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Recombination Processes and Holes and Electrons Lifetimes¹

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In the semiconductor with indirect band gap, such as silicon, recombination on a deep center determines the lifetime of electrons and holes. In this article lifetime is calculated in dependence of both recombination processes, Shockley-Read Hall and Auger. The calculations of lifetime are made for gold in silicon, taking into account both deep levels and neglecting one of them. It is found that in the most cases gold, although having two deep levels, will act as a single level deep impurity. Exceptions are high injection levels where both deep energy levels have influence on recombination process. According to the measured values of lifetime it is confirm that the capture coefficients are temperature dependent and that the both recombination processes, Shockley-Read-Hall and Auger have significant influence on a lifetime.

Key words: recombination, deep impurity, lifetime

1 INTRODUCTION

The lifetime depends on a recombination process. The recombination and it's opposite - a generation process - are processes where electron goes from conduction to valence band and vice versa. An electron can travel directly from one band to another, or its transition can be supported by deep energy level introduced into the band gap. In the semiconductor with indirect band gap, such as Si, Ge, GaP, the probability of direct transition between valence and conduction bands is very small, because it is phonon participated. In such a semiconductor the deep impurity must be added. The deep impurity having energy layer deep in the band gap acts as a recombination center The aim of such centers, often called traps, is to enable fast recombination and short electrons' and holes' lifetime.

When moving from one band to another electron changes its energy; for generation an electron must receive a certain amount of energy while in recombination the energy will be taken away from it. The most popular and the simplest model of recombination is Shockley-Read-Hall, but it did not take into consideration the energy involved in the process. There are several models of recombination processes; the difference between them is in the way of removing the excess energy: the main are Auger, optical, multiphonon and cascade [1]. In this work we will focus only on the *Shockley-Read-Hall* and *Auger* recombination processes. The lifetimes of minority and majority carriers are calculated, assuming single level deep impurity and impurity with two deep levels. In all calculations I have used simulation program of my own design. The numerical results are compared with the experimentally obtained lifetimes.

2 SHOCKLEY-READ-HALLAND AUGER RECOMBINATION

In recombination and generation processes the certain amount of energy is involved. In the Shock-ley-Read-Hall process we do not have to take into consideration how required energy is provided, whereas in the Auger process we do.

In the Shockley-Read-Hall recombination process only two particles are considered, an electron and a hole. The Auger recombination is such a process where three particles are involved; two of them in the process of generation or recombination, and the third that takes or gives some energy. The probability of a recombination is proportional to the concentrations of all involved particles; in the case of Shockley-Read-Hall recombination the probability that the process will take place is proportional to the product of concentrations of the electrons and the holes $n \cdot p$, while in the case of the Auger process probability is proportional to $n^2 \cdot p$ or $n \cdot p^2$. Accordingly, it can be concluded that the Auger process will be more significant as concentrations of electrons and holes become greater.

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If only Shockley-Read-Hall recombination is assumed four processes are possible:

- 1. the electron from conduction band can be trapped by an empty trap,
- 2. a filled trap can emit an electron in the conduction band,
- 3. an empty trap can emit a hole in the valence band (in fact, an empty trap will attract an electron from the valence band) and
- 4. a trap filled with an electron can trap a hole (which means such a trap will emit an electron in the valence band).

In an Auger recombination process we have all four mentioned processes, but in each of these certain amount of energy will be given to, or taken from, an electron or a hole. So, in this case, there are eight Auger processes.

Those events are shown in Figure 1.



Fig. 1 Recombination processes

3 THE CARRIERS' LIFETIME

For the certain disturbance from equilibrium in carrier density Δn or Δp , the recombination and generation processes will tend to revert back the semiconductor into equilibrium condition. The lifetimes of electrons τ_n and of holes τ_p are defined as [2, 3]:

$$\tau_n = \frac{\Delta n}{\mathrm{d}n/\mathrm{d}t} \qquad \tau_p = \frac{\Delta p}{\mathrm{d}p/\mathrm{d}t} \tag{1}$$

 Δn , Δp – excess number of electrons and holes, dn/dt and dp/dt – rate of recombination of electrons or holes.

The rate of recombination of electrons and holes depends on the magnitude of the disturbance and on the recombination process.

3.1 The deep impurity with one deep energy level

The recombination and generation processes depend on the capability of a recombination center to capture or emit an electron. These capabilities are described by capture and emission rates. The electron and hole capture in a Shockley-Read-Hall process are described by an electron c_n (cm³s⁻¹) or a hole capture rate c_p (cm³s⁻¹) [2, 3]. In the Auger process [4, 5] those capture rates will have two additional subscripts -A is for Auger and the third letter determines the third particle involved in the process; e. g. c_{Anp} (cm⁶s⁻¹) is the capture rate for an electron while a certain amount of energy is given to the hole. The electron and the hole emission from the trap are described by the emission rate e_n , e_p (s⁻¹) for the Shockley-Read-Hall recombination and e_{Anx} , e_{Apx} (cm³s⁻¹) for the Auger recombination.

In the steady-state conditions net change of the electrons in the conductance band and the holes in the valence band equals zero; from that conditions connection between capture and emission rate can be obtained [3]:

for Shockley-Read-Hall recombination:

$$e_n = c_n \cdot n_T \qquad e_p = c_p \cdot p_T \tag{2}$$

for Auger process:

 $e_{Ann} = c_{Ann} \cdot n_T \qquad e_{Anp} = c_{Anp} \cdot n_T \qquad (3a)$

$$e_{Apn} = c_{Apn} \cdot p_T \qquad e_{App} = c_{App} \cdot p_T. \tag{3b}$$

Concentrations n_T and p_T are concentrations of electrons or holes if the Fermi level is equal to the deep impurity energy level $E_F = E_T$.

The mathematical calculations for obtaining the recombination rate are described in details in [3, 4, 6]. A deep energy level can have an electron or can be empty; if there is an electron it can be send to the conduction band, or if the level is unoccupied it can capture an electron from the conduction band. Shortly, the net change of the electrons' density in the conduction band can be given as a sum of emission process (electrons go to the conduction band) minus capture process (electrons go from the conduction band), using relations (2) and (3). The

same is valid for a net change of the holes' density in the valence band.

The rate of the disappearance of electrons and holes by recombination in the steady state condition is determined as:

$$\frac{dn}{dt} = \frac{dp}{dt} = \frac{n \cdot p - n_i^2}{\tau_{p0} \cdot (n + n_1) + \tau_{n0} \cdot (p + p_1)}.$$
 (4a)

 N_T is the concentration of the deep impurity.

The times τ_{n0} and τ_{p0} are defined as

$$\tau_{n0} = \frac{1}{(c_n + c_{An})N_T} \quad \text{and} \quad \tau_{p0} = \frac{1}{(c_p + c_{Ap})N_T}.$$
(4b)

The capture coefficients c_n and c_p that have been described earlier, are related to the Shockley-Read-Hall recombination process, while the capture coefficients related to the Auger process are:

$$c_{An} = c_{Ann} \cdot n + c_{Anp} \cdot p \qquad c_{Ap} = c_{Apn} \cdot n + c_{App} \cdot p.$$
(4c)

n, p – nonequillibrium concentrations of electrons and holes.

The times τ_{n0} and τ_{p0} are the minimum possible lifetimes for the electrons in the *p*-type of semiconductor, and for the holes in the *n*-type. As it can be seen, if only Shockley-Read-Hall recombination exists those minimum possible lifetimes depend only on the concentration of recombination center N_T (and its capture capacity), while in the case of Auger recombination, according to equation (4), those lifetimes depend on the concentrations of electrons *n* and holes *p* as well.

3.1.1 Calculation of the lifetime

According to the expressions (1) and (4) lifetime will be determined when excess concentration of electrons and holes are known. All nonequilibrium concentrations n, p, N_T are given as a sum of equilibrium n_0 , p_0 , N_{T0} , and excess concentrations Δn , Δp , ΔN_T :

$$n = n_0 + \Delta n, \quad p = p_0 + \Delta p, \quad N_T = N_{T0} + \Delta N_T.$$
 (5)

Those expressions for excess carriers concentrations must be inserted in (4). We shall presume the condition of a neutrality on a semiconductor with the resulting condition:

$$\Delta n + \Delta N_T^- = \Delta p + \Delta N_T^+. \tag{6}$$

The deep impurity can be either of a donor type or of an acceptor type. If it is of a donor type it will be neutral when its energy level is occupied by an electron and will be ionized positively when the level is empty. The atom of acceptor type is neutral when its level is unoccupied or it is negatively charged when the level is filled with an electron. In (6) it will be:

$$\Delta N_T^- \neq 0$$
 and $\Delta N_T^+ = 0$ if a deep impurity is
acceptor type, or
 $\Delta N_T^- = 0$ and $\Delta N_T^+ \neq 0$ if a deep impurity is
donor type.

To obtain electrons or holes lifetime we must solve equations (4) and (6). Using (4) and (6) the solution for Δn or Δp is obtain in the form of a polynom of 2th degree if only Shockley-Read-Hall recombination is taken into account, or 3th degree if both, Shockley-Read-Hall and Auger recombinations are considered. In the calculation the minority excess concentrations is proposed, and as a solution we obtain the excess concentration of majority carriers. The solution is obtained using simulation program of our own rendered in Fortran.

3.2 The deep impurity with two deep energy levels

If the deep impurity introduces more than one deep energy level situation will be much more complex. The most common deep impurity used as a recombination center is gold. Gold in silicon exhibits two deep energy levels, one of a donor type (neutral when occupied), and the other which behaves as an acceptor (neutral when empty). The mathematical procedure is the same as the one described in detail in [3, 6], and the obtained expression for an excess concentration for majority carriers is of the 5th degree if both recombination processes, Shockley-Read-Hall and Auger, are taken into account. This expression can not be solved analytically. If only Shockley-Read-Hall recombination is considered the expression is of the 3th degree.

3.3 The dependence of lifetime on the injection level

3.3.1 Low injection level

The semiconductor is in the low injection level condition if the non equilibrium concentration of minority carriers is lower than the equilibrium concentrations of the majority carriers. If we presuppose a single level recombination center, in the *n*-type of semiconductor under the low injection will be valid:

$$p = p_0 + \Delta p \doteq \Delta p \ll n_T, p_T \ll n = n_0 + \Delta n \doteq n_0.$$

In this case the lifetime of a holes, a minority carriers, will be equal to:

$$\tau_p \approx \tau_{p0} \approx \frac{1}{N_T \cdot (c_p + c_{Apn} \cdot n_0)}.$$
 (7a)

The lifetime of the majority carriers is longer than the lifetime of the minority carriers.

$$\tau_n \approx \tau_p \left[1 + \frac{(c_p + c_{pn} \cdot n_0) N_T}{(c_n + c_{nn} \cdot n_0) n_0} \right].$$
(7b)

In the both cases, calculation and experiment confirm that if the deep impurity introduces two energy levels, at the low level injection only one level is important for a recombination process, and the minority carriers' lifetime will be equal to the τ_{p0} or τ_{n0} [3, 6, 8].

The minority carriers' lifetime as a function of a gold density is calculated and shown in Figure 2. The lifetimes are considered first using both deep levels introduced by gold in silicon band gap and then only one of the two.





b) n-type

Fig. 2 Lifetime of a minority carriers in a silicon doped with shallow impurity and gold

Gold in silicon introduces two deep energy levels, one is acceptor type and the other is donor type. Their positions and a capture coefficients at T == 300 K are [3, 7]:

$$E_A = E_c - 0.54 \text{ eV},$$

$$c_n = 5 \cdot 10^{-9} \frac{\text{cm}^3}{\text{s}}, \quad c_p = 1 \cdot 10^{-8} \frac{\text{cm}^3}{\text{s}},$$

$$E_D = E_v + 0.35 \text{ eV},$$

$$c_n = 3.5 \cdot 10^{-9} \frac{\text{cm}^3}{\text{s}}, \quad c_p = 3 \cdot 10^{-8} \frac{\text{cm}^3}{\text{s}}.$$

 E_{ν} and E_{c} are the energies of a bottom and a top of a bandgap.

Calculations of lifetimes presented in Figure 2 have been obtained presupposing the low injection level and Shockley-Read-Hall process only. As it can be seen if the density of a deep impurity is lower than the shallow impurity density, only one level is important for recombination process, the one closer to the Fermi level of a semiconductor. In the *p*-type recombination goes through the donor level E_D , the lower one, while in the *n*-type the important deep level is higher one, the acceptor level E_A .

3.3.2 High injection level

Under the high injection level the concentrations of minority and majority carriers become equal:

$$p \doteq \Delta p \doteq n \doteq \Delta n \implies n_T, p_T.$$

The lifetimes of electrons and holes tend to be equal $\tau_n \approx \tau_{p0}$ too. For recombination through one deep energy level lifetimes will be [3, 6]

$$\tau_n \approx \tau_p \approx \tau_{n0} + \tau_{p0} =$$

$$= \frac{1}{N_T} \left[\frac{1}{(c_n + c_{nn} \cdot \Delta n + c_{np} \cdot \Delta p)} + \frac{1}{(c_p + c_{pn} \cdot \Delta n + c_{pp} \cdot \Delta p)} \right].$$
(8a)

For recombination center with two energy levels E_{T1} and E_{T2} those lifetimes will be somewhat shorter then in the case of one energy level and are expressed as:

$$\tau_n \approx \tau_p = \frac{\tau_{n01} \cdot \tau_{n02} + \tau_{p01} \cdot \tau_{n02} + \tau_{p02} \cdot \tau_{n01}}{\tau_{p01} + \tau_{n02}}.$$
 (8b)

The lifetime at the high injection level is longer than at the low injection. That is valid in both cases, taking into account both deep energy levels or only one of them, as can be seen according to equations (7) and (8). This has also be demonstrated on Figure 3, where the lifetime as a function of a disturbance of a minority carriers' density Δn or Δp are shown.



10^{-6} 10^{-7} $10^{$

Fig. 3 The lifetimes of a minority carriers as a function of the injection level

Calculated lifetimes given in Figure 3 are for gold in silicon taking into account first the both and than only the one deep level. As it can be clearly seen from Figure 3 at the low level injection only one level is important for recombination process, as it was already shown in Figure 2. The lifetime rises with the rise of injection level. At the very high injection levels both energy levels have influence on recombination process. The lifetime is shorter when both levels are considered than when only one is taken into account.

5 EXPERIMENTALLY AND THEORETICALLY OBTAINED LIFETIME

5.1 Description of the experiment

In the experiment described in [8] the power $p+pnn^+$ diode was used. On the base of a given position of a Fermi level as $E_F = E_c - 0.35$ eV, the shallow donor concentration in an *n*-region was estimated to be $N_D \doteq 10^{14}$ cm⁻³. This was done using relation

$$E_F = E_c - kT \cdot \ln \frac{N_c}{n}$$

with T = 300 K, $N_c = 3.81 \cdot 10^{19}$ cm⁻³ [13] and $n \doteq N_D$.

To such a structure various deep impurities were added. Because gold is the best described deep impurity, it is used here for comparison between theoretically and experimentally obtained lifetimes. In [8] at low injection level measured lifetime was $\tau_p \approx 1.8$ µs; using (4b), neglecting Auger recombination the gold concentration is estimated as $N_T \doteq 6 \cdot 10^{13}$ cm⁻³.

The measurement of the lifetime was made as a function of a current density in the interval from 5 mA/cm^2 to 0.5 A/cm^2 . To connect current with carriers' density the Shockly relation was used:

$$J_p = q \cdot D_p \cdot \frac{\Delta p}{L_p}$$

$$D_p = \frac{kT}{q} \cdot \mu_p$$
$$L_p = \sqrt{D_p \cdot \tau_p}$$

 τ_p is lifetime of holes and μ_p its mobility.

where:

Using T = 300 K, $N_D \doteq 10^{14}$ cm⁻³, holes mobility $\mu_p \doteq 460$ cm²/Vs [13], measured lifetime τ_p (between $\approx 2-3$ µs), after a rough calculation results in an injection level going from $\Delta p \doteq 10^{13}$ cm⁻³ to $\Delta p \doteq 10^{15}$ cm⁻³.

In Figure 4 the lifetime of a holes as a function of an injection level is shown. Measured values are compared with the calculated ones for three different temperatures. The calculated values of lifetimes are obtained inferring that only the acceptor level of gold will take a role in the recombination process in an n-type of silicon and only the Shockley-Read-Hall recombination is considered.

According to the behavior of experimentally obtained lifetime given in Figure 4 we can see that the lifetime will be longer as injection level becomes higher, which was predicted in equation (8). Further on, it is obvious that for all injection levels, as temperature raises the lifetime rises as well. This is the consequence of the temperature dependence of capture coefficients [8]. According to measured lifetimes a capture coefficient must decrease as temperature increases. The exact temperature dependence of a capture coefficient is not known, but it is predicted in [9, 10] for the Shockley-Read-Hall recombination:

$$c = c (300) \cdot \left(\frac{300}{T}\right)^{3/2}$$
. (9)



Fig. 4 Silicon doped with gold density of $6 \cdot 10^{13}$ cm⁻³

Looking at Figure 4 it can be seen that the difference among the measured and the calculated lifetimes becomes greater as injection level rises. Calculated values rise faster then measured, which implies that the capture coefficients depend on the injection level, that means on to the carriers' density, and the Auger recombination must be considered too. Involving the Auger recombination into the calculation it becomes very complex. To make it simpler it is usual to predict that the Auger capture coefficients for an electron when the energy is exchange with other electron is the same as in the case when the third particle is a hole. The same is valid for capture coefficients of a hole. Those coefficients are expressed as a part of the capture coefficients for the Shockley-Read-Hall recombination according to [4, 5]:

$$c_{Ann} = c_{Anp} = \frac{c_n}{a \cdot n_i} \tag{10a}$$

$$c_{Apn} = c_{App} = \frac{c_p}{a \cdot n_i}.$$
 (10b)

In Figure 5 the measured lifetimes at a room temperature (17 °C) are shown and compared with the calculated values obtained considering both types of recombination, Shockley-Read-Hall and Auger.



Fig. 5 The lifetime as a function of an injection level at $T = 17 \degree C$

It can be seen that for low injection the slope of a lifetime vs. injection level is almost the same for measured and calculated values. This is obtained using in (10) parameter $a = 10^5$.

The difference between measured and calculated lifetimes at high injection levels still exists, but is smaller than it was predicted by the Shockley-Read--Hall recombination (compare Figures 4 and 5). This can be attributed to the influence of a second deep energy level introduced by gold in silicon.

6 CONCLUSION

The deep impurity added into a semiconductor in order to support the recombination process will have, according to (4) shorter lifetime as its density is higher. But, the density of deep impurity must not be too high, in comparison with the shallow impurity, if we wish to avoid its influence on to the semiconductor resistivity [11, 12].

Owing to the measured values presented in [8] it has been confirmed that the multilevel deep impurity, such as gold in silicon, can be treated as a single level. This is valid until the very high injection level is reached when both levels become important for recombination process. Than, of course, two levels are more effective than only one and the exact lifetime is shorter than those calculated with only one level, as can be seen in Figures 3, 4 and 5.

The comparison between measured and calculated values, given in Figure 4 gave us more interesting information about the recombination process. As it is already mentioned, only the Shockley-Read-Hall recombination has been taken into account. Bearing this in mind the obtained difference between measured and calculated lifetimes implies that the recombination processes depend on the carriers' concentrations, which means that the Auger type of recombination has certain influence on to the recombination process. The lifetime in the semiconductor must be modeled taking into account the Shockley-Read-Hall and the Auger recombination with the aim to achieve calculated value close to the real one, as it has been done and present in Figure 5.

The measured values also confirm that the recombination process is temperature dependent. The lifetime is longer as the temperature is higher.

In the end it must be pointed out that the recombination of free carriers in a semiconductor trough the recombination centers has never been the subject of a greater interest. As it was stated 20 years ago [9] »...The problem is a difficult one and the understanding was restricted to a global and heuristic interpretation...«. Today, the situation is almost the same. That is why there are no data about capture coefficients for deep impurities, with the exception of gold. To find out the capture coefficients' temperature dependence, the values of Auger coefficients and all relevant data for recombination process, many more experiments like those described in [8] must be done.

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Rekombinacijski procesi i vremena života šupljina i elektrona. Poluvodičima s indirektnim zabranjenim pojasom, kakav je silicij, dodaju se duboke primjese s ciljem da bi se postiglo određeno vrijeme života elektrona i šupljina. U članku je razmatrano vrijeme života uzimajući u obzir dva osnovna tipa rekombinacijskih procesa, Shockley-Read-Hallov i Augerov. Pri proračunu je kao duboka primjesa uzeto zlato, koje u silicij unosi dvije duboke energetske razine. Računski je pokazano, a i eksperimentom potvrđeno, da je u većini slučajeva za rekombinacijski proces bitna samo jedna duboka razina i to ona koja je bliža Fermijevoj razini poluvodiča. Iznimka je rad poluvodiča pri visokoj injekciji kada se rekombinacija obavlja preko obje razine. Eksperimentom je potvrđeno da koeficijenti zarobljavanja ovise o temperaturi, te da oba rekombinacijska procesa, Shockley-Read-Hallov i Augerov, treba uzeti u obzir pri proračunu vremena života. Pri proračunima je korišten vlastiti program, kojim je moguće, osim proračuna vremena života uzeti u obzir i ostale efekte koje duboka primjesa ima na električka svojstva poluvodiča, kao npr. utjecaj na vodljivost poluvodiča, na širinu i na kapacitivnost osiromašenog sloja.

Ključne riječi: rekombinacija, duboka primjesa, vrijeme života

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