{(2)})}} \quad (1.24)$$

(Fig. 5), where the expression for τ_0 agrees with (1.8) obtained by Shockley and Read for small concentrations of centers of one type (recombination centers — $A_e A_h \neq 0$). Therefore, for the case in question we have $\tau_0 = \tau_r$, i.e., the recombination time introduced by Fan.³⁵

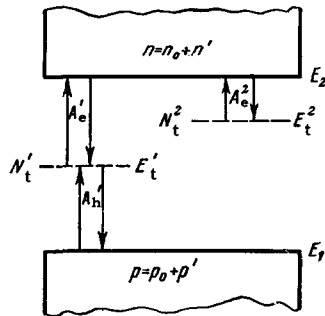


FIG. 5

It is assumed that the lifetime for steady-state processes (τ^{st} , see reference 2) is determined either by measuring the steady-state photoconductivity³⁹ or the diffusion length.⁴⁰ As indicated, a number of authors^{1,3,41-44} assume that the lifetime determined by measuring the diffusion length is equal to $\tau_{min, c.}^{st}$. Leaving aside the fact that such an assumption is incorrect (the times are obtained under conditions which exclude diffusion), it is not clear what lifetime will determine diffusion in semiconductors with intrinsic conductivity.

It is, therefore, necessary to make a special study of the diffusion of electrons and holes in semiconductors. A simplified analysis has been made by van Roosbroeck⁴⁵ and Hoffman³ for the case $n' = p'$, when the diffusion of carriers of both types in semiconductors can be treated in an analogous manner to ambipolar diffusion^{46,47} in gases and plasmas (the fluxes and concentrations of both types of carrier are equal). In this case the expression for the diffusion length $1/K_2$ has the form

$$\left(\frac{1}{K_2}\right)^2 = D\tau,$$

where

$$D = \frac{D_e D_h (n_0 + p_0)}{D_e n_0 + D_h p_0} \quad (1.25)$$

is the ambipolar diffusion coefficient and τ is the common lifetime for electrons and holes.

Thus, when $n' = p'$, there occurs not independent diffusion of electrons and holes in the semiconductor, but diffusion of electron-hole pairs, just as in ambi-

polar diffusion. The electrical field created by the motion of carriers slows down the rapid particles and accelerates the slow ones. We note that the motion of electrons and holes, considered separately for each type of particle, is due both to diffusion and to the field created by the motion (diffusion and field terms are present in the expressions for the electron and hole currents).

Lashkarev,^{48,49} by considering steady-state processes in semiconductors with mixed conductivity, showed that the diffusion of electrons and holes is determined by a common characteristic length ("the diffusive displacement length" $1/K_0$). He obtained the value of $1/K_0$ in the general case when trapping and recombination centers were present as

$$K_0^2 = C \left(\frac{n_0}{D_e} + \frac{p_0}{D_h} \right), \quad (1.26)$$

where C is some constant determined by the recombination law. Lashkarev, in considering the variation of the constant C with the semiconductor parameters, limits himself to a special case. In fact he considers the case of almost filled donor centers and almost empty centers, i.e., when the acceptor levels are situated somewhat above the donors. In the majority of cases just the opposite occurs: the donors are just below the conduction band and the acceptors just above the valence band, i.e., far below the donors (Fig. 6).

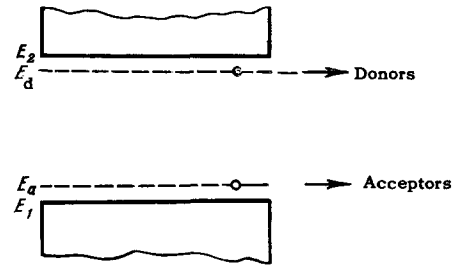


FIG. 6. $N_D \rightarrow$ donors, $N_A \rightarrow$ acceptors.

By considering the one-dimensional case, Lashkarev showed that the diffusion of electrons and holes in the absence of an external field is determined by the equation

$$\frac{d^2 F}{dx^2} - K_0^2 F = 0, \quad (1.27)$$

where $F = p_0 n' + p' n_0$.

In this way Lashkarev showed that in semiconductors with an arbitrary concentration of centers, diffusion is always bipolar and is described by (1.27) and by the characteristic length $1/K_0$, which is the same for electrons and holes. Thus, he shows that electrons

*Lashkarev obtains the distribution of holes and electrons in the quasi-neutral region from the equations

$$F = p' n_0 + n' p_0, \quad u = s p' - n',$$

where s describes the filling of the centers and u is proportional to the value of the space charge. The variables F and u have been written in our notation.

and holes should have a common effective lifetime, which can be determined from $1/K_0$ by assuming that the carrier diffusion in semiconductors is characterized by a common effective mobility for holes and electrons, i.e.,

$$\frac{1}{K_0} = \sqrt{\frac{kT}{q} \mu_{\text{eff}} \tau_{\text{eff}}}$$

Therefore, according to Lashkarev, the diffusion of electrons and holes in semiconductors, as distinct from the steady-state processes of Shockley and Read,² has a single characteristic time which is completely determined by the kinetic equations and does not require the introduction of an additional hypothesis about minority carriers.

The essential property of bipolar diffusion is the absence of charge transfer ($I_e + I_h = 0$) and the existence of a gradient of generated non-equilibrium pairs (non-uniform generation). Consequently, the fact that the concentrations of free non-equilibrium electrons and holes are not equal (the condition for ambipolar diffusion) does not mean that bipolar diffusion (the diffusion of non-equilibrium electron-hole pairs with arbitrary ratio of n' and p') is absent. In fact, in both cases non-equilibrium pairs are always generated in one part of the semiconductor and recombined in another. Therefore, because a concentration gradient of generated pairs is present and charge transfer is absent ($I_e + I_h = 0$), diffusive motion of non-equilibrium pairs (bipolar diffusion) always proceeds independently of carrier capture ($p' \neq n'$, $n'_t \neq 0$). Haynes and Hornbeck³⁰ have shown experimentally that on the whole the diffusion length is not changed by the presence of trapping centers.

Jonscher⁵⁰ has considered theoretically the effect of carrier capture on the diffusion process. The analysis he made of the continuity equation for minority carriers in a quasi-neutral region of a semiconductor⁵¹ shows that carrier capture has an important effect on the drift term $\mu_e E \frac{\partial N}{\partial x}$ (in the field E created during diffusion). He thus concludes that the greatest effect of carrier capture occurs at large injection levels ($n' \sim n_0 + p_0$), and appears as an increase of the diffusion length by a factor of $\sqrt{2}$. However, it should be pointed out that the problem has been incorrectly solved by Jonscher. In point of fact he considers that the diffusion length is constant at large injection levels, which, according to reference 45, is not the case. The very concept of a diffusion length has meaning only when it is a constant, and thus can only be true at small injection levels, i.e., when it is appropriate to neglect the drift term [it is of the order $p'/(n_0 + p_0)$].*

$$*) \mu_e E \frac{\partial n}{\partial x} = \frac{D_{\Delta p}}{p + b_n} \left(\frac{\partial p}{\partial x} - b \frac{\partial n}{\partial x} \right) \frac{\partial n}{\partial x} \\ \sim \frac{D_e}{p_0} \left(\frac{\Delta n}{L_D} \right)^2, \text{ where } n' = \Delta n e^{-\frac{x}{L_D}}$$

Comparison with the remaining terms of the continuity equation for electrons also gives the value of $[p'/(n_0 + p_0)]$.

Therefore, following Jonscher, it can be assumed that carrier capture in no way affects carrier diffusion in the absence of an external field.

The analysis of the main papers on non-equilibrium processes thus leads us to the conclusion that there is not a single characteristic time for electronic processes in semiconductors which is independent of the conditions which destroy thermodynamic equilibrium ($\tau_{\text{min. c.}}^{\text{st}}$). On the contrary, semiconductors are complex systems which contain charge carriers of two types, as well as localized centers of different nature, and should have several characteristic times for electronic processes. Depending on the external conditions, one or other of these times dominates. Shockley⁴³ and Bemsky⁴⁴ arrived at similar conclusions in their recent reviews. They, however, started by dividing all non-equilibrium processes into steady-state and non-steady-state, and considered that $\tau_{\text{min. c.}}^{\text{st}}$ is determined by measuring the diffusion length.

It should be pointed out that such a simplified division of all electronic processes in semiconductors into steady-state and non-steady-state ones does not embrace all the diversities of these processes. Such a division does not, in fact, take into account the processes by which carriers spread through the volume of the semiconductor (diffusion, drift) due to non-uniform generation and external field. Such processes take place under both steady-state and non-steady-state conditions.

It is, therefore, more correct to divide the electronic processes occurring in semiconductors into the following groups:

- 1) steady-state processes under conditions of uniform generation (the times τ_h^{st} , τ_e^{st}) (Shockley and Read,² Hoffman,³ Kalashnikov³⁷);
- 2) steady-state processes with non-uniform generation (bipolar diffusion, the basic parameter being the diffusion length) (Lashkarev,^{48,49} van Roosbroeck⁴⁵);
- 3) non-steady-state processes with uniform generation;
- 4) non-steady-state processes with non-uniform generation.

The consideration of these processes presents us with the following problems:

1. The majority of the authors mentioned consider that the lifetime of any steady-state process is determined by measuring the diffusion length. It is assumed that this time is $\tau_{\text{min. c.}}^{\text{st}}$, i.e., the time that characterizes processes which exclude diffusion. Consequently, by considering bipolar diffusion, it is necessary to find in the general case the characteristic time that determines the diffusion of carriers in semiconductors with a system of centers having different levels.

2. When studying the growth and decay of non-equilibrium carriers under conditions of uniform generation, most authors either introduce a τ not connected with the semiconductor parameters, or limit themselves to a simplified treatment of particular cases.^{29, 30, 32, 35} It is of interest, therefore, to consider non-

steady-state processes occurring under conditions of uniform generation in the general form, to obtain the characteristic times, and to analyze them in detail for a number of cases of special interest, in particular: a) when the semiconductor has centers of only one type with a common energy level; b) when the semiconductor has many types of centers, but the concentration of one type of center predominates and the concentration of the remaining types is small; c) when the concentrations of all the centers contained in the semiconductor are small.

3. As remarked, the greatest interest attaches to non-equilibrium processes at small generation levels, when the lifetimes are constants which characterize the semiconductor (monomolecular recombination). However, by studying the variation of lifetime on non-equilibrium carrier concentration, the possibility arises of determining the different recombination modes (monomolecular, bimolecular, et al.). It is, therefore, of interest to obtain in a general form the decay law of the non-equilibrium carrier concentration in semiconductors which also determines $\tau(n')$. A rigorous solution of the problems mentioned has been given in references 25, 36, 38, and 52. They also constitute the principal contents of the second and third portions of the present review.

2. CHARACTERISTIC TIMES DETERMINED FROM THE DIFFUSION LENGTH

The conditions of uniform and steady-state generation as considered in references 2 and 3 are not, in fact, satisfied. Under steady-state conditions generation is almost always non-uniform throughout the volume of the semiconductor (e.g., the formation of non-equilibrium carriers by light). In this case the basic parameter of the electronic processes is the diffusion length and the characteristic times associated with it. The kinetic equations describing these processes are (see reference 52):

$$G = \sum_{j=1}^{j=m} (A_e^j p_t^j n - B_e^j n_t^j) - \frac{1}{q} \operatorname{div} \mathbf{I}_e, \quad (2.1a)$$

$$G = \sum_{j=1}^{j=m} (A_h^j n_t^j p - B_h^j p_t^j) + \frac{1}{q} \operatorname{div} \mathbf{I}_h, \quad (2.1b)$$

$$\left. \begin{aligned} \frac{1}{q} \mathbf{I}_e &= \mu_e n \mathbf{E} + D_e \operatorname{grad} n, \\ \frac{1}{q} \mathbf{I}_h &= \mu_h p \mathbf{E} - D_h \operatorname{grad} p, \\ p_t^j + n_t^j &= N_t^j, \\ A_e^j p_t^j n - B_e^j n_t^j &= A_h^j n_t^j p - B_h^j p_t^j, \\ j &= 1, 2, \dots, m, \end{aligned} \right\} \quad (2.1c)$$

$$\operatorname{div} \mathbf{E} = \frac{4\pi q}{\epsilon} \left(p - n - \sum_{j=1}^{j=m} n_t^j + \sum_{i=1}^{i=l} N_h^i \right). \quad (2.1d)$$

where

$$B_e^j = A_e^j n_t^j \text{ and } B_h^j = A_h^j p_t^j$$

are the thermal release constants for electrons and holes from centers (see Fig. 1), A_e^j , A_h^j are the capture coefficients for electrons and holes, N_t^j are the total concentration of centers, p_t^j and n_t^j are the concentration of full and empty centers. The superscript j , which all the enumerated quantities have, indicates the center type (all centers of the j -th type have a common energy level E_t^j); n_t^j and p_t^j are given by formulae (1.6); I_e , I_h are the current densities for electrons and holes; μ_e , D_e , μ_h , D_h are mobilities and diffusion coefficients for electrons and holes, \mathbf{E} is the field strength inside the semiconductor, ϵ is the dielectric constant, q is the magnitude of the electronic charge, G is the generation rate (or level) for non-equilibrium pairs, N_d^i is the concentration of donors of the i -th type (having an energy level E_d^i).

By rewriting the system of equations (2.1) in terms of the non-equilibrium carrier concentrations n' and p' ($n = n_0 + n'$, $p = p_0 + p'$, $n_t^j = n_{t0}^j + n_{tj}^j$ etc.), by linearizing* and transforming to the variables:

$$\xi = \frac{p' n_0 + n' p_0}{n_0 + p_0}, \quad (2.2a)$$

$$\eta = \frac{kT \mu_e n' - \mu_h p'}{q \mu_e n_0 + \mu_h p_0}, \quad (2.2b)$$

Eqs. (2.1) transform to the system

$$\left. \begin{aligned} \nabla^2 \xi - k_2^2 \xi &= -\frac{G}{D}, \\ \nabla^2 \eta - k_1^2 \eta &= -M_1^2 \xi, \end{aligned} \right\} \quad (2.3)$$

with the boundary condition

$$\left. \begin{aligned} \frac{\partial \xi}{\partial N} \Big|_{\sigma} &= -\alpha_0 \xi \Big|_{\sigma}, \\ \frac{\partial \eta}{\partial N} \Big|_{\sigma} &= 0, \end{aligned} \right\} \quad (2.4)$$

where $1/k_1$ and $1/k_2$ are the Debye and diffusion lengths with

$$k_2^2 = \frac{D_e n_0 + D_h p_0}{D_e D_h (n_0 + p_0)} \frac{1}{\tau_0} = \frac{1}{D \tau_0} = \frac{1}{D_e \tau_e} = \frac{1}{D_h \tau_h}, \quad (2.5)$$

and D is the ambipolar diffusion coefficient ($n' = p'$) introduced by van Roosbroeck.⁴⁵ $\alpha_0 = S/D$, where S is the surface recombination rate for non-equilibrium pairs, M_1^2 is a constant having the dimensions of charge and depending on the concentration of centers. Finally, $\partial/\partial N$ signifies differentiation in the direction normal to the boundary surface σ . The time τ_0 is given by

$$\frac{1}{\tau_0} = \sum_{j=1}^{j=m} \frac{1}{\tau_0^j} = \sum_{j=1}^{j=m} A_e^j A_h^j \frac{p_{t0}^j (p_0 + p_1^j) + n_{t0}^j (n_0 + n_1^j)}{A_h^j (p_0 + p_1^j) + A_e^j (n_0 + n_1^j)}. \quad (2.6)$$

*Linearization is possible: 1) for non-equilibrium carrier concentrations small in comparison with the concentration of majority equilibrium carriers:

$$n' \ll n_0 + p_0, \quad p' \ll n_0 + p_0;$$

2) for small space charge:

$$\left| \frac{Q}{q} \right| = \left| \left(1 + \sum_{j=1}^{j=m} \frac{\tau_{n_0}^j n_{t0}^j}{(n_0 + p_0) \tau_0^j} \right) p' - \left(1 + \sum_{j=1}^{j=m} \frac{\tau_{p_0}^j p_{t0}^j}{(n_0 + p_0) \tau_0^j} \right) n' \right| \ll n_0 + p_0.$$

We note that the time τ_0^j agrees with the Shockley-Read formula obtained for the particular case of a small concentration of one type of center [Eq. (1.8)].

As shown in references 38 and 52, the variable ξ is the effective concentration of non-equilibrium pairs, and η is some potential determining the bipolar diffusion field $\nabla\eta$.

The kinetics of steady-state processes with non-uniform generation are thus described by two equations [the pair (2.3)]. The first of these expresses the diffusion, recombination, and generation processes of non-equilibrium pairs, and the second expresses the space charge formation and relaxation processes.

The solution of these equations in the one-dimensional case (semi-infinite specimen) for a semiconductor illuminated by visible light ($\lambda \gg k_2$, $G = G_0 e^{-\lambda x}$, $k_1 \gg k_2$),^{53*} in the quasi-neutral region⁵¹ is:

$$\xi = G_0 \tau_0 \frac{k_2^2}{\lambda^2} \frac{\lambda + \alpha_0}{k_2 + \alpha_0} e^{-k_2 x} = G_{\text{eff}} \tau_0,$$

$$\eta \approx \frac{kT}{q} G_0 \frac{\mu_e^{\text{st}} - \mu_h \tau_h^{\text{st}}}{\mu_e n_0 + \mu_h p_0} \frac{k_2^2}{\lambda^2} \frac{\lambda + \alpha_0}{k_2 + \alpha_0} e^{-k_2 x} = \frac{kT}{q} G_{\text{eff}} \frac{\mu_e \tau_e^{\text{st}} - \mu_h \tau_h^{\text{st}}}{\mu_e n_0 + \mu_h p_0},$$

$$p' \approx G_{\text{eff}} \tau_h^{\text{st}}, \quad n' \approx G_{\text{eff}} \tau_e^{\text{st}}, \quad (2.7)$$

where λ is the absorption coefficient for the light.

Consideration of the solutions (2.7) shows that along with processes described by the times τ_e^{st} and τ_h^{st} , bipolar diffusion takes place, which is expressed in the exponential variation of G_{eff} with specimen thickness. In the photoelectric method of measuring the lifetime,⁴⁰ the absorption path of a non-equilibrium pair $1/k_2$ is determined from measurements of $G_{\text{eff}}(x)$, and there is a common diffusion length for electrons and holes. Because the non-equilibrium processes are steady-state ones, carrier capture ($n_t' \neq 0$) has no effect on the bipolar diffusion. This is expressed in the fact that the basic parameter, the absorption path of a non-equilibrium pair $1/k_2 = \sqrt{D\tau}$, does not explicitly depend[†] on the presence and state of trapping centers ($A_e^j A_h^j = 0$). Consequently, the lifetime τ_0 determined by measuring the diffusion length does not depend on the presence and state of the trapping centers in the semiconductor.

Non-uniform generation causes carrier motion (diffusion), due to which space charge is formed. This space charge attains its maximum magnitude close to the surface at a depth of the order of the Debye length. At large depths it becomes small (the quasi-neutral region),⁵¹ and in this case

$$\left| \frac{Q}{qn'} \right| \ll \frac{\tau^{\text{rel}}}{\tau_e} \ll 1, \quad (2.8)$$

*The inequality $k_1 \gg k_2$ (diffusion length much greater than the Debye length) means the neglect of the space charge region⁵¹ formed close to the illuminated surface. According to reference 54, $1/k_1 \leq 7 \times 10^{-5}$ cm, which gives a lower limit for the value of $\tau(k_2 \leq k_1/10)$, of 10^{-9} sec.

†For large concentrations of centers the mobilities μ_e and μ_h change because of the additional scattering at these centers.

where

$$\tau^{\text{rel}} = \frac{\epsilon}{4\pi q (\mu_e n_0 + \mu_h p_0)},$$

and τ_e and τ_h are given by (2.5). The value of the space charge is related to the greatest concentration of non-equilibrium carriers and the corresponding times τ_e , τ_h . From the expression for the space charge*

$$Q = G_{\text{eff}} \tau^{\text{rel}} \left(\frac{\tau_e^{\text{st}}}{\tau_e} - \frac{\tau_h^{\text{st}}}{\tau_h} \right) = G_{\text{eff}} \tau_h^{\text{rel}} \left(1 - \frac{\tau_h^{\text{st}}}{\tau_h} \right)$$

$$= G_{\text{eff}} \tau_e^{\text{rel}} \left(1 - \frac{\tau_e^{\text{st}}}{\tau_e} \right) \quad (2.9)$$

it follows that when

$$\left. \begin{aligned} \tau_e^{\text{st}} &= \tau_e, \\ \tau_h^{\text{st}} &= \tau_h \end{aligned} \right\} \quad (2.10)$$

the semiconductor is neutral at any point. In this case the diffusion fluxes of electrons and holes are equal (the electrons, which move more rapidly, are captured more, while the holes, which move more slowly, are captured less).

When the filling of the centers is arbitrary [Eq. (2.10) is not satisfied], the space charge formed sustains bipolar diffusion; the equality of electron and hole fluxes $\frac{1}{q} |I_e| = \frac{1}{q} |I_h|$ is preserved due to the appearance of conduction currents. The field $\nabla\eta$ formed holds back the rapid and weakly captured carriers, and speeds up the slow carriers strongly captured by the centers. Carrier capture by centers strongly affects the value of the field and can even change its sign, since it changes the times τ_e^{st} and τ_h^{st} . But we also note that the field $\nabla\eta$, created by the motion of non-equilibrium electrons and holes relative to one another, is so small that it does not change the bipolar diffusion at any depth in the semiconductor [see (2.3)].

Thus, in the general case of semiconductors with a system of centers of different types, steady-state processes are determined both by the times τ_e^{st} and τ_h^{st} , and by the time τ_0 , which does not depend on the concentration of trapping centers. The times τ_e^{st} and τ_h^{st} can be determined by measurements of the photo-e.m.f. (the Dember-effect voltage⁵⁵ $-\eta|_{x=0}$) and the non-equilibrium conductivity of the specimen (if μ_e , μ_h , and G_0 are known). The time τ_0 is calculated from measurements of the diffusion length.

The times τ_e and τ_h determine the conditions during the fulfilling of which the semiconductor remains neutral at every point in the case of non-uniform generation.

*Equation (2.10) is obtained from the expressions for the space charge $\frac{Q}{q} = -\frac{\epsilon}{4\pi q} \frac{d^2\eta}{dx^2}$ and the identity

$$\frac{n_0 \tau_h^{\text{st}} + p_0 \tau_e^{\text{st}}}{(n_0 + p_0) \tau_0} = \frac{n_0 \tau_h + p_0 \tau_e}{(n_0 + p_0) \tau_0} = 1.$$

3. NON-STEADY-STATE PROCESSES

As shown in reference 38, the kinetic equations which describe non-steady-state electronic processes occurring during uniform generation of non-equilibrium carriers can, for the general case of a semiconductor with a system of centers of different types, be written in the following form:

$$\left. \begin{aligned} \frac{dn}{dt} &= G - (np - n_0p_0) \sum_{j=1}^{j=m} \frac{A_e^j A_h^j N_t^j}{A_e^j (n_0 + n_1^j) + A_h^j (p_0 + p_1^j)} - \\ &\quad - \sum_{j=1}^{j=m} \frac{A_e^j (n_0 + n_1^j) \frac{dn_t^j}{dt}}{A_e^j (n_0 + n_1^j) + A_h^j (p_0 + p_1^j)}, \\ \frac{dp}{dt} &= G - (np - n_0p_0) \sum_{j=1}^{j=m} \frac{A_e^j A_h^j N_t^j}{A_e^j (n_0 + n_1^j) + A_h^j (p_0 + p_1^j)} - \\ &\quad - \sum_{j=1}^{j=m} \frac{A_h^j (p_0 + p_1^j) \frac{dp_t^j}{dt}}{A_e^j (n_0 + n_1^j) + A_h^j (p_0 + p_1^j)}, \end{aligned} \right\} (3.1a)$$

$$\left. \begin{aligned} p_t^j + n_t^j &= N_t^j, \\ \frac{dn_t^j}{dt} &= (A_e^j p_t^j n - A_h^j n_t^j p) - (A_h^j n_t^j p - A_e^j p_t^j p_t^j), \end{aligned} \right\} (3.1b)$$

$$p - n = \sum_{j=1}^{j=m} n_t^j - \sum_{i=1}^{i=k} N_d^i. \quad (3.1c)$$

After separating all the concentrations into equilibrium and non-equilibrium parts ($n = n_0 + n'$, $p = p_0 + p'$, $n_t^j = n_{t0}^j + n_{tj}^j$), and discarding terms quadratic in the non-equilibrium concentrations, we arrive at a system of equations linear in n' , p' , and n_{tj}^j .

We consider the solutions of such a linearized system for the special cases of most importance. Let the concentrations N_t^j of all types of centers be small, with the exception of one ($j = 1$). Then, for $\tau_1 \ll \tau_2$, the solution giving the non-equilibrium carrier concentration decay ($G = 0$) with initial conditions corresponding to the steady-state situation is

$$\left. \begin{aligned} n' &= G\tau_1 e^{-\frac{t}{\tau_1}} + G(\tau_e^{st} - \tau_1) e^{-\frac{t}{\tau_2}}, \\ p' &= G\tau_1 e^{-\frac{t}{\tau_1}} + G(\tau_h^{st} - \tau_1) e^{-\frac{t}{\tau_2}}, \\ n_{t1}^j &= -p_{t1}^j = G(\tau_h^{st} - \tau_e^{st}) e^{-\frac{t}{\tau_2}}. \end{aligned} \right\} (3.2)$$

The solution obtained contains four time parameters. Two of them: τ_e^{st} and τ_h^{st} — characterize steady-state processes occurring during uniform generation. The two other time parameters are

$$\frac{1}{\tau_1} = A_e^1 p_{t0}^1 + A_h^1 n_{t0}^1 + A_e^1 (n_0 + n_1) + A_h^1 (p_0 + p_1) + \frac{1}{\tau_0^*}, \quad (3.3)$$

$$\frac{1}{\tau_2} = \frac{1}{\tau_0} \frac{A_e^1 (n_0 + n_1) + A_h^1 (p_0 + p_1) + \frac{A_e^1 p_{t0}^1 n_0 + A_h^1 n_{t0}^1 p_0}{n_0 + p_0}}{\frac{1}{\tau_0^*} + A_e^1 (n_0 + n_1) + A_h^1 (p_0 + p_1) + A_e^1 p_{t0}^1 + A_h^1 n_{t0}^1}, \quad (3.4)$$

*The concentrations of non-equilibrium carriers n_{tj}^j captured by centers of the remaining types N_t^j ($j \neq 1$), can be neglected.

where

$$\frac{1}{\tau_0^*} = \sum_{\substack{j=2 \\ j \neq 1}}^{j=m} \frac{1}{\tau_0^j}$$

and the sum is taken over all types of center except the first. If the capturing centers (A_e^1, A_h^1, N_t^1) are so effective that in the denominator of (3.4) $1/\tau_0^*$ can be neglected, the expressions given for τ_1 and τ_2 coincide with the analogous formulae obtained when the semiconductor has centers of only one type.²⁵ However τ_0 , which enters into the relationships mentioned, has a different meaning. In (3.4) τ_0 is determined by recombinations through all the centers. Therefore, as well as recombination centers ($A_e^j A_h^j \neq 0$), it is possible in a semiconductor to have trapping centers ($A_e^j A_h^j = 0$) which can be capturing centers (these centers will not contribute to τ_0). For a semiconductor with only one type of center this does not occur. Analysis made in reference 38 shows that for large concentrations of capturing centers the relaxation time of the non-equilibrium excess τ_2 (the larger time) is smaller than the lifetime of carriers in centers τ_f .³⁵ For this reason, after the disappearance of the excess n' and p' , thermodynamic equilibrium is established not at once, but after the re-establishment of the concentration of minority equilibrium carriers captured by centers, which occurs after a time $\tau_f \gg \tau_2$.

Thus, when there are large concentrations of trapping centers, a decrease of the conductivity should occur during pulsed illumination of the semiconductor by visible light (negative photoconductivity⁵⁶).

If the concentrations of all types of centers are small, then, as shown in references 25 and 38

$$\left. \begin{aligned} \tau_h^{st} \approx \tau_e^{st} \approx \tau_0 \approx \tau_2 \\ n' \approx p' \approx G\tau_0 e^{-\frac{t}{\tau_0}}, \end{aligned} \right\} (3.5)$$

i.e., a single lifetime exists for electrons and holes.

The smaller time τ_0 ^{25,38} is the time to establish quasi-steady-state decay,⁵⁷ and the larger time τ_2 is the relaxation time of the generated excesses n' and p' . This time is strongly dependent on the presence of trapping centers in the semiconductor. Such a time is also measured in experiment, e.g., when measuring the lifetime by the pulse method.⁵⁸ Non-steady-state processes with uniform generation are realized in all cases when the decay or growth of non-equilibrium carrier concentration occurs, and diffusive carrier motion in the semiconductor can be neglected.

Therefore, as is seen from formula (3.4), all methods using the decay of non-equilibrium carrier concentrations in semiconductors give lifetimes greatly dependent on the presence and state of trapping centers in the semiconductor.

For the case of small concentrations of one type of

center ($n' \approx p'$), Eqs. (3.1) give a decay law³⁶

$$\exp \left\{ -\frac{t}{\tau_{p_0} + \tau_{n_0}} \right\} = \frac{n'}{\Delta n} \left(1 + \frac{n_0 + p_0}{n'} \right)^{1 - \frac{\tau_0}{\tau_{p_0} + \tau_{n_0}}} \quad (3.6)$$

which is valid for any generation levels. Here $\Delta n = n' |_{t=0}$.

In certain ranges simple kinetic recombination modes dominate the non-equilibrium carrier concentration change; this leads to approximately exponential, hyperbolic, or linear decay laws. Besides the well-known monomolecular ($\tau = \text{const}$) and bimolecular ($\tau = A/n'$) recombination modes in semiconductors, constant recombination rate occurs, which corresponds to a lifetime proportional to the non-equilibrium carrier concentration: $\tau = An'$. This mode of recombination occurs at low temperatures in semiconductors for which the capture cross section of minority carriers is much greater than the majority carrier cross section. When there are definite relationships between the constants and the temperature, given by $\tau_0 = \tau_{p_0} + \tau_{n_0}$, the non-equilibrium carrier concentration decay proceeds according to a monomolecular mode throughout its entire duration.

We thus complete the analysis of the characteristic times of the principal electronic processes in semiconductors. We now proceed to consider the various experimental methods of determining these times.

4. EXPERIMENTAL METHODS OF DETERMINING THE LIFETIME

It should be pointed out that the different methods of measuring the lifetime ought in the general case to determine different characteristic times. In other words, the lifetime τ , measured on the same specimen by different methods, will have different values. The methods of measuring τ are, therefore, divided into the following groups, according to the non-equilibrium processes to which they correspond:

1. Methods based on steady-state processes occurring during uniform generation of non-equilibrium carriers (e.g., the determination of τ from measurements of the steady-state conductivity). These methods measure τ_e^{st} and τ_h^{st} .
2. The use of steady-state diffusion processes for measuring the lifetime τ_0 — the characteristic lifetime of steady-state processes during non-uniform generation.
3. Methods of determining the lifetime of non-steady-state processes occurring during uniform generation of non-equilibrium carriers in the volume of the semiconductor — the growth and decay constants of non-equilibrium carrier concentrations (the time τ_2).
4. Methods in which non-steady-state processes under conditions of non-uniform generation are used for determining the lifetime. To this group belong

all methods in which the drift of injected carriers is used, and a number of others.

The simplest method of determining the lifetime from diffusion length measurements (processes of the second group; time τ_0) is the photoelectric method, where the diffusion length of non-equilibrium carriers created in the semiconductor by light is found by measuring the distribution in the depth of the semiconductor either of the photo-emf^{59,60,61} or of the photoconductivity⁴⁰ (Fig. 7). In both cases the results are distorted by the effect of metallic contacts.

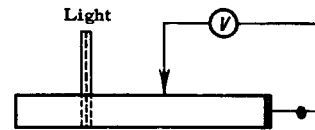


FIG. 7

Harrick^{62,63} developed a variant of the contactless photoelectric method. He made use of the change in the transparency of germanium in the infrared region of the spectrum^{64,65} caused by the scattering of light at free carriers. Thus a measurement of the distribution of the transmission coefficient along a specimen gives us the distribution of non-equilibrium carriers in the volume of the semiconductor, i.e., the diffusion length (Fig. 8) without any distortion introduced by probe contacts. The author showed that measurements of the transmission coefficient perpendicular to the direction of diffusion (the change of transmission in the direction of diffusion — detector A) determined the lifetime of bulk recombination (in this case surface recombination plays an insignificant part), while measurements of the transmission along the direction of carrier diffusion (detector B) can give the surface recombination rate at the side faces of the specimen. The contactless photoelectric method thus allows separate determinations to be made⁶³ of the bulk lifetime and the surface recombination velocity S.

Other modifications of the photoelectric method are those in which quantities are measured which depend on the diffusion length. Such a method is the

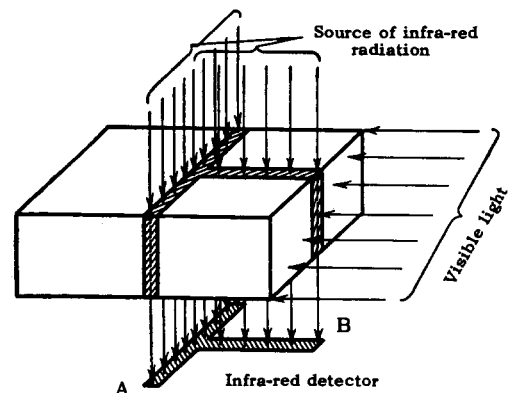


FIG. 8

determination of the lifetime from measurements of the transverse Kikoin-Noskov⁶⁶⁻⁷⁰ photomagnetic effect voltage V_H (Fig. 9)

$$V_H \approx \frac{c_e + c_h}{\mu_e n_0 + \mu_h p_0} G \sqrt{D\tau} \frac{d}{l}, \quad (4.1)$$

where c_e and c_h are the Hall angles for electrons and holes, which are, respectively,

$$c_e = \frac{\mu_e H B}{c}, \quad c_h = \frac{\mu_h H B}{c},$$

$\mu_e H$, $\mu_h H$ are the Hall mobilities for electrons and holes, B is the magnetic induction, l is the width of the specimen, and d is the thickness of the specimen.

An interesting modification of the photoelectric method was proposed by Smirnov.⁷¹ He developed a method of determining the lifetime by measuring the collection coefficient α^* in a photocell with a plane p-n junction. For small surface recombination rates and small diffusion lengths L_D ($d/L_D \geq 2$)

$$\alpha = 2e^{-\frac{d}{L_D}},$$

where d is the distance between the illuminated surface and the p-n junction (Fig. 10). We note that this method can measure lifetimes of the order 10^{-8} sec (the lower limit is determined by the ability to measure small currents).

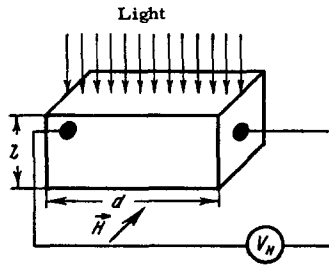


FIG. 9

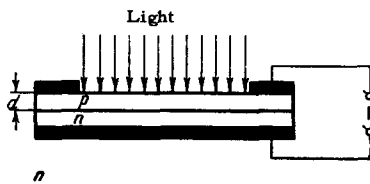


FIG. 10.

The lifetimes of steady-state processes with uniform generation (τ_h^{st} , τ_e^{st}) are measured directly from the steady-state photoconductivity of the specimen

$$\Delta\sigma = q(\mu_e \tau_e^{st} + \mu_h \tau_h^{st}) G_{\text{eff}} \frac{W}{l^2} \approx q(\mu_e + \mu_h) G_0 \tau \frac{W}{l^2} \quad (4.2)$$

(if the concentration of centers is small), where W is the volume of the semiconductor, and l is the length of the specimen.

* α is the ratio of the number of carriers providing the short circuit current to the number of carriers created by the light close to the illuminated surface.

In reference 72 a similar method was developed in detail, and more accurate formulae were obtained in which the effect of surface recombination is taken into account:

$$\tau_{\text{eff}} = \frac{n'}{G} = \tau \left(1 - \frac{S L_h}{D + S L_h} e^{-Z_0/L_h} \right).$$

Here Z_0 is the thickness of the specimen, L_h is the diffusion length of non-equilibrium holes (minority carriers), and S is the surface recombination velocity.

It should be noted that the steady-state photoconductivity method can also measure small times, which is impossible by the usual photoelectric method, because of inhomogeneities in the volume of the semiconductor (as Lashkarev⁵⁹ has shown, to use the photoelectric method it is necessary for the diffusion length to be much larger than the dimensions of the collector region, which gives lengths greater than 4×10^{-3} cm or times exceeding 2.5×10^{-7} sec. The steady-state photoconductivity method has the shortcoming that it is applicable either for the condition $n' = p'$, or when one of the carrier types is almost completely captured ($p' \gg n'$ or $n' \gg p'$). In the general form the problem becomes indeterminate because

$$\Delta\sigma = qG(\mu_e \tau_e^{st} + \mu_h \tau_h^{st}) \frac{W}{l^2} *$$

(i.e., there is one relation to determine two quantities, τ_e^{st} and τ_h^{st}). In concluding the consideration of methods using steady-state processes (the first and second groups), we point out that in fact non-steady-state processes are used for convenience in all these methods, since the generation of carriers is modulated, but, because the length of the generation pulse is chosen to be much greater than any of the characteristic times, it can be taken that a steady state is established in the course of a single pulse.

It should also be pointed out that the method proposed by Adam⁷³ (see Fig. 7), using the motion of an illuminating spot, does not in the general case measure the lifetime of steady-state processes (more accurately, the time τ_0). The idea of this method is that during the motion of the illuminating slit, the instantaneous distribution of non-equilibrium conductivity (characteristic lengths L_1 , L_2) becomes asymmetrical on either side of the slit, and it therefore becomes possible to determine both the diffusion coefficient D and the lifetime τ . The formulae obtained by Adam:

$$\tau = \frac{L_1 - L_2}{v}, \quad D = \frac{v}{\frac{1}{L_2} - \frac{1}{L_1}},$$

where v is the speed with which the light spot (slit) moves, are true only under the assumption that the time required to establish a quasi-steady-state distribution of free electrons and holes is small com-

*It is here assumed that uniform generation of non-equilibrium carriers takes place through the entire volume of the semiconductor, i.e., the thickness of the specimen must be small in comparison with $1/\lambda$ (the penetration depth of the light) or $G = \text{const} = G_{\text{eff}}$.

pared with the lifetime. We know that this is always fulfilled only when $n' \approx p'$. We note, however, that if, for a large concentration of centers, the time $\tau_t = 1/A_e p_{t0}^*$ which is the time taken to establish a quasi-steady state, is much less than the lifetime $\tau = \tau_r$, determined from the diffusion length, and in addition the time taken for the spot to traverse the entire length of the semiconductor t_w is much less than the lifetime of carriers in centers τ_f , then the formulae given for D and τ are also applicable. The transition from a steady state to a quasi-steady state actually occurs after a time $\tau_t = 1/A_e p_{t0}^*$. After this time there is established in a given volume element non-equilibrium filling of the centers, the change of which is determined by the time $\tau_f \gg \tau_t$. If in this case $\tau_f \gg \tau \gg \tau_t$, then for spot motion with a velocity of the order of the diffusive spreading rate $vD = \frac{\sqrt{D\tau}}{\tau}$, the quasi-steady state (i.e., the instantaneous

distribution of carriers throughout the volume) can be established in each volume element of the semiconductor. Because the time is small in comparison with the lifetime of carriers in centers τ_f , carrier capture does not change this distribution, i.e., as in steady-state processes it will not affect carrier diffusion (the establishment of the instantaneous distribution proceeds much more rapidly than diffusive spreading, which, in its turn, also proceeds much more rapidly than the release of carriers from centers; $t_w \ll \tau_f$). In reference 30 an exactly analogous case is considered for silicon ($\tau_t \approx 10^{-7}$ sec, $\tau_f \approx 10^{-3}$ sec, $\tau \sim 10^{-5}$ sec, $t_w \sim 10^{-4}$ sec).

The measurement of the characteristic times of non-steady-state processes (the time τ_2) is in the simplest case performed by a pulse method.⁵⁸ In this method non-equilibrium carriers are injected into the specimen by an external field. The time during which these carriers spread out throughout the volume (the duration of the injecting pulse T_i) should be much less than the lifetime. After the cessation of the pulse (the establishment of a uniform distribution), the decay of non-equilibrium conductivity proceeds only due to recombination and capture, which is determined by the time τ_2 . One variety of the pulse method is the determination of the lifetime by the decay of photoconductivity created by penetrating radiation (for example, infrared radiation³⁰).

A large group of methods are used under conditions of non-steady-state and non-uniform generation. Such methods are, for example, the determination of the lifetime by photoconductive decay in the presence of the usual surface generation of non-equilibrium pairs.⁷⁴ In the paper quoted the case is considered of the semiconductor with no centers ($n' \approx p'$), and the effects of a field E (the presence of electrical current) and of

*In the case taken the semiconductor has trapping centers that capture electrons.

surface recombination are taken into account. In the simplest case (Fig. 11) the expression for the decay constant agrees with the well-known Shockley formula:¹

$$\gamma_0 \approx \frac{1}{\tau} + S \left(\frac{1}{B} + \frac{1}{C} \right) + \frac{\pi^2 D}{A^2} \approx \frac{1}{\tau} + S \left(\frac{1}{A} + \frac{1}{C} \right),$$

since $A \gg B$ and $A \gg C$. Thus, taking into account non-uniform generation and non-steady-state processes increases the decay due to the absorption of carriers at the surfaces of the semiconductor (surface recombination).

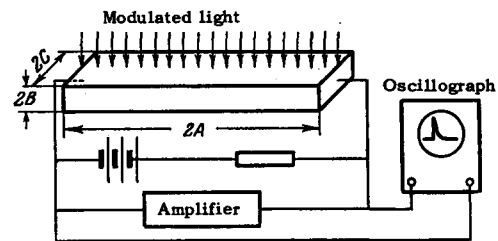


FIG. 11

Another method in which the processes mentioned occur was proposed by Many.⁷⁵ In this method the non-equilibrium conductivity is created by a voltage pulse applied to a specimen contact. But, in distinction from the pulse method,⁵⁸ the duration of the injecting pulse is here chosen to be much greater than the lifetime ($T_i \gg \tau$). Straightforward calculations lead to the following relationship for determining the lifetime:

$$\frac{\Delta\sigma}{\sigma} = \frac{(b+1)\gamma I\tau}{q(bn_0+p_0)\mu_h} (1 - e^{-t/\tau}), \quad (4.3)$$

where σ is the specimen conductivity in the absence of the injecting current pulse I , $\Delta\sigma$ is the excess (non-equilibrium) conductivity created by the pulse of injected non-equilibrium carriers, and γ is the injection coefficient. Thus, by measuring the growth of non-equilibrium conductivity, we determine the lifetime. We note that the picture considered is, according to Shockley^{1*} true when carrier diffusion is neglected (equilibrium is established between the concentration of carriers drawn in by the field and recombination in the bulk). This puts both upper and lower limits on the measurable values of τ . The condition that diffusive smearing can be neglected actually determines the lower limit of the injecting field: $V_D = \sqrt{D/\tau} \leq \mu E$, which leads to

$$\tau \geq \frac{kT}{q} \frac{1}{V} \frac{l}{\mu E}, \quad (4.4)$$

where V is the voltage applied to the specimen, l is the specimen length. This gives the lower limit of measurable values as $\tau \sim 10^{-6}$ sec. On the other hand,

*As Shockley showed,¹ when diffusion is neglected, the non-equilibrium conductivity depends only on the total number of injected carriers, but not on their distribution throughout the volume of the semiconductor.

in the Many method, τ is determined by measuring the growth of non-equilibrium conductivity in the specimen [see (4.3)]. Consequently,

$$\tau \ll T_i = \frac{l}{\mu E}. \tag{4.5}$$

Therefore, the limits of measured values of τ for the Many method are given by the inequalities

$$\frac{kT}{q} \frac{1}{V} \frac{l}{\mu E} \ll \tau \ll \frac{l}{\mu E}. \tag{4.6}$$

We note that the upper limit of the inequality (4.6) depends essentially on the surface recombination velocity S , since

$$\frac{1}{\tau} \gg \frac{1}{T_i} > \frac{S}{l} \quad \text{or} \quad S < \mu E, \tag{4.7}$$

which is the condition for neglecting S in comparison with bulk recombination.

Thus, the absence of diffusion ($V_D \ll \mu E$) ensures conditions equivalent to uniform generation of non-equilibrium carriers in the bulk of the semiconductor, and the large spreading time ($T_i \gg \tau$) allows the relaxation of non-equilibrium carriers to be considered to occur only due to their capture and recombination. Thus T_i should remain small [see the inequality (4.7)] so that the surface recombination velocity can still be neglected. In fact, for large values of the time t ($t > T_i$) we obtain

$$\frac{1}{\tau} + \frac{1}{T_i} \approx \frac{1}{\tau}.$$

When $t \leq T_i$ and diffusion is neglected, relaxation also occurs by recombination and capture, since the non-equilibrium carriers fill only part of the specimen volume. For stronger fields, when the spreading time T_i is comparable with the lifetime, and also for large surface recombination velocities, calculations^{76,77} show that the lifetime measured by the decay of non-equilibrium conductivity will depend also on the field and the surface recombination velocity.

Another very well known method of this type is the drift method⁷⁸ (see Fig. 4). In this method one measures the variation of signal amplitude at the collector with the time the carriers take to cross between the collector and the emitter, i.e., with the value of the field which moves them. Neglecting the diffusive spread of the injected carriers, it can be assumed that the change of collector signal amplitude is caused only by recombination and capture processes. Thus, in this method, too, the conditions correspond to uniform and non-steady-state generation.

Another modification of this method was proposed by Spitzer⁷⁹ — the conductivity modulation method. The use of only one point contact (Fig. 12) makes it possible to measure the distribution of τ throughout the volume of the specimen (each time the lifetime is determined in a small region adjacent to this contact). By making a detailed analysis of this method, Iglitsyn and co-workers⁸⁰ obtained a relationship between the meas-

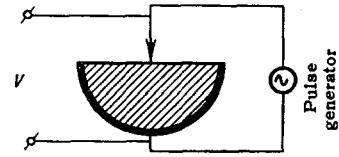


FIG. 12

ured quantities (the current through the contact, the lifetime, the minority carrier mobility, the resistance); when this is satisfied, the conditions are equivalent to uniform non-steady-state generation.

Thus, both the drift method and Many's method measure the time τ_2 which characterizes non-steady-state electronic processes under uniform generation. This time depends strongly on the presence and state of trapping centers in the semiconductors.

Of the other well-known methods of measurement, mention should be made of the determination of the lifetime by measuring the storage (the recovery time t_R) of a forward current pulse I_f on instantaneously reversing the diode voltage (Fig. 13)⁸¹⁻⁸⁵ and also the phase^{86,87,89} and frequency⁸⁸ methods.

We remark that only in particular cases (for example, in the drift and Many methods), when the spreading of carriers due to diffusion can be neglected, are conditions established in the semiconductor which approximate uniform non-steady-state generation. In the general case, to determine the characteristic times of these processes (non-uniform and non-steady-state generation), a rigorous solution of the kinetic equations is necessary.

It should also be pointed out that the work of Sah and Shockley⁹⁰ is not included in this review. They* studied the recombination statistics when centers with

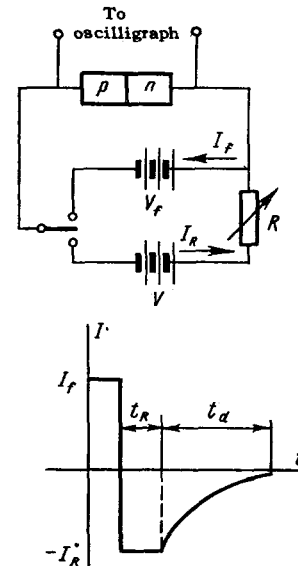


FIG. 13

*S. G. Kalashnikov and co-workers did similar work, independently of Shockley and Sah, and they also obtained experimental support for the theory.⁹¹

several levels were present. In the majority of cases of practical interest the distance between the energy levels of a given center is much greater than kT . From the theory of Sah and Shockley it follows that the levels then act independently, i.e., similarly to the case in which each center has only one energy level. Consequently, under the usual conditions of bulk recombination, this theory gives nothing new as compared with the Shockley-Read treatment.

CONCLUSION

The survey of the electronic processes in semiconductors allows the following conclusions:

1. A semiconductor is a complex system, containing charge carriers of both types, as well as localized centers of various natures, and has several characteristic times. Each of these times corresponds to a definite electronic process, and is completely determined from the kinetic equations of these processes.

Electronic processes in semiconductors can be divided into the following main groups: steady-state processes occurring under conditions of both uniform generation ($G = \text{const}$) and non-uniform generation [$G = f(x, y, z)$] of non-equilibrium carriers, as well as non-steady-state occurring under the same two generation conditions.

2. Electronic processes which occur under conditions of uniform and steady-state generation are characterized by the times τ_e^{st} , τ_h^{st} .^{2,37,38} In a number of cases these times can be determined by measuring the steady-state photoconductivity.^{60,72}

3. The analysis given of the solutions of the equations which describe steady-state non-equilibrium processes occurring under conditions of non-uniform generation shows that in this case, in addition to processes determined by the times τ_e^{st} and τ_h^{st} , bipolar diffusion (motion of non-equilibrium pairs) occurs, which is characterized by the length $1/k_2$, equal for electrons and holes (the absorption path of non-equilibrium pairs). This absorption path (diffusion length) is determined by the ambipolar diffusion coefficient

$D = \frac{D_e D_h (n_0 + p_0)}{D_e n_0 + D_h p_0}$ and the time τ_0 which is given by^{2,38,52}

$$\frac{1}{\tau_0} = \sum_{j=1}^{j=m} \frac{1}{\tau_0^j} = \sum_{j=1}^{j=m} A_e^j A_h^j \frac{p_{t0}^j (p_0 + p_1^j) + n_{t0}^j (n_0 + n_1^j)}{A_h^j (p_0 + p_1^j) + A_e^j (n_0 + n_1^j)}$$

The quantity τ_0 does not here depend on the concentration of trapping centers. Therefore, all methods based on measuring the diffusion length determine a lifetime which does not depend on the presence and state of trapping centers in the semiconductor.

4. The consideration of the kinetic equation solutions for non-steady-state processes in the most important particular cases³⁸ shows that τ_1 and τ_2 are the characteristic times of these processes. The formula³⁸ for the larger time τ_2 , which is measured ex-

perimentally,⁵⁸ gives its variation on the state and presence of trapping centers in semiconductors.

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