Recombination of Electrons and Donors in n-Type Germanium. B*

G. ASCARELLI
Istituto Superiore di Sanità, Rome, Italy

AND

S. RODRIGUEZ
Department of Electrical Engineering, Princeton University, Princeton, New Jersey

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A study is made of two possible recombination mechanisms for electrons and ionized donors in Ge. The first consists of two successive transitions ending in the ground state of the donor and having an excited state as an intermediate level. Two phonons are emitted. The second mechanism is that of impact recombination. It is shown that the first mechanism is dominant at liquid helium temperatures for electron concentrations less than 4×10^{-15} cm^{-3}. At higher concentrations impact recombination dominates the rate of approach to equilibrium.

I. INTRODUCTION

IN a previous paper,[1] the authors have discussed several mechanisms for the recombination of electrons and ionized impurity donors in semiconductors. The rate at which electrons in the conduction band recombine with the donor centers can be described by means of an average recombination cross section. It was found in A that the dominant recombination mechanism is one in which the electrons experience two successive transitions. The first is a capture in an excited state of the donor, while the second is a transition from the excited state to the ground state. Both processes are accompanied by emission of phonons. The results of the work in A were applied to germanium doped with arsenic and antimony.

The object of the present paper is twofold. Firstly, we give a more intuitive picture of the recombination process described in A. Secondly, we discuss the recombination of electrons and donors by means of impact, i.e., the inverse process to impact ionization. Section II is devoted to the first question, while Sec. III deals with the second.

As in A we assume a simple parabolic conduction band with effective mass m^*. We designate the stationary states of a donor by a suffix j which represents the set of quantum numbers nlm in the ordinary hydrogenic model. An s state with principal quantum number n is designated simply by the suffix n. The notation used in this paper is the same as that of A. It is convenient, however, to list the symbols used:

V = volume of the crystal.
E_j = energy of an electron in the bound state j.
E_c = energy of an electron at the bottom of the conduction band.
$I_j=E_c-E_j$ = ionization energy of an electron in state j.
$\epsilon=\frac{1}{2}m^*v^2$ = kinetic energy of an electron with velocity v in the conduction band.
ζ = Fermi energy.
$f(\epsilon)$ = Probability for a state of kinetic energy ϵ to be occupied by an electron [in this work we assume $E_c-\zeta\gg kT$ so that $f(\epsilon)=\exp\left(\frac{\zeta-\epsilon-E_c}{kT}\right)$].
k = Boltzmann's constant.
T = absolute temperature.
N = concentration of electrons in the conduction band.
N_∞ = equilibrium concentration of electrons in the conduction band.

$$N_\infty=N_c\exp[(\zeta-E_c)/kT]. \quad (1)$$

$$N_c=2(m^*kT/2\pi\hbar^2)^{\frac{3}{2}}. \quad (2)$$

$n(\epsilon)$ = density of electron states per unit volume of the crystal and per unit energy range at ϵ.
N_A = concentration of acceptors.
N_D = concentration of donors.
f_j = probability for the bound state j to be occupied by an electron.

$$f_j=g_j\exp\left(\frac{\zeta-E_j}{kT}\right)\left[1+\sum_j g_j\exp\left(\frac{\zeta-E_j}{kT}\right)\right]^{-1}. \quad (3)$$

g_j = degeneracy of state j.
$\langle v\rangle$ = average thermal velocity of the electrons.
$a^*=K\hbar^2/m^*e^2$ = effective Bohr radius.
e = charge on the electron.
K = dielectric constant of the material.
E_i = ionization energy for a donor in its ground state.
w_j = probability per unit time for an electron in state j to make a transition to the ground state.

II. RECOMBINATION WITH EMISSION OF PHONONS

Let us consider a two-step recombination process such as the one described in A. An electron in the conduction band is first captured in an excited state j of the donor, and subsequently experiences a transition from j to the ground state. In both transitions the excess energy is carried away by phonons.

Let us focus our attention on an electron in a highly excited state of a donor center. To fix the ideas, let it be the s state with $n=10$. The time it takes this electron to lose or gain energy of the order of kT is approximately equal to the mean free time τ for electrons in the conduction band (i.e., about 10^{-10} sec at 4°K). However, the time required for it to make a transition to the ground state is of the order of 10^{-6} sec. In

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[1] G. Ascarelli and S. Rodriguez, Phys. Rev. 124, 1321 (1961). This paper is referred to as A in the present work. It contains references to other pertinent work.

TABLE I. Values of w_n and β_n.

n	w_n(As) (sec^{-1})	w_n(Sb) (sec^{-1})	β_n (sec^{-1})
2	0.408×10^{9}	1.71×10^{9}	4.56×10^{5}
3	0.409×10^{8}	1.71×10^{8}	4.53×10^{8}
4	1.16×10^{7}	4.86×10^{7}	7.29×10^{9}
5	0.487×10^{7}	2.04×10^{7}	2.44×10^{10}
6	2.50×10^{6}	1.05×10^{7}	
7	1.45×10^{6}	6.09×10^{6}	
8	0.921×10^{6}	3.86×10^{6}	
9	0.621×10^{6}	2.60×10^{6}	
10	4.38×10^{5}	1.83×10^{6}	
11	3.21×10^{5}	1.34×10^{6}	
12	2.42×10^{5}	1.01×10^{6}	

Table I we give the results of a calculation of the transition probability for an electron in a state ns to emit a phonon and fall into the ground state. Also, for comparison, we give the rate β_n of thermal ionization for some low-lying states at 4°K. These results are obtained from A [Eq. (23) and Table I of that paper, respectively]. This fact, namely, that an electron in a high excited state of the donor center suffers a large number of transitions to and from the conduction band before experiencing a transition to the ground state, implies that this state of the donor is occupied by an electron with a probability equal to the thermal equilibrium distribution that would obtain if the lower lying states were absent. This situation is reached in a time of the order of a few conductivity relaxation times τ, and we shall refer to it as the pseudo-equilibrium situation. We can describe this case by a pseudo-Fermi level ζ'. The recombination time is the time required for ζ' to approach the equilibrium Fermi level.

The lowest excited state whose population is governed by the pseudoequilibrium distribution is the state of lowest n for which β_n exceeds w_n. We refer to this state as the critical or bottleneck state. From Table I we see that at $T=4$°K the critical state is the one characterized by $n=3$. This argument shows that at liquid helium temperatures the rate of recombination is determined mainly by the state $3s$. The reasons why s states are the most important in governing the approach to equilibrium have been discussed in A and shall not be repeated here.

If f_j' designates the probability for the state j to be occupied by an electron in the pseudoequilibrium situation and N' is the corresponding concentration of electrons in the conduction band, then the cross section for recombination of electrons and donors is

$$\sigma=(\textstyle\sum_j' f_j' w_j)/N'\langle v\rangle. \tag{4}$$

The sum over j extends over all states having energy equal to or larger than that of the critical state, but whose size is smaller than the average distance between impurities [such sums will be distinguished from sums over all j by a dash as indicated in Eq. (4)]. However, since w_j is larger for s states than for states with $l\neq0$ and decreases very rapidly with increasing n, it is a good approximation to write

$$\sigma=f_{n_0}'w_{n_0}/N'\langle v\rangle, \tag{5}$$

where n_0 is the principal quantum number of the critical state.

In general, f_j' and N' are given by Eqs. (3) and (1), respectively, where we replace ζ by ζ'. We find

$$f_j'=(N'x_j/N_c)(1+N'x/N_c)^{-1}, \tag{6}$$

where

$$x_j=g_j\exp(I_j/kT), \tag{7}$$

and

$$x=\textstyle\sum_j' x_j. \tag{8}$$

The probability for a center to have captured an electron in pseudoequilibrium is

$$\textstyle\sum_j' f_j'=(N'x/N_c)(1+N'x/N_c)^{-1}. \tag{9}$$

Because of the large probability of re-excitation for states above the critical state, $\sum_j' f_j'\ll1$ so that $N'x/N_c\ll1$. This implies

$$f_j'\simeq(N'g_j/N_c)\exp(I_j/kT). \tag{10}$$

Therefore, from Eqs. (5) and (10)

$$\sigma\simeq\frac{2w_{n_0}}{N_c\langle v\rangle}\exp\left(\frac{I_{n_0}}{kT}\right)=\frac{\pi^2\hbar^3w_{n_0}}{m^*(kT)^2}\exp\left(\frac{E_i}{n_0^2kT}\right). \tag{11}$$

Taking $m^*=2\times10^{-28}$ g, $E_i=0.0117$ eV, and $T=4$°K, we find

$$\sigma=3.4\times10^{-13}\text{ cm}^2 \quad\text{for As-doped Ge,}$$
$$=1.4\times10^{-12}\text{ cm}^2 \quad\text{for Sb-doped Ge.}$$

These results are in good agreement with the results of the more elaborate calculation given in A. In fact, we found there that the recombination cross section at 4°K was 7.36×10^{-13} cm^2 for As-doped Ge and 1.51×10^{-12} cm^2 for Sb-doped Ge.

It is possible to take into account the fourfold degeneracy of the bound states arising from the fact that the conduction band of Ge has four equivalent minima, in the manner described in A, by multiplying these cross sections by 4. The reader is referred to that work for further details.

III. IMPACT RECOMBINATION

In the present section we study the rate of recombination by the process of impact, i.e., that which is the opposite of impact ionization. The rate of impact recombination can be expressed in terms of the cross section for impact ionization, if one makes use of the principle of detailed balance. Let $\sigma_i(j,\epsilon)$ be the cross section for the ionization of an impurity center origin-

ally in state j by an incident electron of kinetic energy ϵ. The number of centers in state j ionized per unit time is

$$\nu_j = VN_D^{(j)} \int_{I_j}^{\infty} n(\epsilon) f(\epsilon) v \sigma_i(j,\epsilon) d\epsilon. \quad (12)$$

Here $N_D^{(j)}$ is the concentration of donor centers in state j. The number of electrons captured per unit time in state j is

$$\nu_j' = \alpha_{ij} N^2 (N_A + N) V, \quad (13)$$

and the corresponding cross section for impact capture is

$$\sigma_{ij} = \nu_j'/N(N_A+N)V\langle v\rangle = \alpha_{ij} N/\langle v\rangle. \quad (14)$$

Equation (13) is nothing more than the definition of the quantity α_{ij}. In thermal equilibrium, we must have

$$\nu_j = \nu_j'$$

so that

$$\alpha_{ij} = \frac{N_D f_j}{N_\infty^2 (N_A + N_\infty)} \int_{I_j}^{\infty} n(\epsilon) f(\epsilon) v \sigma_i(j,\epsilon) d\epsilon. \quad (15)$$

After some transformations

$$\alpha_{ij} = \frac{8\pi\hbar^3}{m^{*2}(kT)^3} \exp\left(\frac{I_j}{kT}\right) \int_{I_j}^{\infty} \epsilon \sigma_i(j,\epsilon) \exp\left(-\frac{\epsilon}{kT}\right) d\epsilon. \quad (16)$$

If $I_j \gg kT$, the rate α_{ij} of impact recombination is determined by the rate of change of the impact ionization cross section in the vicinity of the threshold energy I_j. This question has been discussed theoretically by Wannier[2] and by Geltman.[3] Using Coulomb wave functions, Geltman is able to show that near the threshold the cross section for impact ionization of hydrogen increases linearly with the energy of the incident electron above the threshold. Wannier establishes with the aid of a more general argument that the cross section increases with the power 1.127 of the same quantity. In this work we shall assume the linear dependence to be valid for simplicity, and because both results would give approximately the same answer in our particular problem. Fite and Brackmann[4] have made absolute determination of the cross section for impact ionization of atomic hydrogen by electrons confirming the theoretical results. Let us then write, for the cross section for impact ionization, the relation

$$\sigma_i(j,\epsilon) = \gamma_{ij} \pi a^{*2} (\epsilon - I_j)/I_j. \quad (17)$$

Here, γ_{ij} is a number. Using S-wave scattering, Geltman[3] finds that, for the ground state $\gamma_{i1} = 0.598$, while experimentally Fite and Brackmann find $\gamma_{i1} = 1.061$. From (17), (16), and (14) and assuming $I_j \gg kT$, we find

$$\sigma_{ij} = 2\pi a^{*2} (N/N_c) \gamma_{ij} [1 + (2kT/I_j)] \simeq 2\pi a^{*2} (N/N_c) \gamma_{ij}. \quad (18)$$

The total impact recombination cross section is

$$\sigma_i = \textstyle\sum_j \sigma_{ij} S_j, \quad (19)$$

where S_j is the sticking probability of an electron in state j. If we assume that $\gamma_{ij} = \gamma$, a constant independent of j, we find, at 4°K

$$\sigma_i = 2\pi S a^{*2} \gamma (N/N_c), \quad (20)$$

where only s states are taken into account since the sticking probabilities for states with angular momentum higher than zero are considerably smaller than those for s states. The quantities S can be obtained from Table IV in A. At 4°K for As-doped Ge, $S = 2.08$ and for Sb-doped Ge, $S = 2.28$.

It is interesting to compare the result (18) with the one obtained using the Born approximation

$$\sigma_i(\epsilon) = (\pi e^4 C/\epsilon E_i K^2) \ln(\epsilon/\lambda E_i), \quad (21)$$

for the ionization cross section of a donor center in the ground state by an electron of kinetic energy ϵ. Here, $C = 0.285$ and $\lambda = 0.012$ are constants.[5] We find, after some transformations,

$$\sigma_{i1} = \frac{2\pi e^4 C}{K^2 kT E_i} \frac{N}{N_c} \left[-\ln\lambda + \frac{kT}{E_i} - \left(\frac{kT}{E_i}\right)^2 \right], \quad (22)$$

or approximately

$$\sigma_{i1} = 2.52(\pi N e^4/N_c K^2 kT E_i). \quad (23)$$

While (18) yields

$$\sigma_{i1} \simeq 10^{-12} (N/N_c) \text{ cm}^2, \quad (24)$$

Eq. (23) gives

$$\sigma_{i1} \simeq 6.3 \times 10^{-10} (N/N_c T) \text{ cm}^2. \quad (25)$$

We see that the use of the Born approximation overestimates the cross section for impact recombination by a factor of the order of 100 at $T = 4$°K. Because at 4°K the cross section for recombination is of the order of 10^{-12} cm^2, impact recombination only becomes important for concentrations $N > N_c = 4 \times 10^{15}$ cm^{-3}. It is worthwhile to make the final remark that Eq. (18) cannot be but an overestimate of the average cross section. In fact, the cross section (17) gives the behavior of $\sigma_i(j,\epsilon)$ in the vicinity of the threshold I_j, but at higher energies the cross section deviates from the linear behavior in such a way that it bends towards the energy axis (see reference 4). When $I_j \gg kT$, our approximations are accurate.

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