Steady-State Recombination via Donor-Acceptor Pairs*

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The steady-state recombination rate for recombination via donor-acceptor pairs is worked out using a phenomenological model similar to that employed by Shockley and Read for single, isolated defects. Simplified expressions are given for the extrinsic case, for very small injection levels, and for very large injection levels. The effect of pair recombination on diode current and injection electroluminescence is also considered. The results are compared with the Shockley-Read mechanism wherever meaningful comparisons can be made.

I. INTRODUCTION

IF by some means a nonequilibrium carrier density is produced in a semiconductor, the system will tend to revert to equilibrium by recombination or its inverse, regeneration. Recombination can occur either by direct electron-hole annihilation or by indirect processes involving interactions between electrons and holes with crystalline imperfections such as impurities, dislocations, or vacancies.[1] The direct process is usually very inefficient in comparison with recombination at imperfections.[2]

The most widely and successfully applied model for recombination in semiconductors is the phenomenological model of Shockley, Read, and Hall.[3] In this model, the recombination process is imagined to consist of alternate capture of electrons and holes by the recombination center, and generation is imagined to consist of alternate emission of electrons and holes. The steady-state lifetime is calculated in terms of the capture and emission probabilities. The latter are activation processes, i.e., they are governed by the activation energy E_A of the defect under consideration [$\propto \exp(-E_A/kT)$]. This model has been extended to include the transient lifetime[4] for the case of singly ionizable defects and the steady-state lifetime of defects capable of more than two charge states.[5]

The importance of close donor-acceptor pairs as effective recombination centers has been demonstrated by Prenner and Williams[6] with ZnS phosphors and by Thomas and Hopfield[7] and others with GaP. This recombination mechanism appears also to be present in germanium and silicon[8] and may also be responsible for the broad 1.28-eV emission from GaAs diodes.[9]

The transient properties of recombination via donor-acceptor pairs has been worked out by Thomas, Hopfield, and Calbow.[10] Their results provide a valuable technique for studying recombination of this type when the donor-acceptor transition is radiative. It would also be helpful to know the steady-state properties of pair recombination in order to assess the effect of pair recombination on various steady-state phenomena (e.g., diode properties,[11] photoluminescence, and electroluminescence[12]). In this paper the steady-state recombination rate (or lifetime) is calculated for close-pair recombination along the lines suggested by Shockley *et al.*,[3,5] and several limiting cases for which the expressions are greatly simplified are then considered. The effect of pair recombination on diode current-voltage characteristics is also considered.

II. CALCULATION OF RECOMBINATION RATE

The model employed is very simple. It is assumed that the donor can capture an electron and the acceptor a hole (in either order) and that there is a nonvanishing probability that the electron can make the transition from the donor to the nearby acceptor. We are interested in the net recombination rate resulting from this mechanism. If we consider the donor-acceptor pair as a single defect, it is seen to be quite similar to a flaw of the Sah-Shockley type,[5] having three possible charge states $(+1, 0, -1)$ and two energy levels, except that the pair

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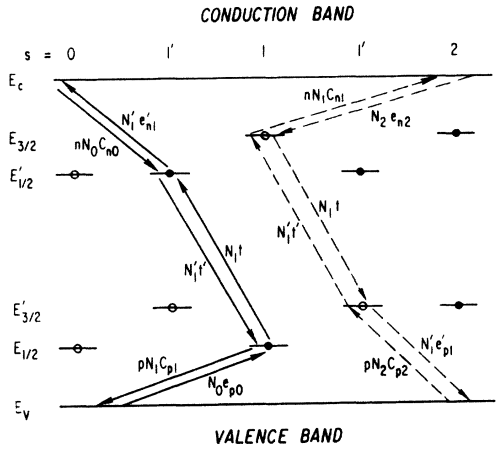

FIG. 1. Energy-level diagram depicting the various transitions giving rise to recombination or generation via a donor-accptor pair. The unperturbed donor and acceptor levels are $E_{1/2}'$ and $E_{3/2}'$ and the perturbed levels are $E_{1/2}$ and $E_{3/2}$, respectively. The s value denotes the occupancy of the complex, $s=1'$ meaning the donor is occupied and the acceptor is not.

defect has an additional energy level. Since the middle charge state has associated with it two possible configurations (neglecting spin degeneracy), we can speak of the configuration when the donor is occupied and the acceptor unoccupied as the excited state.

The model is illustrated diagrammatically in Fig. 1, where s designates the charge state, or occupancy, of the pair and is arbitrarily taken as zero for strongly p-type material. It is necessary to consider two possible paths in Fig. 1. In the left-hand path, only the two lower charge states are considered, i.e., the possible s values are 0, 1, and 1′, where 1′ refers to the excited state of the neutral condition. This path is most important for p-type material when both levels tend to be unoccupied. In this case, an excess electron starting from the conduction band and cascading to the valence band causes the center to go through the following transitions: $(s=0)\rightarrow(s=1')\rightarrow(s=1)\rightarrow(s=0)$. In the right-hand path, s is limited to 1, 1′, and 2, and an excess hole cascading from the valence band to the conduction band causes the center to go through the following transitions: $(s=2)\rightarrow(s=1')\rightarrow(s=1)\rightarrow(s=2)$. Both paths have one section in common, viz., $(s=1')\rightarrow(s=1)$, but in steady state the net rate of centers entering the common section from the left is equal to the rate of those leaving on the left (although they may not be the same centers); the same is true for the right. In Fig. 1, when a transition is represented as a hole rather than an electron transition, dashed lines are used.

The energy levels, labeled $E_{3/2}$ and $E_{3/2}'$ in Fig. 1, are higher, respectively, than $E_{1/2}'$ and $E_{1/2}$ (the notation is similar to that of Sah and Shockley[5]). This shift is due to the Coulombic interaction and amounts to about q^2/Kr, where q is the electronic charge, K the dielectric constant, and r the distance between the donor and acceptor. The unperturbed donor activation energy E_D is approximately equal to E_c, the bottom of the conduction band, less $E_{1/2}'$, since $E_c-E_{1/2}'$ is the energy required to remove an electron from a donor when the nearby acceptor is unoccupied, hence, neutral. Similarly, the acceptor activation energy is $E_A\approx E_{3/2}'-E_V$, where E_V is the top of the valence band. The energy corresponding to the $1'\rightarrow 1$ transition is, of course,

$$E\approx E_g-(E_A+E_D)+\frac{q^2}{Kr}. \tag{1}$$

as already pointed out by Thomas and Hopfield and others.[7] In Eq. (1), E_g is the energy gap. The quantities to the left or right of the arrows in Fig. 1 are expressions for the corresponding transition rates. We have adopted the nomenclature of Sah and Shockley[5] in a slightly modified form to accommodate the excited state. The quantities N_0, N_1', N_1, and N_2 are the concentrations of the pairs in the states $s=0$, 1′, 1, and 2, respectively. The notations for capture probability and emission probability are C for capture and e for emission, with the first subscript designating electron (n) or hole (p) and the second subscript designating the value of s before the event; e.g., C_{n0} is the capture probability for electrons by a pair in the state $s=0$ and e_{p1}' is the probability that a pair in the state $s=1'$ will emit a hole. Since the energies $E_{1/2}'$, etc., correspond to transitions between two adjacent s values, the subscript used is the average, i.e., $\frac{3}{2}$ for $(s=1)\rightarrow(s=2)$, etc. Here, again, the prime indicates that one end of the transition is the $s=1'$ state.

A. Assumptions

The following conditions are assumed: (a) All excited states, other than state 1′ described earlier, have very fast relaxation times.[8] (b) No transitions occur directly between the donor and valence band or the acceptor and conduction band. (c) All pairs considered have the same separation unless otherwise stated. (d) Each pair is isolated from all other pairs.

Assumption (b) is most likely to be valid for shallow donors and acceptors and for large energy gaps. Assumption (c) is made for mathematical convenience. The effect of a statistically varying separation is to broaden the energy levels $E_{1/2}$ and $E_{3/2}$ and to necessitate considering a distribution of capture constants for C_{n1} and C_{p1} and of emission probabilities e_{p0} and e_{n2}, rather than discrete values of these parameters. This also, of necessity, broadens the $1'\rightarrow 1$ transition. (The parameters $E_{1/2}'$, $E_{3/2}'$, C_{n0}, C_{p2}, and, consequently, e_{n1}' and e_{p1}' are unaffected by the separation to first order.) Assumption (d) can be considered a fairly good approximation even for a random distribution (no ion pairing) since each donor is most likely to interact with its nearest acceptor. If the donor and acceptor concentrations are too large, this assumption may break down, and the levels $E_{1/2}'$ and $E_{3/2}'$ will no longer represent the unperturbed donor and acceptor levels. If the donor and

TABLE I. Analogous terms.

$n \leftrightarrow p$	$n_{1/2}' \leftrightarrow p_{3/2}'$
$C_{n0} \leftrightarrow C_{p2}$	$n_{3/2} \leftrightarrow p_{1/2}$
$C_{n1} \leftrightarrow C_{p1}$	$t' \leftrightarrow t'$
$e_{n2} \leftrightarrow e_{p0}$	$t \leftrightarrow t$
$e_{n1}' \leftrightarrow e_{p1}'$	$N \leftrightarrow N$

acceptor concentrations are not equal, the concentration of the minority impurity becomes the effective pair concentration N.

B. Calculation

The principle of detailed balance[2,13] requires that in equilibrium each transition and its inverse (Fig. 1) occur at equal rates, i.e.,

$$\begin{aligned} e_{n1}'N_1' &= nC_{n0}N_0, \\ e_{n2}N_2 &= nC_{n1}N_1, \\ N_1 t &= N_1' t', \\ e_{p0}N_0 &= pC_{p1}N_1, \\ e_{p1}'N_1' &= pC_{p2}N_2, \end{aligned} \tag{2}$$

where t and t' are, respectively, the probability of the transition $1' \rightarrow 1$ and its inverse. From these relationships we find the following two useful equations connecting the capture constants and the emission probabilities:

$$n_i^2 C_{n0} C_{p1} t' = e_{p0} e_{n1}' t, \tag{3}$$

$$n_i^2 C_{n1} C_{p2} t' = e_{p1}' e_{n2} t, \tag{4}$$

where n_i is the intrinsic carrier density. The net steady-state recombination rate U is

$$U = N_1' t' - N_1 t, \tag{5}$$

since, regardless of which path in Fig. 1 is followed, the transition $1' \rightarrow 1$ must occur in order to bring about recombination. It is convenient to divide U into two components,

$$U = U_{1/2} + U_{3/2}, \tag{6}$$

where $U_{1/2}$ is the net rate of $0 \rightarrow 1'$ transitions and $U_{3/2}$ represents the $2 \rightarrow 1'$ transitions. From Eqs. (5) and (6) and the fact that the transition rate into a state is equal to the transition rate out of it, we can write six independent equations. One possible set is

$$\begin{aligned} nC_{n1}N_1 - e_{n2}N_2 &= U_{3/2}, \\ nC_{n0}N_0 - e_{n1}'N_1' &= U_{1/2}, \\ t'N_1' - tN_1 &= U_{3/2} + U_{1/2}, \\ nC_{n1}N_1 + e_{p1}'N_1' - (pC_{p2} + e_{n2})N_2 &= 0, \\ (nC_{n0} + e_{p0})N_0 - pC_{p1}N_1 - e_{n1}'N_1' &= 0, \\ N_0 + N_1 + N_1' + N_2 &= N. \end{aligned} \tag{7}$$

These equations can be solved for $U_{3/2}$, $U_{1/2}$, and, consequently, U as functions of the capture constants, emission probabilities, and carrier densities. The resulting expressions are complicated but can be simplified considerably by the application of Eqs. (3) and (4).

It is sometimes convenient to express the emission probabilities in terms of a temperature-dependent parameter with dimensions of "carrier density," multiplied by an appropriate capture constant. This enables one to calculate the emission probabilities if the capture constants are known. We therefore define $n_{1/2}'$ as the carrier density when the Fermi level F is at $E_{1/2}'$, and $p_{3/2}'$ as the carrier density when $F = E_{3/2}'$. Then, since for nondegenerate statistics

$$n = n_i \exp\left(\frac{F - E_i}{kT}\right), \tag{8}$$

where E_i is the intrinsic Fermi level, we have

$$n_{1/2}' = n_i \exp\left(\frac{E_{1/2}' - E_i}{kT}\right) = n \exp\left(\frac{E_{1/2}' - F}{kT}\right). \tag{9}$$

From the principles of statistical mechanics[5,13] it can be shown that, in equilibrium,

$$\frac{N_0}{N_1'} = \exp\left(\frac{E_{1/2}' - F}{kT}\right). \tag{10}$$

Hence, from Eqs. (2), (9), and (10), it follows that $e_{n1}' = n_{1/2}' C_{n0}$. Expressions for the other three emission probabilities are obtained in the same manner. The four expressions are

$$\begin{aligned} e_{n1}' &= n_{1/2}' C_{n0}, \quad & e_{n2} &= n_{3/2} C_{n1}, \\ e_{p0} &= p_{1/2} C_{p1}, \quad & e_{p1}' &= p_{3/2}' C_{p2}. \end{aligned} \tag{11}$$

From Eqs. (3), (4), (7), and (11), the following expression is obtained for the steady-state recombination rate

$$\begin{aligned} U = \{ & N(np - n_i^2) t' [(nC_{n0} + p_{1/2}C_{p1}) C_{n1} C_{p2} + (pC_{p2} + n_{3/2}C_{n1}) C_{n0} C_{p1}] \} \\ & \div \{ (pC_{p2} + n_{3/2}C_{n1}) [np + n_{1/2}' p_{1/2}) C_{n0} C_{p1} + t' pC_{p1} + n_{1/2}' C_{n0} (t + pC_{p1})] \\ & + (nC_{n0} + p_{1/2}C_{p1}) [(np + n_{3/2}p_{3/2}') C_{n1} C_{p2} + t' nC_{n1} + p_{3/2}' C_{p2} (t + nC_{n1})] \\ & + (t + t')(nC_{n0} + p_{1/2}C_{p1})(pC_{p2} + n_{3/2}C_{n1}) + nn_{1/2}' (pC_{p2} + p_{1/2}C_{p1}) C_{n0} C_{n1} + pp_{3/2}' (nC_{n0} + n_{3/2}C_{n1}) C_{p1} C_{p2} \}. \end{aligned} \tag{12}$$

Although Eq. (12) is cumbersome, the symmetry between analogous n and p quantities is obvious. Analogous quantities are given in Table I. If a transformation is performed by replacing each term by its analogous term, Eq. (12) remains unchanged. For example, if Eq. (12) were simplified for p-type material by neglect-

[13] See, for example, C. Kittel, *Elementary Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1958).

ing certain unimportant terms, then the corresponding expression for n-type material could be obtained by performing this transformation.

III. SPECIAL CASES

We will first consider the relative magnitude of t' and t. From Eqs. (3), (4), and (11),

$$\frac{t'}{t}=\frac{p_{1/2}n_{1/2}'}{n_i^2}=\frac{p_{3/2}'n_{3/2}}{n_i^2}, \tag{13}$$

whence, from Eq. (9) and similar relations,

$$\frac{t'}{t}=\exp\left(\frac{E_{1/2}'-E_{1/2}}{kT}\right)=\exp\left(\frac{E}{kT}\right), \tag{14}$$

where E is the energy associated with the (1',1) transition. Thus, for fairly large energy gaps and shallow donors and acceptors, t' is much greater than t and we can neglect the terms multiplied by t in the denominator of Eq. (12).

A. Extrinsic Case

For the extrinsic p-type case, the equilibrium hole concentration, p_0, is much greater than the equilibrium electron concentration, n_0; i.e., $p_0 \gg n_0$. For moderately to strongly p-type material such that

$$p \gg p_{1/2}, \quad \text{and} \quad p \gg n_{3/2}\frac{C_{n1}}{C_{p2}}, \tag{15}$$

while $C_{n1}<C_{n0}$ or C_{p2} and for moderate injection levels such that

$$n_i \ll n \ll \frac{C_{n1}}{C_{n0}}n_{3/2}, \quad \text{and} \quad n \ll (n_{1/2}'p_{1/2}+np)\frac{C_{n0}}{t'}, \tag{16}$$

Eq. (12) reduces to

$$U \approx \frac{nNC_{n0}t'}{(n+n_{1/2}')C_{n0}+t'}. \tag{17}$$

If, furthermore, $t' \gg (n+n_{1/2}')C_{n0}$, Eq. (17) becomes

$$U \approx nNC_{n0}. \tag{18}$$

Expressions analogous to Eqs. (17) and (18) can be obtained for n-type material by substituting as shown in Table I. Note that Eq. (18) is the same expression as that obtained for Shockley-Read centers in strongly p-type material. The condition that C_{n1} or $C_{p1}<C_{n0}$ or C_{p2} is highly favored because of Coulomb attraction.

The temperature dependence of Eq. (17) implies a thermal quenching effect. The only strongly temperature-dependent term is

$$n_{1/2}'=N_c \exp[-(E_c-E_{1/2}')/kT],$$

where N_c is the effective density of states in the conduction band and E_c is the bottom of the conduction band. Thus, U is essentially constant at sufficiently low temperatures, but at higher temperatures $n_{1/2}'C_{n0}$ eventually overtakes the other terms and U decreases with increasing temperature with an activation energy of E_D or E_A according to whether the material is p or n type.

B. Very Large Injection Levels

For very large injection levels the donors and acceptors become essentially nonionized (state 1') and the recombination rate is determined solely by the transition probability t'. The asymptotic solution of Eq. (12) for large n and p is

$$U=Nt'\left(1+\frac{t'+n_{1/2}'C_{n1}+p_{3/2}'C_{p1}}{nC_{n1}+pC_{p1}}\right)^{-1}. \tag{19}$$

This leads to the saturation value of Nt' at sufficieatly high injection levels.

C. Carrier Lifetime for Small Injection

The small injection lifetime τ is by definition

$$\tau=\delta n/U, \tag{20}$$

where δn is the excess hole and electron concentration. Because of charge neutrality

$$n=n_0+\delta_n, \qquad p=p_0+\delta_n. \tag{21}$$

For the extrinsic p-type case ($p_0 \gg n_0$), Eq. (12) then gives

$$\tau_n \cong \frac{p_0^2C_{p2}X+p_0(XY+n_{1/2}'p_{1/2}C_{n1}C_{p2})+n_{1/2}'p_{1/2}ZC_{n1}}{Nt'p_0(p_0C_{p2}C_{n0}+C_{n1}Z)}, \tag{22}$$

where

$$X=t'+n_{1/2}'C_{n0},$$
$$Y=p_{1/2}C_{p2}+n_{3/2}C_{n1},$$
$$Z=p_{1/2}C_{p2}+n_{3/2}C_{n0}.$$

Equation (22) is quite accurate as long as, in addition to the extrinsic condition, the following conditions are satisfied:

$$n \ll t'/C_{n0},$$
$$p_{1/2} \gg n_i(C_{n0}/C_{p1}),$$
$$n_{3/2} \gg n_i(C_{n0}/C_{n1}).$$

The latter two conditions will nearly always be fulfilled if the donor and acceptor levels are not too close to the center of the gap. The analogous equation for extrinsic n-type material is obtained through a transformation based on Table I.

To illustrate the variation of τ_n as a function of majority carrier density, Eq. (22) is plotted in Fig. 2 for a hypothetical semiconductor in which $E_A=E_D=0.1$ eV. The electron and hole effective masses are 0.078 m_0 and 0.4 m_0, respectively, $t'=3\times10^6$ sec^{-1}, $n=10^{15}$ cm^{-3},

$r=44$ Å, $K=10$, $C_{n0}=C_{p2}=10^{-6}$ cm^3/sec, and $C_{n1}=C_{p1}=10^{-8}$ cm^3/sec. As in the case of the Shockley-Read statistics, the extrinsic lifetime is a monotonically decreasing function of the majority carrier density. [This can be verified generally by differentiating Eq. (22).] For Shockley-Read statistics, the extrinsic lifetime reduces to

$$\tau_n=\tau_{n0}(1+p_1/p_0),$$

where τ_{n0} is the lifetime for strongly p-type material and p_1 is the hole density when the Fermi level is at the recombination level. For purposes of comparison, we let $\tau_{n0}=1/NC_{n0}$ and $p_1=p_{3/2}'$ and obtain the two curves labeled SR-78°K and SR-300°K. The main differences, qualitatively, seem to be a "bump" for intermediate carrier densities and the much greater temperature dependence for pair recombination.

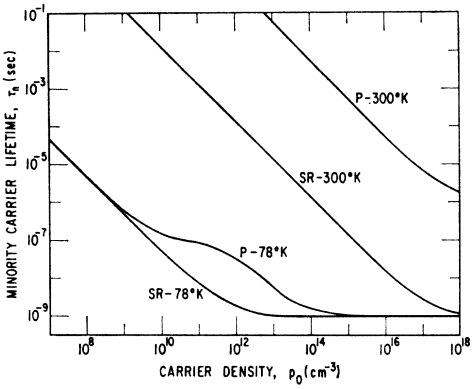

FIG. 2. Low-level minority-carrier lifetime for a hypothetical semiconductor, the characteristics of which are described in the text. The curves labeled P-78°K and P-300°K are for pair recombination at 78 and 300°K, respectively; SR-78°K and SR-300°K are for Shockley-Read statistics at these temperatures.

D. Application to Diodes

If recombination through pairs is the major process in a diode, then its effect on the voltage current curves should be pronounced. Since the region near the junction in diffused diodes is heavily compensated, it is conceivable that recombination via pairs is an important conduction mechanism in some cases. Even if pair recombination is not the major process for current flow, it may be the major process giving rise to injection luminescence in some cases.

1. *Reverse Bias*

In the case of reverse bias, n and p are negligible in the space charge region where the electric field quickly removes them. The reverse current is proportional to the generation rate which, from Eq. (12), is

$$-U=\frac{Nt}{1+t'/(n_{1/2}'C_{n0}+p_{3/2}'C_{p2})}, \tag{23}$$

where it has been assumed that t is very much smaller than t', $n_{3/2}C_{n1}$, and $p_{1/2}C_{p1}$. Equation (23) indicates that the form of the reverse current-voltage characteristics is the same as for Shockley-Read traps.[11] However, if the reverse current is measured as a function of temperature, Eq. (23) implies an activation energy of E if $t'\ll n_{1/2}'C_{n0}+p_{3/2}'C_{p2}$. But, at sufficiently low temperatures, this inequality is reversed and the activation energy lies in the range of $(E+E_D)$ to $(E+E_A)$. This result is somewhat similar to that obtained for a Shockley-Read trap,[11] in which case the generation rate has an activation energy equal to the energy difference between the trap and the farther band edge.

If the pair separations are treated as statistical variables, it can be shown that a plot of $\ln(-U)$ versus $1/T$ shows a similar behavior, except that the slopes obtained correspond approximately to infinite separation.

2. *Forward Bias*

In the space charge region, $np=n_i^2\exp(qV/kT)$, where V is the applied bias minus the IR drop. For a moderate or large bias such that $qV/kT\gg 1$ and both carrier densities in the space charge region are much greater than any of the quantities $p_{1/2}$, $n_{1/2}'$, $p_{3/2}'$, or $n_{3/2}$, we obtain from Eq. (12)

$$U=\frac{Nt'n_i\exp(qV/2KT)}{n_i\exp(qV/2kT)+Q}, \tag{24}$$

where

$$Q=\frac{\gamma(C_{p1}/C_{n0})(t'+C_{n0}n_{1/2}')+(1/\gamma)(C_{n1}/C_{p2})(t'+C_{p2}p_{3/2}')+t'+C_{n1}n_{1/2}'+C_{p1}p_{3/2}}{\gamma^{1/2}C_{p1}+\gamma^{-1/2}C_{n1}},$$

and $\gamma=p/n$.

Equation (24) must be integrated over the space charge region to obtain an expression for the recombination-generation current. However, since U peaks sharply near the center of the junction, the current is proportional to the value of U at its maximum. It is easy to show graphically that if $C_{n1}\ll C_{n0}$ and $C_{p1}\ll C_{p2}$ there are two maxima in Eq. (24) corresponding approximately to

$$\gamma=\frac{C_{n1}(t'+C_{p2}p_{3/2}')}{C_{p2}(t'+C_{n1}n_{1/2}'+C_{p1}p_{3/2}')},$$

and

$$\gamma=\frac{C_{n0}(t'+C_{n1}n_{1/2}'+C_{p1}p_{3/2}')}{C_{p1}(t'+C_{n0}n_{1/2}')}.$$

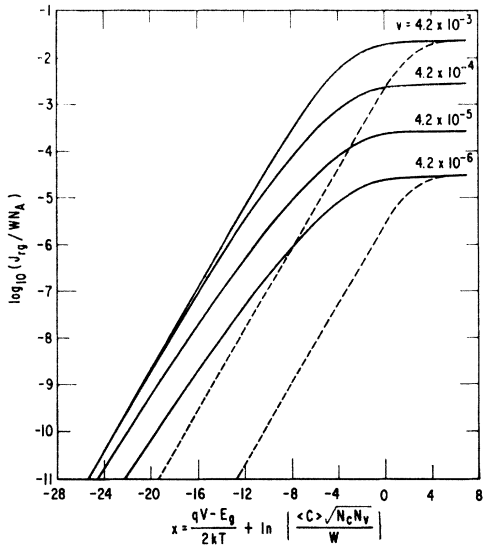

FIG. 3. Plots of the quantity J_{rg}/WN_A, which is proportional to the recombination-generation current in the depletion region of a diode in which pair recombination predominates. Each curve is labeled with the parameter v, which is proportional to the majority defect concentration, donors in this case. The solid curves are for the low-temperature regime, the dashed curves for the high-temperature regime.

Therefore, the recombination-generation current J_{rg} is approximately

$$J_{rg}\propto\frac{Nt'n_i\exp(qV/2kT)}{n_i\exp(qV/2kT)+Q'}, \tag{25}$$

where Q' is the smaller of

$$2\left(\frac{(t'+C_{n1}n_{1/2}'+C_{p1}p_{3/2}')(t'+C_{p2}p_{3/2}')}{C_{n1}C_{p2}}\right)^{1/2},$$

and

$$2\left(\frac{(t'+C_{n1}n_{1/2}'+C_{p1}p_{3/2}')(t'+C_{n0}n_{1/2}')}{C_{p1}C_{n0}}\right)^{1/2}.$$

Thus, the recombination-generation current in the space charge region varies as $e^{qV/2kT}$ as long as $qV/2kT$ is not too large or Q' is not too small. However, as the bias is increased, J_{rg} should eventually saturate unless other processes are encountered before saturation (strictly speaking the current would have a slight voltage dependence resulting from the change in depletion width). The saturation occurs rather abruptly, over a voltage range of less than 10 kT/q. Since the diffusion current has a steeper slope [$J_{\text{diff}}\propto\exp(qV/kT)$], it may overtake the space charge current before the saturation region is observed.

More realistically, the donor-acceptor separation may be nearly random. In this case, one would expect a more gradual transition to saturation. Equation (25), then, can be written in the form (for $N_A<N_D$)

$$J_{rg}\propto\int_0^\infty\frac{P(r)Nt'n_i\exp(qV/2kT)dr}{n_i\exp(qV/2kT)+Q'}, \tag{26}$$

where $P(r)dr$ is the probability that the distance between the acceptor and its closest donor is between r and $r+dr$. This probability can easily be shown to be

$$P(r)=4\pi r^2N_D\exp(-\tfrac{4}{3}\pi N_Dr^3). \tag{27}$$

Since t' is expected to be proportional to the square of the overlap of the hole and electron wave functions, we write

$$t'=W\exp[-(r/R)], \tag{28}$$

where W and R are constants, R being of the order of the radius of the larger state. If $t'\ll C_{n1}n_{1/2}'+C_{p1}p_{3/2}'$ (high-temperature regime), then Q' is independent of t' and Eq. (25) has the same form as Eq. (24) with Q' replacing Q. But if t' is much greater than $C_{n0}n_{1/2}'$ or $C_{p2}p_{3/2}'$ (low-temperature regime), then

$$Q'\cong t'/\langle C\rangle, \tag{29}$$

where $\langle C\rangle$ is the larger of $(C_{n1}C_{p2})^{1/2}/2$ and $(C_{p1}C_{n0})^{1/2}/2$. By substituting Eq. (29) into Eq. (26) and utilizing Eqs. (27) and (28), the recombination-generation current can be expressed as

$$\frac{J_{rg}}{WN_A}\propto e^x\int_0^\infty\frac{\exp(-z)dz}{1+\exp[x+(z/v)^{1/3}]}, \tag{30}$$

where

$$x=(qV-E_g)/2kT+\ln[\langle C\rangle(N_cN_v)^{1/2}/W],$$
$$v=\tfrac{4}{3}\pi N_DR^3,$$
$$z=v(r/R)^3.$$

The right-hand side of Eq. (30) has been evaluated by means of a computer. The results are plotted in Fig. 3 as a function of x for various values of the parameter v, assuming $\langle C\rangle$ is independent of the separation r. The curves for the high-temperature regime ($t'\ll C_{n1}n_{1/2}'+C_{p1}p_{3/2}'$) are shown as dashed lines (the quantity $\langle C\rangle Q'/W$ is taken to be 10). It is seen that in the low-temperature regime the slope of $\ln J_{rg}$ can be less than $q/2kT$ over an extended range if N_D or R is relatively small. (A reasonable estimate for R might be about 10 Å, in which case the value 4.2×10^{-5} for v corresponds to $N_D=10^{16}/\text{cm}^3$.) Equation (30) also implies that in the low-temperature regime the quantity $\beta=2[d(\ln J_{rg})/dx]^{-1}$ is independent of temperature, provided the current is kept constant.

For the diffusion current, assuming electron injection into a heavily doped p-type region, we utilize Eq. (17) with $n=n_p\exp[(qV/kT)-(x/L)]$. The quantity n_p is the equilibrium minority carrier density on the p side, and L is the electron-diffusion length. This gives for the

diffusion-current density J_D

$$J_D=q\int_0^\infty U(x)dx,$$

$$=q\int_0^\infty\int_0^\infty \frac{P(r)t'(r)NC_{n0}n_p\exp(qV/kT)\exp(-x/L)}{C_{n0}n_p\exp(qV/kT)\exp(-x/L)+n_{1/2}'C_{n0}+t'(r)}drdx. \quad (31)$$

Integrating first with respect to x yields

$$\frac{J_D}{qNL3vW}=\int_0^\infty \zeta^2\exp(-\zeta-v\zeta^3)\times\ln\left[1+\frac{\exp(y)}{A\exp(-\zeta)+1}\right]d\zeta, \quad (32)$$

where

$$\zeta=r/R,$$
$$y=[qV-(E_{1/2}'-E_V)]/kT+\ln(N_V/p_p),$$
$$A=W/C_{n0}n_{1/2}'.$$

From inspection of Eq. (32) it is seen that the diffusion current is proportional to $\exp(y)$ at a small bias and tends to saturate at large bias, although complete saturation does not occur. At very large bias the current varies linearly with bias.

The transition voltage region where the current is proportional to neither $\exp(y)$ nor y is centered about the transition voltage V_{tr} obtained by setting $\exp(y)=(A+1)$. This gives

$$qV_{tr}=E_g+kT\ln\left[\frac{p_p}{N_cN_V}\left(\frac{W}{C_{n0}}+n_{1/2}'\right)\right].$$

Thus, if $E_{1/2}'$ is very shallow, such that $n_{1/2}'$ is comparable to N_c, the transition will not occur until the applied voltage is approximately equal to E_g/q; however, this range is difficult to explore because of heating effects and the IR drop. For a deeper level, such that $n_{1/2}'\ll W/C_{n0}$, the transition should occur considerably below E_g/q if the reasonable condition $W/(N_cC_{n0})\ll 1$ obtains.

Equations (26) and (32) show that pair recombination can result in a forward current composed of a space-charge component that tends to saturate with voltage and a diffusion component that becomes linear at high voltages. These two components vary as $\exp(qV/\beta kT)$ at low voltages, with $\beta=2$ for the space-charge current and $\beta=1$ for the diffusion current. This result suggests a possible explanation for those experimental results that indicate values of β greatly in excess of 2 over certain voltage ranges. Such effects have been seen, for example, in GaAs[14] and in GaP.[15] Shockley-Read recombination[11] predicts $\beta\leqq 2$.

IV. SUMMARY AND CONCLUSIONS

If it is assumed that the dominant recombination mechanism is pair recombination, rather than the usual Shockley-Read (S-R) mechanism, a number of interesting similarities and differences arise. Thus, for fairly strongly extrinsic material, pair recombination and S-R recombination give essentially the same results, provided the transition probability, t' (see Fig. 1), is sufficiently large ($t'\gg n_{1/2}'C_{n0}$) and the minority carrier density (injection level) is not too high. But, as the injection level increases, recombination via pairs tends to saturate, Eq. (19), whereas recombination via S-R centers may proceed at a slower rate but never completely saturates. The low level pair recombination rate also deviates from S-R recombination as the majority carrier density decreases (see Fig. 2).

As temperature increases, pair recombination shows a thermal quenching effect, Eq. (17). Such a thermal quenching effect has been seen in the 1.28 eV electroluminescence of Zn-diffused GaAs diodes[9] and suggests that this band is due to pair recombination in which one of the levels is about 0.06 eV from a band edge.

As suggested above, diodes offer a possible means of demonstrating pair recombination. The reverse voltage current dependence should be about the same for either pair recombination or S-R recombination, but the reverse current as a function of temperature appears to be more complicated in the case of pair recombination. The forward current tends to saturate at high voltages for pair recombination within the depletion region and becomes linear with large applied bias for diffusion current. This result might explain voltage-current curves with slopes less than $qV/2kT$,[14,15] as well as the saturation of the 1.0 and 1.28 eV electroluminescence of GaAs diodes.[9]

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