

# Recombination statistics of non-equilibrium carriers in the model of semiconductor with donor-acceptor pairs possessing variable recombination activity

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**Abstract.** The recombination rate of non-equilibrium carriers has been calculated for the model of the semiconductor with donor-acceptor pairs, the recombination activity of which decreases during excitation. It has been shown that, even at a very low inertia of intra-complex exchange, this process can lead to decreasing the recombination rate. The obtained results demonstrate a principal distinction from the classical Shockley–Read statistics.

**Keywords:** recombination, donor-acceptor pairs, decrease of recombination activity.

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## 1. Introduction

It is well-known expression for the recombination rate of non-equilibrium carriers, obtained by W. Shockley and W. Read and which has long become classic:

$$U = N_R \frac{c_n c_p (pn - n_i^2)}{c_n (n + n_1) + c_p (p + p_1)}. \quad (1)$$

Here,  $U$  is the rate of recombination of non-equilibrium carriers;  $N_R$  – concentration of deep impurity centers through which recombination occurs;  $p$  and  $n$  – the concentrations of free holes and electrons, correspondingly;  $n_i$  – intrinsic concentration;  $c_n$  and  $c_p$  – the capture coefficients of free electrons and holes by the impurity level  $E_R$ ;  $n_1$  and  $p_1$  are the Shockley–Read statistical factors for electrons and holes:

$$n_1 = N_c e^{\frac{E_c - E_R}{kT}}, \quad p_1 = N_v e^{\frac{E_v - E_R}{kT}}, \quad (2)$$

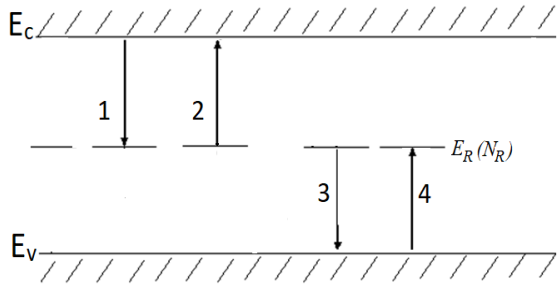
$N_c$  and  $N_v$  are the density of states in the conduction and valence gaps, correspondingly.

When deriving Eq. (1), a number of simplifying assumptions were made, the main of which are as follows:

1. Recombination proceeds through singly charged impurity centers, each of which can be either neutral or singly charged (see Fig. 1).

2. The process of carrier exchange between gaps and recombination centers is assumed to be inertialess. In other words, the time of carrier fixation by impurities is considered insignificant as compared to that inherent to capture (or emission) of the carrier by the center.

It is well known that most of semiconductor materials have a more complex spectrum of impurities. Therefore, after publication of the work by W. Shockley and W. Read, many authors developed certain recombination models, trying to take into account the more complex nature of recombination centers. In particular, many works have been devoted to recombination going through paired recombination complexes, for which it is necessary to take into account the inertia of intra-complex exchange. First of all, these are complexes of the type of donor-acceptor pairs, but they can be pairs of another nature, in particular, an impurity + vacancy type or an interstitial atom + impurity. In [1], the attempt was made to summarize these models and obtain an expression for the recombination rate going through pair complexes. Similar models were also considered in [2-4].



**Fig. 1.** Scheme of recombination through the simple single-level Shockley-Read trap. (1)  $c_n N_R (1 - f_R) n$ , (2)  $c_n N_R f_R n$  – exchange of the trap level with the conduction band. (3)  $c_p N_R f_R p$ , (4)  $c_p N_R (1 - f_R) p$  – exchange of the trap level with the valence band.

**2. Models and experimental technique**

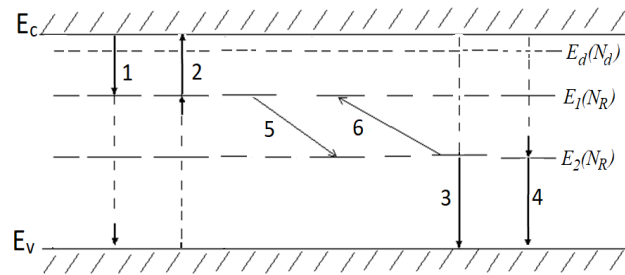
The scheme of recombination going through the pair complex is shown in Fig. 2.

For all these models, the recombination rate can be written as:

$$U = N_R \times \frac{c_{n1} c_{p2} (pn - n_i^2)}{c_{n1}(n + n_{11}) + c_{p2}(p + p_{12}) + \frac{c_{n1} c_{p2}}{c_{12}} (pn + p_{12}n + n_{11}p + p_{12}n_{11})} \quad (3)$$

where  $c_{n1}$  is the electron capture coefficient by the level  $E_1$ ,  $c_{p2}$  – hole capture coefficient by the level  $E_2$ ,

$$n_{11} = N_c e^{-\frac{E_c - E_1}{kT}}, \quad p_{12} = N_v e^{-\frac{E_v - E_2}{kT}} \quad (4)$$



**Fig. 2.** Scheme of recombination through the pair recombination complex. Dashed lines show unaccounted transitions. (1)  $c_{n1} N_R (1 - f_1)$ , (2)  $c_{n1} N_R f_1 n_{11}$  – exchange between the level  $E_1$  and conduction band. (3)  $c_{p2} N_R f_2 p$ , (4)  $c_{p2} N_R (1 - f_1) p_{12}$  – exchange between the level  $E_2$  and valence band. (5)  $c_{p2} N_R f_1 (1 - f_2)$ , (6)  $c_{12} N_R f_2 (1 - f_1) e^{-\frac{E_2 - E_1}{kT}}$  – exchange between the levels  $E_1$  and  $E_2$ , where  $(c_{12})^{-1} = \tau_{ii}$  is the time of intra-complex exchange.

are the analogues of the Shockley-Read statistical factors (see (2)) for the impurity levels  $E_1$  and  $E_2$ ,  $c_{12}$  – coefficient describing the exchange of electrons between the components of the pair complex.

When deriving Exp. (3), it was assumed that the concentration of impurities  $N_R$  at the levels  $E_1$  and  $E_2$  is the same, and that the distance between the levels  $E_1$  and  $E_2$  is small, so  $\exp\left(\frac{E_1 - E_2}{kT}\right)$  can be ignored. From the

formula (3), it can be seen that in the case when  $c_{12} \rightarrow \infty$ , i.e., the time of intra-complex exchange

$$\tau_{ii} = \frac{1}{c_{12}} \rightarrow 0, \text{ the latter term in the denominator (3) will}$$

be negligible and the recombination rate through pair complexes takes the form:

$$U = N_R \frac{c_{n1} c_{p2} (pn - n_i^2)}{c_{n1}(n + n_{11}) + c_{p2}(p + p_{12})}. \quad (5)$$

**3. Experimental results and discussion**

Comparison of (5) and (1) leads us to the conclusion that under conditions of almost inertialess exchange between the components of the complex  $E_1$  and  $E_2$ , the rate of recombination through donor-acceptor pairs does not differ from the rate of recombination through the simple single-level Shockley-Read traps. Similar results were obtained in all recombination statistics that considered two-level recombination complexes, regardless of their specific nature. But none of these works considered the possibility of changing the capture coefficients of free carriers in the process of excitation of the material. Meanwhile, such experimental facts have long been known. A very common type of intra-complex processes is charge interaction of the components that form the complex with each other, so in CdS [5, 6] the Coulomb interaction of the associated donor and acceptor components causes a significant difference in the values of coefficients for free carrier capture by complexes. One specific example of the pair recombination complex is donor-acceptor pairs in which the components are located at the closest distances in the crystal lattice. For example, in GaP, the near donor-acceptor pair forms the Zn-O complex. In different silicon carbide polytypes (6H, 4H, 3C), pronounced acceptor-donor pairs are formed by nitrogen atoms (donor) with aluminum or boron. In  $\beta$ -SiC, the acceptor-donor boron-carbon vacancy pair is responsible for green luminescence; similar close associates also exist in other wideband semiconductors.

The intercomponent charge interaction should show itself, in particular, in the dependence of the free carrier coefficient capture by the recombination complex on the degree of filling of its components by captured carriers.

So, in our model of the simple pair complex, the coefficient of capture of free electrons by the level  $E_1$  can turn out to be the function of filling the component  $E_2$  by captured electrons, i.e.,  $c_{n1} = c_{n1}(f_2)$ , where  $f_2$  is the probability of filling the level  $E_2$  by electrons. Indeed, if the levels  $E_1$  and  $E_2$  are sufficiently close by their energy, then, due to the simple Coulomb interaction,  $c_{n1}$  – the electron capture coefficient by level  $E_1$  – can directly depend on filling the level  $E_2$  by electrons, the larger the level filling by holes, i.e., the larger  $(1 - f_2)$ , the more difficult the capture of electrons by the level  $E_1$ . For example, consider a very simple approximation of this process. Let it be,

$$c_{n1} = c_{n0}(1 - \alpha\sqrt{p}), \quad (6)$$

where  $\alpha$  is the coefficient describing the process of inhibition of electron capture by the level  $E_1$ . In this case, the emission of electrons from the level  $E_1$  in the conduction band remains the same:  $c_n = c_{n0} n_{11}$ .

Then the recombination rate (5) takes the form:

$$U = N_R \frac{c_{n0}(1 - \alpha\sqrt{p})c_{p2}(pn - n_i^2)}{c_{n0}(1 - \alpha\sqrt{p})n + c_{n0}n_{11} + c_{p2}(p + p_{12})}. \quad (7)$$

At the high level of excitation, when

$$p \approx n \gg n_{11}, p_{12} \quad (8)$$

(5) takes the form

$$U = N_R \frac{c_{n1}c_{p2}}{c_{n1} + c_{p2}} p, \quad (5a)$$

i.e., the recombination rate increases linearly with increasing the level of excitation, like to that in the Shockley–Read statistics.

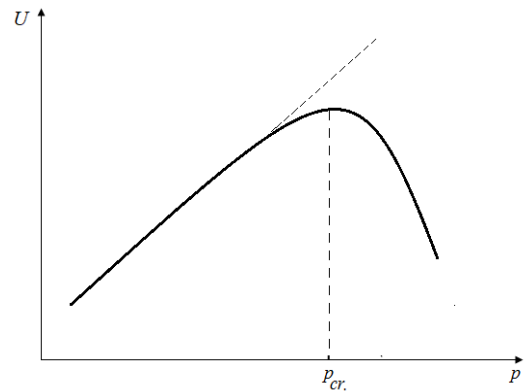
But if  $c_{n1}$  depends on the level of excitation, according to the law (6), then under conditions (8), the recombination rate (7) will take the form:

$$U \approx N_R \frac{c_{p2}c_{n0}}{c_{n0} + c_{p2}} p \left[ 1 - \left( 1 - \frac{c_{n0}}{c_{n0} + c_{p2}} \right) \alpha\sqrt{p} \right]. \quad (7a)$$

Studying this expression to the maximum allows one to find the critical concentration, at which the decrease of the recombination rate begins:

$$p_{cr} = \frac{4}{9 \left( 1 - \frac{c_{n0}}{c_{n0} + c_{p2}} \right) \alpha^2}. \quad (9)$$

Qualitatively, this result is shown in Fig. 3.



**Fig. 3.** Qualitative dependence of the change of the recombination rate on the level of excitation under the conditions of dependence  $c_n(p)$  (6). The dotted line shows the dependence  $U(p)$  corresponding to the formula (5a).

#### 4. Conclusion

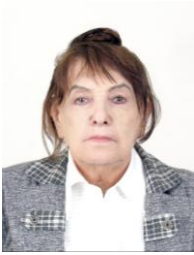
Thus, the presence of the pair recombination complex under the conditions of decreasing activity of one of the components can lead to a decrease of the recombination rate of non-equilibrium carriers upon strong excitation of the material.

It should be emphasized that this decrease is possible even at the negligible inertia within the complex electronic exchange. This result is not possible within the framework of the Shockley–Read statistics, where the recombination rate increases linearly at increasing concentration of free carriers at a high level of excitation.

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## Статистика рекомбінації нерівноважних носіїв у моделі напівпровідника з донорно-акцепторними парами зі змінною активністю рекомбінації

А.Ю. Лейдерман, А.К. Утеніязов, М.Т. Нсанбаєв

**Анотація.** Швидкість рекомбінації нерівноважних носіїв була розрахована для моделі напівпровідника з донорно-акцепторними парами, активність рекомбінації яких знижується під час збудження. Було показано, що навіть при дуже низькій інерційності внутрішньокмплексного обміну цей процес може призвести до зниження швидкості рекомбінації. Отримані результати демонструють принципову відмінність від класичної статистики Шоклі-Ріда.

**Ключові слова:** рекомбінація, донорно-акцепторні пари, зниження активності рекомбінації.

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