

RECOMBINATION PROCESSES IN SEMICONDUCTORS

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SUMMARY

Recombination of electrons and holes may take place in the host crystal or at impurity centres, the energy being removed by radiation of a light quantum, by multiphonon emission, or by an Auger process. The probabilities for each of these six processes are discussed. While the lifetime in semiconductors is usually determined by multiphonon recombination at impurity centres, Auger recombination in the host crystal can be expected to dominate in small-band-gap crystals containing large concentrations of free carriers. Radiative recombination in the host crystal may limit the lifetime in semiconductors where band-to-band transitions are direct, provided that the specimens are reasonably free of recombination centres.

LIST OF PRINCIPAL SYMBOLS

- α = Optical absorption coefficient, cm^{-1} .
 B = Recombination probability for radiative or multiphonon recombination, cm^3/sec .
 β = Recombination probability for Auger recombination, cm^6/sec .
 W_g = Band gap of a semiconductor.
 M = Number of recombination centres per unit volume, cm^{-3} .
 n = Free electron concentration, cm^{-3} .
 p = Free hole concentration, cm^{-3} .
 r = Recombination rate, $\text{cm}^{-3} \text{sec}^{-1}$.
 R = Net recombination rate, $\text{cm}^{-3} \text{sec}^{-1}$.
 τ = Lifetime of excess free electrons or holes, sec.
 μ = Index of refraction.

(1) INTRODUCTION

Several mechanisms have been proposed to account for the generation and recombination of electrons and holes in non-metallic crystals. These processes have been studied in the greatest detail in germanium and silicon, but, in addition, considerable information has been obtained from investigations of various other semiconductors. The paper reviews the behaviour to be expected from theoretical considerations of the basic recombination mechanisms and compares these results with the available experimental information.

The following processes are examined:

- (a) Radiative recombination, in which most of the energy is carried away by a quantum of electromagnetic radiation, sometimes with an accompanying lattice phonon.
 (b) Multiphonon recombination, wherein the recombination energy is dissipated by the creation of a number of lattice phonons.
 (c) Auger recombination, which results in the ejection of an energetic electron or hole to help satisfy the laws of energy and momentum conservation.

Each of these processes may be imagined to take place either in the host crystal itself or at an imperfection, making six cases in all to be discussed. Some characteristic features of each are summarized in Table 1.

In the Sections that follow, an attempt is made to provide estimates of the probabilities for each of these processes. The behaviour with respect to variations in temperature and impurity concentration, and such material parameters as energy gap and

Table 1

COMPARISON OF DIFFERENT RECOMBINATION PROCESSES

Process	In host crystal	At impurity centres
Radiative ..	Negligible compared with other processes except with very large carrier concentrations. Not strongly dependent upon temperature and band gap.	Prominent in materials with large band-gaps, e.g. phosphors.
Multiphonon	Improbable process. Not yet seen experimentally.	Dominant process in most semiconducting materials.
Auger ..	Probability increases rapidly with temperature. Favoured by small band-gaps and large carrier concentrations.	Sometimes seen in trapping phenomena. Generally requires large carrier concentrations to be important.

effective mass are discussed. It is hoped that these estimates will provide a convenient framework with which to compare experimental results.

(2) RECOMBINATION RATES AND LIFETIMES

We shall use the symbol r_n to denote the rate per unit volume of disappearance of free electrons due to any given recombination process. Our object is to obtain explicit expressions for this quantity in terms of the electron and hole concentrations, n and p , for each of the processes that we wish to consider. From a knowledge of $r_n(n, p)$ and the corresponding expression for holes we can calculate all the other parameters that are used to describe the kinetics of the recombination of electrons and holes.

By the principle of microscopic reversibility, we know that the recombination and generation rates of each kind of carrier must be in balance at equilibrium for each of the recombination processes taken separately. Therefore the rate of thermal generation of electrons must be given by $r_n(n_0, p_0)$, where n_0 and p_0 represent the equilibrium carrier concentrations. The amount by which the recombination of electrons exceeds the thermal generation rate, and the corresponding expression for holes, may be written in the form

$$R_n = r_n(n, p) - r_n(n_0, p_0) \quad \dots \quad (1a)$$

$$R_p = r_p(n, p) - r_p(n_0, p_0) \quad \dots \quad (1b)$$

Clearly, if several of these processes are simultaneously operative, the total net recombination rate is the sum of the individual rates.

We shall define the lifetime of an electron or hole to be the excess carrier concentration divided by the corresponding net recombination rate.

$$\tau_n = (n - n_0)/R_n = \delta n/R_n \quad \dots \quad (2a)$$

$$\tau_p = (p - p_0)/R_p = \delta p/R_p \quad \dots \quad (2b)$$

No limitations need be placed upon the magnitudes of δn and δp , except that n and p must never be negative. This definition of carrier lifetime is the one which is normally used in semi-

conductor electronics. Although it is generally used only to describe the behaviour of minority carriers, it is equally applicable to the description of the properties of the majority-carrier concentration. Note that it does not represent the time that an electron or hole can expect to survive before being captured; this quantity (the capture lifetime) will be discussed later in this Section.

In the calculation of lifetimes from eqn. (2), it is often necessary to specify the conditions under which they are to be evaluated. If electrons and holes are created within the sample at a constant rate, L per unit volume (by irradiating with penetrating light, for example), the excess carrier concentrations will increase until steady-state values are reached with $R_n = R_p = L$. The quantities that are calculated by using these values in eqn. (2) are known as the steady-state lifetimes. The electron and hole lifetimes may differ considerably in magnitude if the recombination process involves a sufficient concentration of impurity centres.

On the other hand, the transient response following the removal of an external stimulus is calculated from eqn. (1) by noting that $R_n = -dn/dt$, and $R_p = -dp/dt$. Where the time dependence can be described by a simple exponential decay, the use of eqn. (2) leads to constant values for the carrier lifetimes. These transient lifetimes may, however, be quite different from the steady-state lifetimes if charge storage at recombination centres is important. Quite often, a more complicated time-dependence is observed, and the concept of a carrier lifetime becomes less meaningful.

The lifetime as defined by eqn. (2) is only indirectly related to the average time interval, T , that a carrier spends as a free entity between generation and capture processes. The latter quantity, which we shall call the 'capture lifetime', is given by the ratio of the total electron or hole concentration to the corresponding capture rate. The capture lifetime is more directly related to the mechanics of the recombination process and is the quantity that is generally used in analysing the behaviour of photoconductors.

These two definitions of lifetime, as applied to electrons, are compared by the following equations:

$$\tau_n = \frac{\delta n}{R_n(n, p)} = \frac{n - n_0}{r_n(n, p) - r_n(n_0, p_0)} \quad (3a)$$

$$T_n = \frac{n}{r_n(n, p)} \quad (3b)$$

When the carrier concentrations have approximately their equilibrium values, these two lifetimes will generally be quite different, particularly in the case of the majority carrier. In large band-gap materials, only a small stimulus is required to make both the capture rate and the minority-carrier concen-

tration large compared with their equilibrium values. Under these conditions, the two values of minority-carrier lifetime are substantially equal. However, in most instances it is necessary to distinguish between these two definitions of lifetime. The lifetime concept is discussed further by Schottky¹ and Hoffmann.²

(3) RADIATIVE RECOMBINATION IN THE HOST CRYSTAL

Radiation which is presumably due to the recombination of free electrons and holes has been observed in germanium,^{3, 4, 5} silicon,⁵ gallium antimonide,⁶ gallium arsenide,⁶ indium phosphide,⁶ indium antimonide⁷ and cadmium telluride.⁸ In a non-degenerate semiconductor, the rate at which electron and holes disappear by this process is proportional to the product of the electron and hole concentrations.

Thus $r = Bnp$ (4)

and $R = B(np - n_i^2)$ (5)

The radiative lifetimes, calculated using eqn. (2), are

$$\tau_n = \tau_p = \frac{1}{B(n_0 + p_0 + \delta n)} \quad (6)$$

Thus, to a good approximation, the radiative lifetime is inversely proportional to the total concentration of free carriers under all circumstances.

In intrinsic material, the low-level lifetime has a maximum value which is strongly temperature-dependent and varies greatly from one semiconductor to another. Since one generally deals with extrinsic semiconductors, however, a more significant quantity is the low-level lifetime in a sample having a given majority-carrier concentration. For samples having 10^{17} majority carriers/cm³ the room-temperature radiative lifetime may range from a few milliseconds in a semiconductor such as germanium or silicon where radiative transitions are indirect, to a few tenths of a microsecond in materials where the transitions are direct. It should be noted that internal absorption will increase the apparent radiative lifetime in samples which are thick compared with the absorption distance for the recombination radiation.⁹

The capture probability, B , can be evaluated by the method of van Roosbroeck and Shockley,¹⁰ using experimentally determined values of the optical absorption coefficient and the intrinsic carrier concentration. Table 2 summarizes values for B obtained in this manner for several semiconductors. Lifetimes and capture probabilities were calculated from optical data in the references cited, corrected to 300° K where necessary. For the lead salts, n_i was deduced from Chasmar's work.⁶⁴

Analytic expressions for B may be obtained by a direct calculation or by applying van Roosbroeck and Shockley's method

Table 2
FREE CARRIER RADIATIVE RECOMBINATION AT 300° K

Material	W_g	n_i	B	τ (intrinsic)	τ (for 10^{17} majority carriers/cm ³)	Reference
	eV	cm ⁻³ × 10 ¹⁴	cm ³ /sec × 10 ⁻¹²		μs	
Si	1.08	0.000 15	0.002	4.6 h	2500	11, 12
Ge	0.66	0.24	0.034	0.61 sec	150	11, 13
GaSb ..	0.71	0.043	13	0.009 sec	0.37	14
InAs ..	0.31	16	21	15 μs	0.24	15
InSb ..	0.18	200	40	0.62 μs	0.12	16
PbS ..	0.41	7.1	48	15 μs	0.21	17
PbTe ..	0.32	40	52	2.4 μs	0.19	17
PbSe ..	0.29	62	40	2.0 μs	0.25	17

to theoretical or semi-empirical formulae for the optical absorption coefficient. We will make use of the latter procedure here, since a comparison between the calculated and observed absorption coefficients can be helpful in testing the correctness of the calculation.

Direct transitions can occur in those semiconductors where the conduction-band minimum and the valence-band maximum both occur at the same point in momentum space. For such materials, the variation of the optical absorption coefficient, $\alpha(cm^{-1})$, with energy has the form,¹⁸

$$\alpha_{direct} = \frac{2^{3/2} me^2}{3\mu \hbar^2} \left[\frac{m_e m_h}{m(m_e + m_h)} \right]^{3/2} \left(1 + \frac{m}{m_e} + \frac{m}{m_h} \right) \left(\frac{W - W_g}{mc^2} \right)^{1/2} \quad (7)$$

for photon energies, W , slightly greater than the band gap, W_g . μ is the index of refraction, and m_e and m_h are the density-of-states electron and hole effective masses. mc^2 is the electron self-energy, 0.511 MeV.

Indirect transitions occur when the optical absorption threshold involves states of different k -vector. In this case, the optical absorption as analyzed by Bardeen *et al.*¹⁸ and by Macfarlane *et al.*^{19, 20} can be approximated by

$$\alpha_{indirect} = A \left[\frac{(W - W_g - k\theta)^2}{(1 - \varepsilon^{-\theta/T})} + \frac{(W - W_g + k\theta)^2}{(\varepsilon^{\theta/T} - 1)} \right] \quad (8)$$

The constant, A , is essentially independent of temperature. It has values of 2600, 3600, and 2500 $eV^{-2} cm^{-1}$ for Ge, Si, and SiC as determined experimentally.^{12, 13, 21} Corresponding values for θ are 260° K, 600° K, and 1044° K respectively.

In the method of van Roosbroeck and Shockley, the equilibrium rate of radiative recombination is set equal to the total amount of black-body radiation absorbed by the crystal due to band-to-band processes:

$$Bn_i^2 = \int_0^\infty \frac{\mu^2 \alpha W^2}{\pi^2 c^2 \hbar^3 [\exp(W/kT) - 1]} \quad (9)$$

It should be noted that this formula is applicable without modification to crystals in which the Franck-Condon shift is appreciable. Combining this equation with eqn. (7) gives an expression for the capture probability for direct transitions:

$$\begin{aligned} B_{direct} &= \frac{(2\pi)^{3/2} \hbar e^2}{3 m^2 c^2} \mu \left(\frac{m}{m_e + m_h} \right)^{3/2} \\ &\left(1 + \frac{m}{m_e} + \frac{m}{m_h} \right) \frac{W_g^2}{(kT)^{3/2} (mc^2)^{1/2}} \\ &= 0.58 \times 10^{-12} \mu \left(\frac{m}{m_e + m_h} \right)^{3/2} \\ &\left(1 + \frac{m}{m_e} + \frac{m}{m_h} \right) \left(\frac{300}{T} \right)^{3/2} W_g^2 cm^3/sec \quad (10) \end{aligned}$$

where the energy threshold for direct transitions, W_g , is expressed in electron-volts. Values of B calculated for gallium antimonide, indium arsenide and indium antimonide using this equation agree with those in Table 2 within the present experimental uncertainties of the effective masses.

A similar calculation of the capture probability for indirect transitions gives

$$\begin{aligned} B_{indirect} &= \frac{4\pi \hbar^3}{m^3 c^2} A \mu^2 \left(\frac{m^2}{m_e m_h} \right)^{3/2} W_g^2 \coth \frac{\theta}{2T} \quad (11) \\ &= 2.17 \times 10^{-20} A \mu^2 \left(\frac{m^2}{m_e m_h} \right)^{3/2} W_g^2 \coth \frac{\theta}{2T} \end{aligned}$$

In this case, calculated values of the capture probability agree well with those in Table 2, since the parameters A and θ are chosen to fit the measured absorption data.

Examination of eqns. (10) and (11) shows that B_{direct} should vary as $T^{-3/2}$, whereas $B_{indirect}$ can be expected to vary somewhat more slowly than T^{-1} . In neither case, however is a strong temperature dependence to be expected.* The magnitude of B_{direct} should not depend very strongly upon W_g in view of the tendency for small energy gaps to be associated with small effective masses. Thus, for semiconductors in which recombination occurs by a direct radiative transition, $B \approx 30 \times 10^{-12} cm^3/sec$. Most of the III-V, II-VI and lead-salt compounds appear to fall in this category. For indirect transitions, the capture probability is smaller by a factor of 10^3 to 10^4 , a quantity which may vary considerably from one material to another, being dependent upon the nature of the energy surfaces. Similar remarks apply to the extrinsic lifetime, since this quantity is inversely proportional to B .

In the case of germanium, the calculated transition probability is several times too small because of failure to take into account the contribution made by vertical transitions between states near $k = 0$, where the energy gap is greater than the thermal band-gap by a rather small amount, δW_g . For such materials the band gap appearing in eqn. (7) should be replaced by $W_g + \delta W_g$, and the resulting expression for B_{direct} contains an additional factor, $\exp(-\delta W_g/kT)$. As it stands, eqn. (10) represents the recombination probability for that fraction of the total electron concentration that has sufficient thermal energy to attain a zero momentum vector. The total recombination probability for a semiconductor having band edges at different k -values can therefore be written⁹

$$B = B_{indirect} + B_{direct} \exp(-\delta W_g/kT) \quad (12)$$

The direct process tends to become dominant at high temperatures because of the effect of the exponential factor. This occurs somewhat below room temperature in the case of germanium. Optical data for silicon²² show that direct transitions are unimportant below the melting temperature.

Analysis of the electrical characteristics of p - i - n rectifiers shows that the high-level lifetime does not decrease below 10 microsec at carrier concentrations of $10^{18}/cm^3$ in the case of germanium²³ or $10^{17}/cm^3$ in the case of silicon.²⁴ Under these conditions, the radiative lifetimes calculated from eqn. (6) are 30 microsec for germanium and 5000 microsec for silicon. Thus, in neither case is the lifetime limited by radiative recombination, although the margin is rather close in the case of germanium rectifiers.

(4) RADIATIVE RECOMBINATION AT IMPERFECTIONS

This Section will summarize and discuss experimental evidence regarding the probability for radiative capture of free electrons and holes at impurity centres. In this case, both theory and experiment are considerably less reliable than was the case in the preceding Section. Nevertheless, it is felt that some useful generalizations may be made. Transitions between localized impurity levels will not be considered, although this is an important process in phosphor crystals.

The rate of capture of free carriers at an impurity centre is given by

$$r = BNn \quad (13)$$

where B is the capture probability, N the concentration of empty centres, and n the appropriate free-carrier concentration. The

* The strong temperature dependence for the radiative recombination cross-section computed by van Roosbroeck and Shockley¹⁹ can be attributed to lack of reliable data regarding the temperature dependence of α and n_i .

kinetics of recombination due to this mechanism are similar to the case for multiphonon recombination and will be discussed in Section 6.

There is very little direct experimental evidence regarding the magnitude of B for the radiative process. Values in the range 10^{-13} to 10^{-14} cm³/sec are suggested by work involving sulphide phosphors.²⁵ In germanium, an upper limit of 2×10^{-12} cm³/sec has been measured for the total capture probability, including non-radiative transitions of electrons at ionized aluminium centres.²⁶

Optical absorption data may be used to deduce values for B , using detailed balance arguments analogous to those of van Roosbroeck and Shockley:

$$B = \left(\frac{2}{\pi}\right)^{1/2} \frac{\mu^2}{(m_{eff}kT)^{3/2}c^2} \int_{W_i}^{\infty} \sigma W^2 \exp[-(W - W_i)/kT] dW$$

$$= 1.58 \times 10^4 \mu^2 \left(\frac{m}{m_{eff}} \frac{300}{T}\right)^{3/2} \int_{W_i}^{\infty} \sigma W^2 \exp[-(W - W_i)/kT] dW \quad (14)$$

W_i is the threshold energy for ionization, σ is the absorption cross-section for ionization of the impurity centre by light of energy W , and m_{eff} is the effective mass of the free carrier involved. For numerical evaluation, W is expressed in electronvolts and σ in cm².

The optical data are frequently measured at temperatures low enough for the integral in these equations to be determined to a good approximation by the threshold value of the absorption cross-section, σ_i . Under these circumstances, we obtain

$$B \simeq \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{m}{m_{eff}}\right)^{3/2} \frac{W_i^2}{(kT)^{1/2}(mc^2)^{3/2}} \mu^2 c \sigma_i$$

$$\simeq 408 \left(\frac{m}{m_{eff}}\right)^{3/2} \left(\frac{300}{T}\right)^{1/2} \mu^2 \sigma_i W_i^2 \text{ (eV) cm}^3/\text{sec} \quad (15)$$

Measurements have been made^{27, 28, 29} of the optical absorption due to the ionization of holes from column III acceptors in silicon. Recombination probabilities calculated from these data assuming $m_{eff}/m = 0.6$ and α_i independent of temperature are presented in Table 3. Also included are probabilities deduced from data by Kaiser and Fan³⁰ for the first and second ionization of holes from copper in germanium ($m_{eff}/m = 0.36$).

A comparison may be made between these recombination probabilities deduced from optical data and those listed in the fifth column of Table 3, which are calculated from a formula due to Sclar and Burstein:³¹

$$B = \frac{(2\pi)^{3/2}}{3} 2^8 e^{-4} \frac{\hbar e^2}{m^2 c^2} \frac{\mu}{Z^2} \left(\frac{m}{m_{eff}}\right)^{5/2} \frac{W_i}{(kT)^{1/2}(mc^2)^{1/2}}$$

$$= 0.069 \times 10^{-12} \frac{\mu}{Z^2} \left(\frac{m}{m_{eff}}\right)^{5/2} \left(\frac{300}{T}\right)^{1/2} W_i \text{ (eV) cm}^3/\text{sec} \quad (16)$$

where Z is the charge state of the ionized centre. This equation should be applicable to the hydrogen-like donors and acceptors. For most of these impurities, it gives values that are in reasonably good agreement with those deduced from absorption data.

Similar agreement is found for the two copper levels in germanium. For non-hydrogenic impurity centres such as these, however, the agreement must be regarded as fortuitous. Nevertheless, eqn. (16) can serve a useful purpose in providing a yardstick with which to compare experimental values of radiative capture probabilities for deep-level impurities. Comparison with eqn. (10) suggests that radiative recombination at impurity centres should be somewhat less probable than free

Table 3

RADIATIVE RECOMBINATION OF HOLES AT NEGATIVE ACCEPTORS AT 300° K

Recombination centre	W_i	σ_i	B (from σ_i)	B (eqn. 16)	Reference
	eV	cm ² × 10 ⁻¹⁶	cm ³ /sec × 10 ⁻¹⁴	cm ³ /sec × 10 ⁻¹⁴	
B ⁻ in Si . .	0.046	13	2.8	3.8	27, 28
Al ⁻ in Si . .	0.067	6	2.7	5.6	27, 28
Ga ⁻ in Si	0.071	5	2.5	5.9	27, 28
In ⁻ in Si . .	0.15	0.7	1.6	12	28, 29
Cu ⁻ in Ge	0.055	12	11	14	30
Cu ⁻ in Ge	0.25	1.6	30	22	30

carrier recombination in crystals where direct transitions are permitted.

The capture of electrons or holes at neutral hydrogenic impurities involves the radiation of a light quantum of energy nearly equal to the energy gap of the crystal. The probability for this process should be approximately equal to that for radiative recombination of free electrons and holes, to the extent that the carrier which is bound at the neutral centre can be regarded as a 'nearly free' carrier. This viewpoint should be applicable to impurities having ionization energies that are not large compared with kT . Thus, eqn. (10) or (11) may be used to estimate the probability for radiative recombination at neutral hydrogenic impurities in semiconductors where capture occurs by direct or indirect transitions respectively. Haynes has measured radiation resulting from recombination of free carriers at neutral donors and acceptors in silicon.³² His observations are consistent with the foregoing remarks within the rather large experimental uncertainties which are involved.

In general, radiative recombination at impurities is less probable by factors of 10^4 to 10^6 than radiationless recombination in typical semiconductors. Thus, it would appear unlikely that an appreciable fraction of the recombination of free carriers at impurities can be caused to occur by radiative processes in such materials. On the other hand, in large band-gap crystals such as phosphors, the difficulty of disposing of a large amount of energy by means of multiple phonon or other processes is sufficiently great for radiative recombination to be competitive.

(5) MULTIPHONON RECOMBINATION IN THE HOST CRYSTAL

In this process, an electron and a hole annihilate each other, with the simultaneous release of a sufficient number of lattice phonons to account for the recombination energy. The kinetics are similar to the case of radiative recombination, being represented by eqns. (4) and (5). Although estimates of the capture probability for this process have not been made, there are good theoretical reasons for believing that it is very much smaller than that of the radiative process. Up to the present time, there are no experimental results which indicate that this kind of radiationless recombination between a free electron and a hole is of importance.

(6) MULTIPHONON RECOMBINATION AT IMPURITY CENTRES

The mechanism which usually determines the recombination rate in semiconductors is a non-radiative process at impurity centres, the rate of capture being proportional to the product of the carrier concentration and the number of empty centres, as described by eqn. (13). Experimental values for the capture

probability, B , are usually in the range 10^{-6} to 10^{-9} cm³/sec (corresponding to capture cross-sections of 10^{-13} to 10^{-16} cm²), although much smaller values are sometimes observed. The latter correspond to centres which are often called 'traps'. In most cases, B is not strongly temperature dependent, except at very low temperatures. In germanium and silicon, this is the dominant mechanism in the range from liquid air temperature to at least 150°C, and for free carrier concentrations as high as 10^{17} /cm³, whether due to injection or to the presence of donor or acceptor impurities. Recombination having these characteristics will be called 'multiphonon recombination', since there are good reasons to believe that the time-limiting step in the capture process involves the capture or emission of one or more lattice phonons.

Impurities which make effective recombination centres usually give rise to energy levels that are near the middle of the forbidden band. The capture of an electron or hole at such a centre releases an amount of energy which is many times larger than that of a lattice phonon. Since the probability for the simultaneous emission of a large number of phonons is small, calculations based upon a one-step capture process lead to values that are significantly smaller than those usually measured.³³ On the other hand, Gummel and Lax^{34, 35} have calculated values which are comparable in magnitude to those found experimentally by assuming that the free carrier is first captured at shallow excited states of the impurity centre by one or more single-phonon transitions. Having thus become localized at the impurity centre, the fate of the carrier is determined, and therefore the capture probability is insensitive to the time required for further transitions to the ground state.

The time required for decay to the ground state can be an important consideration under some circumstances. In order to account for the behaviour of germanium and silicon rectifiers

at high injection levels, it is necessary to assume that the entire capture process, including the final transition, takes place in a time less than 10^{-11} sec. It is not easy to account for decay times as short as this by a multiphonon process. An alternative mechanism is that the energy is transferred to a nearby electron or hole by an Auger process. This idea is consistent with the observation that crystals having high luminescence efficiencies contain small free-carrier concentrations, thereby suppressing the Auger process sufficiently for radiative transitions to be able to compete.

The kinetics of multiphonon recombination at impurity centres has received considerable attention.^{2, 36-41} We will review briefly some of the characteristic features of this process.

The simplest case concerns the low-level behaviour of a semiconductor where recombination takes place at a single set of energy levels. It is assumed that the equilibrium carrier concentrations are controlled by donors and acceptors which play no part in the recombination process. When the concentration, M , of the recombination centres is sufficiently small, the electron and hole lifetimes are equal and are given by

$$\tau = \frac{\tau_f(n + n_r) + \tau_e(p + p_r)}{n + p} \quad \dots (17)$$

In strongly n -type material, the lifetime has a 'plateau' value, $\tau_f = (MB_n)^{-1}$, which is limited by capture of holes at centres which are full of electrons. A similar plateau lifetime, τ_e , is found in strongly p -type semiconductors, due to electron capture at empty centres. For intermediate concentrations of electrons and holes, the lifetime depends upon the free carrier concentration, generally showing a maximum for intrinsic material, as shown in Fig. 1. The quantity $n_r = n_i^2/p_r$ measures the position of the energy level of the recombination centre in the for-

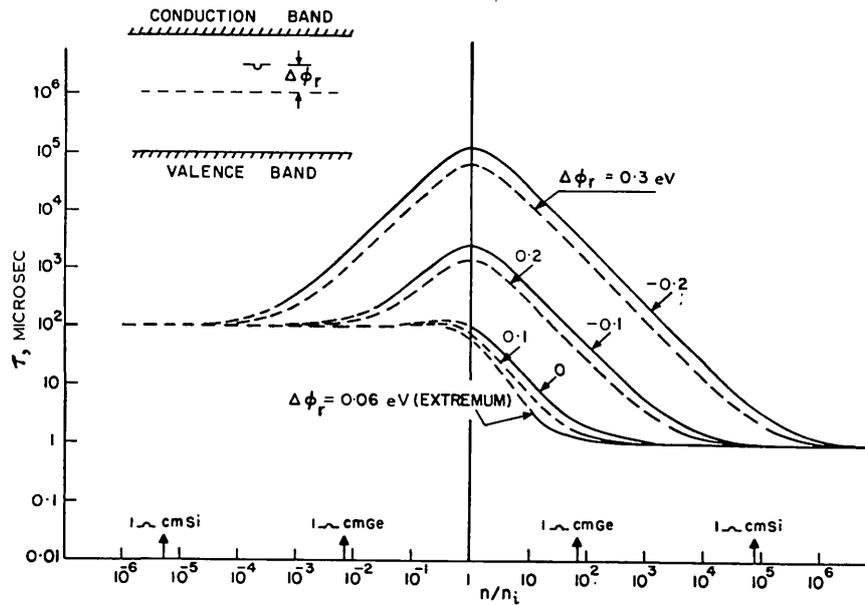


Fig. 1.—Lifetime due to multiphonon recombination at a single set of energy levels.

The dashed portions of the curves indicate regions where less than half of the recombination centres contain electrons.

$T = 300^\circ \text{K}$. $\tau_e = 100$ microsec. $\tau_f = 1$ microsec.

$\Delta\phi_r$	n_r/n_i
0.3	125 000
0.2	2 500
0.1	50
0.06	10
0	1
-0.1	0.02
-0.2	0.0004

bidden band. It is the free-electron concentration that would cause the Fermi level to coincide with this energy level.

Eqn. (17) is valid for $M \ll n_r + p_r$. For larger concentrations of recombination centres, the electron and hole lifetimes differ. The steady-state lifetime for electrons, for example, is given by

$$\tau_n = \frac{\tau_f(n + n_r) + \tau_e(p + p_r) + M\tau_e p_r / (p + p_r)}{p + n + M(p/p_r + 2 + n/n_r)} \quad (18)$$

Two time-constants appear in the transient response of semiconductors containing large concentrations of recombination centres.^{40, 41} The larger of these reduces to eqn. (17) in the limit $M \rightarrow 0$.

Under high-level injection conditions, where the electron and hole concentrations are nearly equal and large compared with M , n_r and p_r , the carrier lifetime assumes a constant value

$$\tau_\infty = \tau_e + \tau_f \quad (19)$$

Two interesting features of the steady-state lifetimes may be mentioned. For an impurity concentration such that $n = n_r \tau_f / \tau_e$, the electron and hole lifetimes are both equal to the high-level lifetime, regardless of the injection level or the concentration of recombination centres. Furthermore, if $n > n_r \tau_f / \tau_e$, the electron lifetime is always equal to or greater than the hole lifetime.

Real recombination centres generally give rise to more than one level in the forbidden band of the semiconductor. Nevertheless, the observed variation of lifetime with free carrier concentration and temperature is similar to that of the one-level model discussed above.⁴² This result is consistent with analyses of centres giving rise to more than one energy level.^{39, 43} Several reviews of the properties of recombination have recently appeared.⁴⁴⁻⁴⁶

Analyses of the response of photoconductors sometimes lead to conclusions regarding carrier lifetime which appear to be at variance with some of the foregoing generalizations. One reason for these differences is that it is customary to assume that the energy gap is sufficiently large compared with kT for thermal excitation of either electrons or holes from the recombination centres to be negligible.^{47, 48} In addition, attention is focused upon cases where the free carrier concentration is small compared with the concentration of recombination centres, whereas the opposite situation is usually considered in dealing with semiconductors. Lack of precise definition of the term 'lifetime' can lead to misinterpretation, as discussed in Section 2.

(7) AUGER RECOMBINATION INVOLVING FREE CARRIERS

Collisions between two free electrons and a hole, or vice versa, may limit the lifetime in semiconductors having small energy gaps, the recombination energy being carried off by the extra electron or hole. The recombination rate for this process may be written

$$r = \beta_n n^2 p + \beta_p n p^2$$

$$\text{or} \quad R = \beta_n (n^2 p - n_0^2 p_0) + \beta_p (n p^2 - n_0 p_0^2) \quad (20)$$

where the coefficient β_n ($\text{cm}^6 \text{sec}^{-1}$) represents the probability when the extra carrier is an electron. Since it is necessary that momentum as well as energy be conserved in such an interaction, the three carriers which initiate the recombination process must have kinetic energies which are significantly greater than thermal, unless the interaction also involves lattice phonons.

We can obtain an estimate of the magnitude of β_n by considering the probability for the inverse process, impact ionization. At thermal equilibrium, the rate at which carriers disappear by Auger recombination is equal to the average over

the Boltzmann distribution of the rate at which pairs are created by electrons that have the necessary thermal energy. Thus,

$$\beta_n n^2 p = \int_0^\infty P(W) \frac{dn}{dW} dW \quad (21)$$

where $P(W)$ is the probability per unit time that an electron having energy W will suffer an ionizing collision. $P(W)$ has been evaluated by Franz.⁴⁹ It has the form

$$P(W) = \frac{me^4}{2\hbar^3} G \left(\frac{W}{W_t} - 1 \right)^\nu \quad (22)$$

G is a dimensionless parameter somewhat smaller than unity which depends in a complicated way upon the band structure of the semiconductor. The exponent, ν , is an integer which is determined by the symmetry in momentum space at the energy threshold, W_t . For the case analysed by Franz, $\nu = 2$, W_t is also dependent upon the band structure; it is generally believed^{49, 50, 51} to be approximately $3W_g/2$. Evaluation of eqn. (21) gives

$$n_i^2 \beta_n = \frac{\nu}{\sqrt{\pi}} \frac{me^4}{\hbar^3} G \left(\frac{kT}{W_t} \right)^{\nu-1/2} \exp(-W_t/kT) \quad (23)$$

Assuming $\nu = 2$ and $G = 0.1$, we obtain

$$n_i^2 \beta_n \simeq 4.67 \times 10^{15} \left(\frac{kT}{W_t} \right)^{3/2} \exp(-W_t/kT) \text{sec}^{-1} \quad (24)$$

It should be emphasized that the approximations made in the derivation of this expression could easily introduce errors of one or two factors of ten. Nevertheless, it should be helpful in providing a semi-quantitative estimate of the magnitude and temperature dependence of the coefficient for Auger recombination. Calculations based upon estimates of the ionization probability by Wolff⁵¹ and Seitz⁵² give results that are in close agreement with eqn. (24). A more detailed calculation for the probability for Auger recombination in InSb has recently been obtained by Beattie and Landsberg.⁵³

Calculating the lifetime from eqns. (2) and (20) we find

$$\tau = \frac{1}{n^2 \beta_n + 2n_i^2 (\beta_n + \beta_p) + p^2 \beta_p} \quad (25)$$

If $\beta_n = \beta_p$, the lifetime has its maximum value at $n = p = n_i$ and decreases as the square of the majority-carrier concentration in the extrinsic ranges. If these two coefficients are unequal, the lifetime will remain at approximately the intrinsic value in either the n -type or the p -type region as the carrier concentration is increased until $p/n = 2\beta_n/\beta_p$, before entering the region of quadratic decrease.

In the intrinsic range the lifetime is given by

$$\tau_i = \frac{1}{3n_i^2 (\beta_n + \beta_p)} \simeq 3.6 \times 10^{-17} \left(\frac{W_t}{kT} \right)^{3/2} \exp(W_t/kT) \text{sec} \quad (26)$$

We note that the intrinsic lifetime is strongly dependent upon temperature and energy gap. The temperature dependence should be more rapid than n_i^{-2} , in most cases varying approximately as n_i^{-3} . This behaviour offers a convenient method for determining experimentally whether the lifetime is limited by Auger recombination or by other processes. Room-temperature intrinsic lifetimes calculated from eqn. (26) are shown in Fig. 2.

For samples which are sufficiently extrinsic, eqn. (25) shows that the lifetime decreases as the square of the majority-carrier

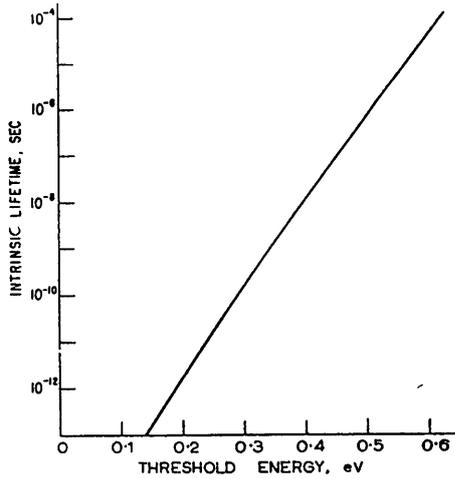


Fig. 2.—Lifetime due to Auger recombination of free electrons and holes in an intrinsic semiconductor at 300° K.

concentration. The temperature dependence in this range is less rapid than in the intrinsic region. Nevertheless, the lifetime should still show a moderately rapid decrease with increasing temperature to the extent that W_i exceeds the energy gap.

Lifetimes which are apparently limited by Auger recombination have been reported for a number of semiconductors. Measurements of InSb by Zitter *et al.*⁵⁴ indicate an intrinsic lifetime which is approximately 2×10^{-8} sec at room temperature and which increases rapidly with decreasing temperature. The behaviour of the lifetime in Te in the intrinsic and extrinsic ranges is likewise characteristic of Auger recombination.⁵⁵ Moss⁵⁶ has reported measurements of lifetime in extrinsic crystals of PbS which show an inverse-square-law dependence upon the majority-carrier concentration. These results are consistent with the behaviour indicated by Fig. 2, within the rather large uncertainties which are involved.

At high injection levels, where $n = p \gg n_i$, the lifetime becomes

$$\tau_{(high-level)} = \frac{1}{n^2(\beta_n + \beta_p)} = \frac{3n_i^2}{n^2}\tau_i \quad (27)$$

Since this lifetime decreases as the square of the carrier concentration, Auger recombination is likely to become the dominant process when large concentrations of carriers are injected into a semiconductor. In the case of germanium at room temperature, eqns. (26) and (27) indicate that the lifetime in the presence of $10^{18}/\text{cm}^3$ injected holes and electrons should be of the order of 1 microsec, assuming $W_i = 3W_g/2$. This is comparable with the lifetime which is observed under these conditions, as noted at the end of Section 3, and indicates that Auger recombination may be of importance in germanium under conditions of very-high-level injection, particularly at elevated temperatures. In semiconductors with smaller band gaps, this mechanism can be expected to be dominant at smaller injection levels.

(8) AUGER RECOMBINATION AT IMPURITIES

The energy released when an electron or hole is captured at an impurity centre can be transferred to another electron or hole which happens to be in the neighbourhood. The capture rates for such an Auger process will be proportional to the product of the two carrier concentrations. The equation analogous to eqn. (13) which describes the rate of capture of

electrons in material having a concentration, N , of empty centres is

$$r_n = N(n^2\beta_{nn} + np\beta_{np}) \quad (28)$$

β_{nn} and β_{np} represent the capture probabilities (cm⁶/sec) for electrons when the energy is carried off by another electron or hole respectively. A similar expression, involving coefficients β_{pn} and β_{pp} , describes the capture of holes at filled centres.

The kinetics of recombination due to Auger recombination at impurities can be worked out using procedures analogous to those which have been applied to multiphonon recombination.^{36, 37} The resulting expression for the net recombination rate under steady-state conditions is given by

$$R = M(np - n_i^2) \left(\frac{n + n_r}{n\beta_{pn} + p\beta_{pp}} + \frac{p + p_r}{n\beta_{nn} + p\beta_{np}} \right)^{-1} \quad (29)$$

M , n_r and p_r have the same significance as in Section 6. When M is small enough for charge storage to be neglected, the free-carrier lifetime under low-level conditions is given by eqn. (17), except that the plateau lifetimes, instead of being independent of the carrier concentration, are given by

$$\begin{aligned} \tau_f^{-1} &= M(n\beta_{pn} + p\beta_{pp}) \\ \tau_e^{-1} &= M(n\beta_{nn} + p\beta_{np}) \end{aligned} \quad (30)$$

Thus, the variation of lifetime with carrier concentration is similar to that for multiphonon recombination, except that it decreases indefinitely with increasing concentration of free electrons or holes.

In the simple situation where all the β -values are equal, the low-level lifetime becomes

$$\tau = \frac{n + n_r + p + p_r}{M\beta(n + p)^2} \quad (31)$$

The high-level lifetime is given by

$$\tau_\infty = \frac{1}{Mn\beta} \quad (32)$$

Values for β have been calculated by Pincherle,⁵⁷ Bess⁵⁸ and Nagae.⁵⁹ The latter estimates a value of 2×10^{-27} cm⁶/sec for β_{nn} or β_{pp} for impurities giving rise to energy levels of approximately $\frac{1}{4}$ eV from the conduction or valence band respectively. β_{np} and β_{pn} should be of this same general magnitude in semiconductors such as germanium and silicon, in which band-to-band transitions are indirect, but may be larger by a factor of 10^4 in materials characterized by direct transitions.

These calculations of Auger recombination coefficients should be regarded as order-of-magnitude estimates, since they depend rather critically upon the wave functions that are used to describe the recombination centre. In general, they indicate that the β -values should vary approximately as the inverse cube of the capture energy, and that they should not be strongly temperature dependent.

The values for the high-level lifetimes in germanium and silicon discussed at the end of Section 3 provide upper limits for the Auger recombination coefficients in these materials. Assuming a concentration of recombination centres of $M = 10^{11}/\text{cm}^3$, eqn. (32) indicates $\beta < 10^{-24}$ cm⁶/sec, a value which is consistent with the theoretical estimates. Values as small as 10^{-32} to 10^{-34} cm⁶/sec are indicated by trapping experiments in silicon.^{60, 61} The smallness of the latter quantities may be attributed to the effects of coulomb repulsion if the trapping centres are suitably charged.⁶²

The foregoing discussion indicates that Auger recombination

at impurity centres in semiconductors can be expected to be negligible in comparison with multiphonon recombination under almost all circumstances. Exceptions to this statement may result from impurities which do not give rise to the shallow excited states that seem to be necessary for multiphonon recombination. Since these shallow states are not to be expected in the case of centres which have a repulsive coulomb field, it is reasonable to suppose that they should behave as traps (i.e. that the capture probability for one type of carrier should be very much smaller than for the other). For such centres, Auger capture of one type of carrier should be observable under suitable circumstances, while the other kind of carrier would be captured by a multiphonon process.

Under certain circumstances, an Auger process having a large capture probability can be expected to occur at impurities which give rise to several charge states.⁶³

(9) CONCLUSIONS

Two of the important recombination processes are intrinsic properties of the semiconductor material. While radiative recombination is well understood and has been unambiguously observed in a number of semiconductors, the experimental evidence regarding Auger recombination is quite meagre. The latter can be expected to become the dominant process in semiconductors with small energy gaps when large carrier concentrations are present. A characteristic feature which can be used to identify it experimentally is a strong temperature dependence, even in the extrinsic range.

With the concentrations of recombination centres that are normally found in most semiconductors, the lifetime is almost invariably limited by multiphonon recombination. Radiative and Auger processes involving impurity centres can sometimes contribute significantly to the recombination rate in large-band-gap materials. In particular, it appears that they can sometimes play an important part as one of the intermediate steps in multiphonon recombination.

The relative magnitudes of these processes at room temperature are compared in Figs. 3 and 4, for germanium and for a hypothetical semiconductor having the same energy gap and intrinsic carrier concentration, but in which band-to-band transitions are direct. A material which closely approximates the latter is GaSb. In these diagrams, (a) represents free carrier radiative recombination with $B = 3.4 \times 10^{-14}$ and $3.0 \times 10^{-11} \text{ cm}^3/\text{sec}$ respectively; (b) represents the Auger process in the host crystal as calculated from eqns. (24) and (25) with $W_i = 1.0 \text{ eV}$. Multiphonon recombination at impurities, (c), is assumed to be the same in both materials and is patterned after the behaviour which is typical of germanium; (d) represents Auger recombination at impurities, as calculated from eqns. (17) and (30). For this process, it is assumed that there are $10^{11}/\text{cm}^3$ recombination centres lying in the middle of the energy gap and that all the β -values are equal to $10^{-27} \text{ cm}^6/\text{sec}$, except that β_{np} and β_{pn} are larger by a factor of 10^4 in the 'direct' semiconductor. Fig. 4 indicates that radiative recombination is likely to be the dominant process in crystals which permit direct band-to-band transitions, provided that the concentration of recombination centres can be made as small as it is in germanium.

It is evident that there are several areas where our understanding of recombination processes is unsatisfactory. This is particularly true for semiconductors having very large concentrations of free electrons or holes. Studies of recombination in large-band-gap semiconductors containing few free carriers should shed light upon some of the mechanisms involved in multiphonon recombination.

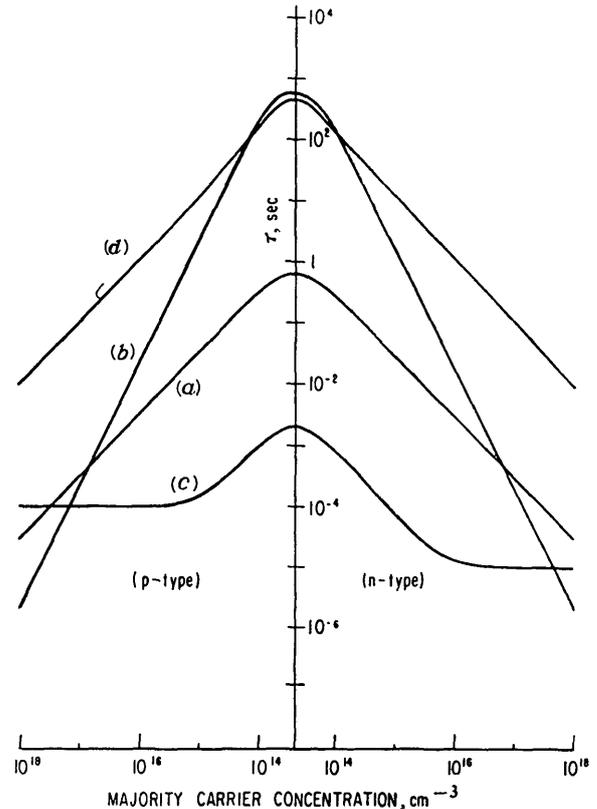


Fig. 3.—Comparison of recombination processes at room temperature in germanium.

Estimated lifetimes as limited by (a) radiative and (b) Auger recombination in the host crystal, and (c) multiphonon and (d) Auger (4) recombination at impurities.

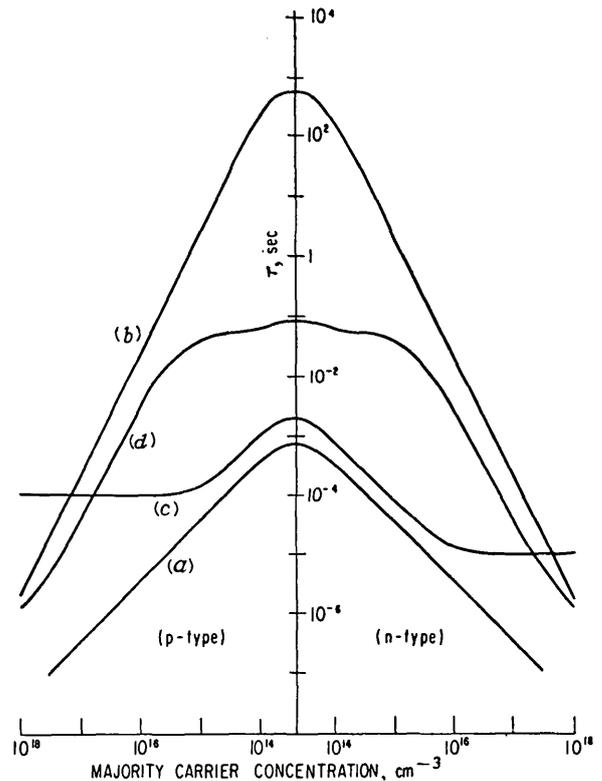


Fig. 4.—Comparison of recombination processes at room temperature in a semiconductor similar to germanium but having direct band-to-band transitions.

Estimated lifetimes as limited by (a) radiative and (b) Auger recombination in the host crystal, and (c) multiphonon and (d) Auger recombination at impurities.

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