DECAY LAW FOR THE CONCENTRATION OF NON-EQUILIBRIUM CHARGE CARRIERS IN SEMICONDUCTORS

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Decay processes are considered for non-equilibrium carriers generated uniformly throughout the volume of a semiconductor. The decay law is found for the concentration of non-equilibrium carriers in a semiconductor containing a small concentration of recombination centers (traps), for arbitrary departures from thermal equilibrium. Approximate expressions for this law are obtained for various ranges of variation of the concentration of the non-equilibrium carriers. These expressions correspond to various kinetic patterns of recombination. It is shown that alongside such well known patterns as the monomolecular and the bimolecular, there is also a type of recombination at a steady rate corresponding to a lifetime proportional to the concentration of the non-equilibrium carriers. This occurs at low temperatures in semiconductors in which the recombination cross-section for the minority carriers is much larger than that for the majority carriers.

A paper by Adirovich and the writer[1] examined the problem of the existence of characteristic times of stationary and nonstationary electronic processes in semiconductors. In this connection a law was obtained for the decay of non-equilibrium carriers in the case of low generation level and arbitrary concentration of traps (recombination centers).

When the concentration of traps is sufficiently large, the characteristic times turn out to be different from the characteristic times of the stationary processes, as found by Shockley and Read.[2] In the present paper a study is made of the kinetics of the nonstationary process of decay of non-equilibrium carriers for the case of small concentration of traps and arbitrary level of generation, and the laws of the process under these conditions are found.

1. STATEMENT AND SOLUTION OF THE PROBLEM

During the process of decay the kinetics of the electronic processes, for uniform generation, are described by the equations*

$$dn/dt = -A_e n p_t + B_e n_t, \quad n_t + p_t = N_t, \quad dp/dt = -A_t p n_t + B_t p_t, \quad p - n - n_t = N_a - N_d - \delta. \qquad (1)$$

The separation of the concentrations into equilibrium and non-equilibrium parts ($n = n_0 + n'$, and so on) leads to the following way of writing this system:

$$dn'/dt = -A_e p_{t0} n' + A_e (n_0 + n_1) n'_t - A_e n' p'_t, \qquad dp'/dt = -A_h n_{t0} p' + A_h (p_0 + p_1) p'_t - A_h p' n'_t,$$
$$p' = n' + n'_t, \quad p'_t = -n'_t, \qquad (2)$$

and linearization of the system with respect to the excess concentrations is possible only in the special case of small levels of generation. We shall carry out the calculation of the decay law in the general nonlinear case by the method used by Adirovich to obtain the decay law for crystalline phosphors.[3]

We assume that the concentrations of electrons and holes localized in the traps (recombination centers) are small in comparison with the corresponding concentrations in the zones. In this case

$$n' \approx p', \qquad (3)$$

$$dn'/dt \approx dp'/dt. \qquad (4)$$

* In the present paper we adopt the notation of Refs. 1 and 2.

Equating the expressions for dn'/dt and dp'/dt from the system (2) and replacing p' by n', we arrive at the following expression for the concentration of non-equilibrium electrons localized in the traps

$$n'_t = \frac{(A_e p_{t0} - A_h n_{t0}) n'}{A_h (n_0 + n_1) + A_h (p_0 + p_1) + (A_e + A_h) n'} . \tag{5}$$

Introducing the lifetimes τ_0, τ_{p0}, τ_{n0},[2]

$$\tau_0 = \tau_0 \frac{n_0 + n_1}{n_0 + p_0} + \tau_{p0} \frac{p_0 + p_1}{n_0 + p_0}; \quad \tau_{n0} = \frac{1}{A_e N_t}; \quad \tau_{p0} = \frac{1}{A_h N_t}, \tag{6}$$

we put the relation (5) in the form:

$$n'_t = (\tau_{p0} p_{t0} - \tau_{n0} n_{t0}) n' / [(n_0 + p_0) \tau_0 + (\tau_{p0} + \tau_{n0}) n']. \tag{7}$$

Substituting n'_t from Eq. (7) into the first equation of the system (2), we get the differential equation

$$-\frac{dn'}{dt} = \frac{(n_0 + p_0) n' + (n')^2}{(n_0 + p_0) \tau_0 + n' (\tau_{p0} + \tau_{n0})},$$

and integration of this under the initial condition $n' = \Delta n$ at $t = 0$ gives the desired decay law

$$\exp\left(-\frac{t}{\tau_{p0} + \tau_{n0}}\right) = \frac{n'}{\Delta n} \left(\frac{1 + (n_0 + p_0)/n'}{1 + (n_0 + p_0)/\Delta n}\right)^{1 - \tau_0/(\tau_{p0} + \tau_{n0})} \tag{8}$$

Let us now determine the physical conditions corresponding to the assumptions (3) and (4), on which the decay law (8) is based. Since $p' = n' + n'_t$, the assumption (3) and (4) are equivalent to the inequalities

$$n'_t \ll n', \quad |dn'_t/dt| \ll |dn'/dt|.$$

From expression (5) it follows that

$$\left|\frac{n'_t}{n'}\right| = \frac{|A_e p_{t0} - A_h n_{t0}|}{|A_e (n_0 + n_1) + A_h (p_0 + p_1) + n' (A_h + A_e)} < \frac{A_e p_{t0} + A_h n_{t0}}{A_e (n_0 + n_1) + A_h (p_0 + p_1)} < \frac{N_t}{a (n_0 + n_1 + p_0 + p_1)},$$

where a is the smaller of the ratios τ_{p0}/τ_{n0} and τ_{n0}/τ_{p0} [see Eq. (6)].

An analogous estimate can also be obtained for the ratio of derivatives $|dn'_t/dt|/|dn'/dt|$. Consequently, at small concentrations of traps[1] $N_t \ll a(n_0 + n_1 + p_0 + p_1)$, Eq. (8) gives the decay law for the concentration of non-equilibrium carriers at arbitrary levels of generation.

This discussion shows that at small concentrations of traps the non-equilibrium concentrations of electrons and holes in the zones are practically the same: $n' = p' + p'_t \approx p'$, not only for $n' \gg N_t$, which is trivial (or $p'_t \leq N_t$), but also at moderate and small levels of generation, and also at any stage of the decay process. Therefore the processes in question can be characterized by a single lifetime of a non-equilibrium electron-hole pair,[4] given by the expressions:

$$\tau = -\frac{n'}{dn'/dt} \approx -\frac{p'}{dp'/dt}. \tag{9}$$

The complicated form of the decay law (8) is due to the fact that τ depends on the level of generation.

According to the Shockley-Read formula[2] τ_0 can be larger or smaller than $\tau_{p0} + \tau_{n0}$. Let us consider separately the two cases

$$\tau_0 \gg \tau_{p0} + \tau_{n0}, \tag{10}$$

$$\tau_0 \lesssim \tau_{p0} + \tau_{n0}. \tag{11}$$

In the first case one can distinguish three ranges of variation of the concentrations in which the decay law is approximated by simpler expressions, corresponding to the monomolecular and bimolecular patterns of recombination. In fact, for large generation levels,

$$n' \gg n_0 + p_0, \tag{12}$$

the decay law (8) can be written in the form:*

$$\left(1 - \frac{\tau_0}{\tau_{p0} + \tau_{n0}}\right) \frac{n_0 + p_0}{\Delta n} - \frac{t}{\tau_{p0} + \tau_{n0}} \approx \ln \frac{n'}{\Delta n} + \frac{n_0 + p_0}{n'} \left(1 - \frac{\tau_0}{\tau_{p0} + \tau_{n0}}\right),$$

* By transforming Eq. (8) by means of the limit relation $(1 + \alpha)^{1/\alpha} \approx e$ for $\alpha \to 0$ and taking logarithms, we get the expression given in the text.

or, using Eq. (10), we get:

$$\frac{n_0+p_0}{n'}+\frac{\tau_{p0}+\tau_{n0}}{\tau_0}\ln\frac{n_0+p_0}{n'}-\frac{n_0+p_0}{\Delta n}-\frac{\tau_{p0}+\tau_{n0}}{\tau_0}\ln\frac{n_0+p_0}{\Delta n}\approx\frac{t}{\tau_0}. \tag{13}$$

Then for

$$\frac{n_0+p_0}{n'}\Big/\left|\ln\frac{n_0+p_0}{n'}\right|\ll\frac{\tau_{p0}+\tau_{n0}}{\tau_0} \tag{14}$$

the decay law is exponential

$$n'\approx\Delta n\exp\{-t/(\tau_{p0}+\tau_{n0})\}, \tag{15}$$

and for

$$\frac{n_0+p_0}{n'}\Big/\left|\ln\frac{n_0+p_0}{n'}\right|\gg\frac{\tau_{p0}+\tau_{n0}}{\tau_0}, \tag{16}$$

it is hyperbolic

$$1/n'\approx t/(n_0+p_0)\tau_0+\text{const.} \tag{17}$$

In virtue of the condition (10) both the inequalities (14) and (16) are compatible with the condition (12) of a high generation level. The monomolecular law (15) corresponds to larger values of the ratio $n'(n_0+p_0)$ than the bimolecular law (17).

For small levels of generation

$$n'\ll n_0+p_0 \tag{18}$$

by steps analogous to those in Eq. (13), Eq. (8) takes the form:

$$\text{const}-\frac{t}{\tau_0}\approx\ln\frac{n'}{\Delta n}+\frac{\tau_{p0}+\tau_{n0}}{\tau_0}\left(1-\frac{\tau_0}{\tau_{p0}+\tau_{n0}}\right)\frac{n'}{n_0+p_0}. \tag{19}$$

Using the relation (10), we get

$$\frac{n'}{n_0+p_0}-\ln\frac{n'}{n_0+p_0}\approx\frac{t}{\tau_0}+\text{const.} \tag{20}$$

But by inequality (18) one always has

$$\frac{n'}{n_0+p_0}\ll\left|\ln\frac{n'}{n_0+p_0}\right|.$$

Consequently, at small concentrations of the non-equilibrium carriers the decay law is given by the exponential

$$n'\approx ce^{-t/\tau_0}. \tag{21}$$

For the opposite relationship between the lifetimes, given by the inequality (11), the conditions (12) and (16) are incompatible, and therefore the bimolecular decay law does not appear. In this case the approximating expressions are exponentials: Eq. (21) for small values of n' and Eq. (15) for large values.

In the case of exact equality

$$\tau_0=\tau_{p0}+\tau_{n0} \tag{22}$$

these two exponentials are the same, and it can be seen from Eq. (8) that the decay law is described by a single exponential

$$n'=\Delta ne^{-t/\tau},\quad \tau=\tau_0=\tau_{p0}=\tau_{n0} \tag{23}$$

throughout its entire course.

Let us consider in particular the case

$$\tau_0\ll\tau_{p0}+\tau_{n0}. \tag{24}$$

In this case, for small values of n', a region of linear decay can be distinguished before the exponential region.

In fact, referring to Eq. (19) and using condition (24), we get the relation

$$\frac{n'}{n_0+p_0}+\frac{\tau_0}{\tau_{p0}+\tau_{n0}}\ln\frac{n'}{n_0+p_0}+\text{const}\approx-\frac{t}{\tau_{p0}+\tau_{n0}}, \tag{25}$$

in which it is possible to satisfy the inequality [cf. Eq. (17)]

$$\frac{n'}{n_0+p_0}\Big/\left|\ln\frac{n'}{n_0+p_0}\right|\gg\frac{\tau_0}{\tau_{p0}+\tau_{n0}}. \tag{26}$$

Consequently, in the range of values satisfying the inequalities (18) and (26), the decay law in the case (24) is of the form:

$$n'\approx\text{const}-t\,(n_0+p_0)/(\tau_{p0}+\tau_{n0}). \tag{27}$$

We note that when (24) is satisfied the exponential decay law holds for

$$\frac{n'}{n_0+p_0}\Big/\left|\ln\frac{n'}{n_0+p_0}\right|\ll\frac{\tau_0}{\tau_{p0}+\tau_{n0}}. \tag{28}$$

2. DISCUSSION OF RESULTS

According to Ref. 4* the inequality (10) is equivalent to

$$n_1\gg n_0\gg p_0\gg p_1\ \text{and}\ p_{t0}\gg n_{t0}, \tag{29a}$$

if the trapping level and the level of the dominant impurity are located in the same half of the forbidden zone, and

$$p_1\gg n_0\gg p_0\gg p_1,\quad n_{t0}\gg p_{t0}, \tag{29b}$$

if they are in different halves.

Similarly, (11) is equivalent to either

$$n_0\gg n_1\gg p_1\gg p_0, \tag{30a}$$

or

$$n_0\gg p_1\gg n_1\gg p_0. \tag{30b}$$

We note that n_1 and p_1 give the amount of thermal ejection of electrons and holes captured in the traps.† Consequently, the inequality (10) corresponds to a greater value of the thermal ejection, and on the other hand when (11) is satisfied thermal ejection does not play any important part.

The exponential decay law corresponds to a monomolecular kinetics of recombination, i.e., to constant lifetime (τ independent of n'). This is realized for small levels of generation [$\tau=\tau_0$, Eq. (21)] and for very large levels [$\tau=\tau_{p0}+\tau_{n0}$, Eq. (5)]. In the former case the equilibrium degree of filling of the traps is conserved; in the latter case the limiting degree of filling of the traps by electrons and holes is determined by the non-equilibrium carriers themselves and depends only on the effective capture cross-sections.††

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* From Eq. (6.2) of Ref. 4 we get for an electron semiconductor $\frac{(1+\alpha_t/y)(1+\gamma/\alpha_t y)}{1+y^{-2}}\gg1+\gamma$, which gives the relation

$$\left[\exp\left(\frac{E_t-F}{kT}\right)-\gamma\right]\left[1-\exp\left(-\frac{E_t+F}{kT}\right)\right]\gg0,$$

which leads to the relations (29a) and (29b). In the treatment of a hole semiconductor one must replace F by $-F$ and γ by $1/\gamma$ ($\gamma=A_h/A_e$).

†Indeed, the constants B_e and B_h for thermal ejection of electrons and holes are determined by the system of equations (1) and the conditions of thermodynamic equilibrium:

$$B_e=A_e n_0 p_{t0}/n_{t0}=A_e n_1\ \text{and}\ B_h=A_h p_0 n_{t0}/p_{t0}=A_h p_1.$$

††Of course, small values of n' can be obtained not only for small generation levels, but also in the late stages of decay for large Δn. Therefore it is more correct to speak of small and large disturbances of thermal equilibrium.

The equality $\tau_0 = \tau_{p0} + \tau_{n0}$ (to which the exponential law (23) corresponds over the whole range of variation of the concentration of the non-equilibrium carriers) holds in two cases:

(a) If the equilibrium filling of the traps coincides with the limiting value corresponding to large generation levels, i.e., for

$$n_{t0}/p_{t0} = n_{t\infty}/p_{t\infty} = \tau_{p0}/\tau_{n0} = A_e/A_h, \tag{31}$$

$$n_{t0} = n_{t\infty} = \tau_{p0}N_t/(\tau_{p0} + \tau_{n0}),\ p_{t0} = p_{t\infty} = \tau_{n0}N_t/(\tau_{p0} + \tau_{n0}). \tag{32}$$

(b) If the equalities

$$n_0 = p_1,\ p_0 = n_1. \tag{32a}$$

hold. In case a the filling of the traps does not depend on n', and therefore the process of recombination occurs by the monomolecular pattern. Case b occurs for location of the trap levels and those of the dominant impurity in different halves of the forbidden zone. Then for small generation levels[4] the recombination is determined not by the equilibrium degree of filling (p_{t0}, n_{t0}) but by the existence of a "thermal barrier." The equalities (32a) also lead at low generation levels to the relations

$$A_e n_0/B_h = \tau_{p0}/\tau_{n0} = n_{t\infty}/p_{t\infty}, \tag{33a}$$

if the lifetime is determined by the recombination of non-equilibrium empty traps with equilibrium electrons (electron semiconductor), and

$$B_e/A_h p_0 = \tau_{p0}/\tau_{n0} = n_{t\infty}/p_{t\infty}, \tag{33b}$$

if the lifetime is determined by the recombination of non-equilibrium filled traps with equilibrium holes (hole semiconductor).

Thus if at small generation levels the ratio of the thermal ejection and recombination of the carriers captured by the traps, expressed by the relations (33a) and (33b), turns out equal to the limiting degree of filling at large generation levels, then also there is monomolecular recombination during the entire course of the process of decay of the non-equilibrium carriers.

According to Eqs. (29a), (29b), and (12) the bimolecular recombination described by the hyperbola (17) occurs for appreciable values of the thermal ejection and for large concentrations of non-equilibrium carriers. The existence of the thermal ejection brings it about that even at large generation levels the filling of the traps is still far from its limiting value given by Eq. (31).

In fact, using Eqs. (7), (10), and (12), we get:

$$p_t = p_{t0} + p'_t = p_{t0} + \frac{\tau_{n0}n_{t0} - \tau_{p0}p_{t0}}{(n_0 + p_0)\tau_0}p', \tag{34a}$$

$$n_t = n_{t0} + n'_t = n_{t0} + \frac{\tau_{p0}p_{t0} - \tau_{n0}n_{t0}}{(n_0 + p_0)\tau_0}n'. \tag{34b}$$

But, unlike the case of small disturbance of thermodynamic equilibrium, for which one can assume that the filling of the traps is still that characteristic of equilibrium, we have here

$$p_{t0} \gg |n'_t| \gg n_{t0}, \tag{35a}$$

if (29a) holds, and

$$n_{t0} \gg |p'_t| \gg p_{t0}, \tag{35b}$$

for the case of (29b).

Consequently in this case the recombination given by the system of equations (2) is determined by terms that are quadratic in the non-equilibrium concentrations. Indeed, according to Ref. 4, if the lifetime is determined by the recombination of the minority carriers, then, using Eqs. (3), (12), and (35a), we get:

$$-\frac{dp'}{dt} \approx A_h p' n'_t \approx \frac{A_h N_t \tau_{p0}}{(n_0 + p_0)\tau_0}n'p' = \frac{(n')^2}{(n_0 + p_0)\tau_0}. \tag{36a}$$

In this case the traps are emptied by thermal ejection, and everything is determined by the recombination of the non-equilibrium holes ($p' \gg n_0 + p_0$) with non-equilibrium filled traps ($n'_t \gg n_{t0}$). But if the determining role is played by the recombination of the majority carriers, then, taking into account the relations (3), (12), (29b), and (35b), we get:

$$-\frac{dn'}{dt} \approx A_e n' p'_t \approx \frac{A_e N_t \tau_{n0}}{(n_0 + p_0)\tau_0} p' n' \approx \frac{(n')^2}{(n_0 + p_0)\tau_0}. \quad (36b)$$

Here, owing to the location of the trap levels and the dominant impurity levels in different halves of the forbidden zone, the traps are filled up, and everything is determined by the recombination of non-equilibrium electrons ($n' \gg n_0 + p_0$) with non-equilibrium empty traps ($p'_t \gg p_{t0}$). Thus we indeed arrive at Eqs. (36a) and (36b), which give the hyperbola (17).

From the relations (7), (12), and (16) one can obtain the inequality

$$a(n_0 + n_1 + p_0 + p_1) / \left| \ln \frac{n_0 + p_0}{n'} \right| \gg n' \gg n_0 + p_0,$$

where a is the smaller of the ratios A_e/A_h and A_h/A_e. Consequently, the best conditions for the bimolecular recombination (the widest range of variation of n') correspond to large values of the thermal ejection (the quantities n_1 and p_1). In fact, the thermal ejection of carriers back into the zones is the main effect hindering the establishment of the limiting degree of filling of the traps. Therefore the greater the thermal ejection, the wider the range of variation of n' in which the filling of the traps is still far from its limiting value even at large levels of generation. The conditions for the greatest thermal ejection are realized at temperatures corresponding to the maximum in the curve of τ_0 as function of the reciprocal temperature $1/T$, in semiconductors having narrow trap levels.

Of particular interest is the region of the linear decay law, corresponding to increase of the lifetime with increase of the generation level. The necessary condition for the realization of such a process is the inequality (24), which can be fulfilled only if τ_{p0} and τ_{n0} are quantities of different orders of magnitude, namely: for an electron semiconductor, if

$$\tau_{n0} \gg \tau_{p0}, \quad (37a)$$

and for a hole semiconductor, if

$$\tau_{p0} \gg \tau_{n0}. \quad (37b)$$

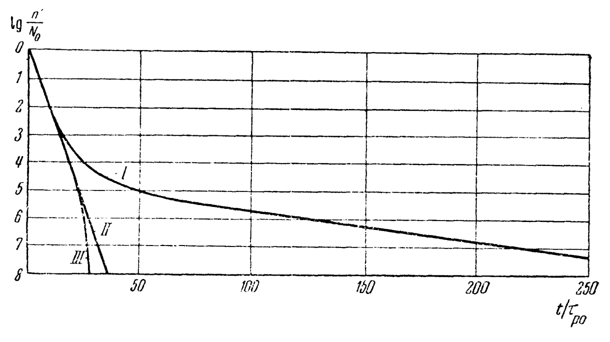
In this case, at low generation levels, according to Eq. (27), a region of variation of n' can be distinguished in which the rate of recombination is constant. Because of the smallness of the thermal ejection of carriers into the zones the limiting degree of filling of the traps is established for small disturbances of thermodynamic equilibrium (i.e., p'_t and n'_t are constants). In this case the system (2) (for an electron semiconductor) takes the form

$$dn'/dt = -A_e(n_0 + n_1)p'_t \approx -A_e n_0 p'_t, \quad dp'/dt = -A_h n_{t0} p' + A_h(p_0 + p_1)p'_t - A_h p' n'_t,$$
$$p' \approx n', \quad p'_t = -n'_t. \quad (38)$$

Substituting into the first equation of the system (38) the value of p'_t given by the relations (32), we get

$$-dn'/dt \approx A_e N_t \tau_{n0} n_0 / (\tau_{p0} + \tau_{n0}) = n_0 / (\tau_{p0} + \tau_{n0}), \quad (39)$$

which for the case considered of an electron semiconductor ($n_0 \gg p_0$) indeed gives the linear decay law (27). Indeed, in this case, because of the smallness of the thermal ejection ($n_0 \gg n_1$) the traps in the equilibrium state are almost completely filled with electrons and everything is determined by the recombination of non-equilibrium empty traps ($p'_t \gg p_{t0}$) with equilibrium electrons ($n = n_0 + n' \approx n_0$, $n' \ll n_0$).



I—$T = T_0 = 300°$ K, II—$T = T_{cr} = 220°$ K, III — $T = 150°$ K

But owing to the limited number of traps and the smallness of the recombination cross-section for an electron in comparison with the corresponding cross-section for holes, the traps are at once filled up with non-equilibrium holes ($p'_t \approx N_t$) and remain in this state for all $n' \gg N_t$. Therefore in the range of variation $n_0 + p_0 \gg n' \gg N_t$ the rate of recombination will be constant, as is indeed expressed by Eq. (39).

We note that the lifetime given by such a scheme of recombination will be proportional to the concentration of non-equilibrium carriers. In fact, by Eqs. (9) and (39), we have:

$$\tau \approx An'.$$

The case (24) is realized at low temperatures in semiconductors in which the recombination cross-section of the minority carriers is much larger than that of the majority carriers.

The diagram shows decay curves of non-equilibrium carriers for a semiconductor with the composition $N_d = 2.5 \times 10^{14}$ cm^{-3}, $N_a = 2.5 \times 10^{13}$ cm^{-3}, $E_1 - E_t = 0.2$ ev, and $A_e = A_h$, for various temperatures.*

CONCLUSIONS

1. The kinetics of the decay of non-equilibrium carriers in semiconductors containing a small concentration of traps is complicated. In some ranges of variation of the concentration of non-equilibrium carriers a dominant part is played by simple recombination schemes, which makes the decay law approximately exponential, hyperbolic, or linear form.

2. Besides the thoroughly studied monomolecular (τ = const) and bimolecular ($\tau = A/n'$) types of recombination kinetics, in a semiconductor there can also occur a situation of constant rate of recombination, which corresponds to a lifetime proportional to the concentration of non-equilibrium carriers, $\tau = An'$. Recombination occurs in this way at low temperatures in semiconductors in which the recombination cross-section of the minority carriers is much larger than that of the majority carriers.

3. Under definite conditions as to the composition and temperature, expressed by the equality $\tau_0 = \tau_{p0} + \tau_{n0}$, the decay of the non-equilibrium carriers follows the monomolecular pattern throughout its entire course.

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* The critical temperature T_{cr} is determined from the equality $\tau_{p0} + \tau_{n0} = \tau_0$, when the decay law throughout its course is the exponential $n' = \Delta n e^{-t/\tau}$.

We have

$$N_0 = 2(2\pi m k T_0/h^2)^{3/2} = 2.5 \times 10^{19}\ \text{cm}^{-3}.$$