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Institute of Physics of Solids and Semiconductors,
Academy of Sciences of the Belorussian SSR, Minsk[1]

Trapping of Minority Carriers in Thermal U$^-$-Donors in n-Si

By

L. F. Makarenko and L. I. Murin

Theoretical studies are made on the trapping behavior of the semiconductor containing U$^-$-donors. The theoretical analysis results are compared with the experimental data for the two sets of bistable thermal donors in n-Si.

Рассмотрена модель прилипания неосновных носителей тока в полупроводнике, содержащем U$^-$-центры. Результаты теоретического анализа сравниваются с экспериментальными данными, полученными для двух видов бистабильных термодоноров в кристаллах n-Si.

1. Introduction

Trapping of minority carriers and slow relaxation of nonequilibrium conductivity in oxygen containing n-Si crystals were investigated and interpreted for the first time in [1]. The authors [1] revealed several types of centres (α-, β- ... traps) which caused slow conductivity relaxation. The obtained data were interpreted in terms of the trapping model developed for crystals with single level traps [2, 3]. However, detailed studies on the temperature dependence of majority carrier concentration in heat-treated crystals of n-Si⟨O⟩ performed by us [4, 5] have revealed the β- and γ-traps to be divalent bistable thermal donors (BTD) with occupancy level inverted order of the first and the second electrons (U$^-$-centre). These results require the development of a new model of photoconductivity which should involve both the existence of multiple-charge conditions for these centres and their inverted level order. This paper is mainly concerned with the analysis of the kinetics of the long-time component of photoconductivity (PC) related to the charge change of BTD.

2. Some Properties of Bistable Thermal Donors

A bistable thermal donor can exist in two configurations with different energy spectra of localized electronic states. In one of them (later on referred to as H) the center is a double donor with shallow levels $E_H(0/+) = E_c - 0.05\text{ eV} \div 0.07\text{ eV}$ and $E_H(+/++) = E_c - 0.14\text{ eV} \div 0.16\text{ eV}$. At the same time the energy required for the electron emission from the neutral BTD to occur in another configuration B exceeds greatly $\Delta E_{2H} = E_c - E_H(+/++)$.

According to [4, 5] BTD is an Anderson negative-U system. Under equilibrium conditions the average number of electrons on the centre is determined at any Fermi level position F_0 by only one parameter, namely the occupancy level $E(0/++)$. At $F_0 > E(0/++)$ BTD will be in a neutral state, the equilibrium occupation probability of this state $f_0^{(0)}$ is about unity; at $F_0 < E(0/++)$ the BTD main state will be the doub-

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[1] P. Browki 17, SU-220726 Minsk, USSR.

ly positively charged state, $f_0^{(++)} \approx 1$. The equilibrium occupation probability of the singly ionized state of BTD will always be small, $f_0^{(+)} \ll 1$.

Owing to the bistability of the neutral state of BTD it is $f_0^{(0)} = f_{0\mathrm{B}}^{(0)} + f_{0\mathrm{H}}^{(0)}$, where $f_{0\mathrm{B}}^{(0)}$ and $f_{0\mathrm{H}}^{(0)}$ are the equilibrium occupation probabilities of the neutral states of B and H configurations of BTD. Since $f_{0\mathrm{B}}^{(0)} \gg f_{0\mathrm{H}}^{(0)}$ it is always $f_0^{(0)} \approx f_{0\mathrm{B}}^{(0)}$. The doubly ionized state of BTD is monostable, therefore $f_0^{(++)} \equiv f_{0\mathrm{H}}^{(++)}$, where $f_{0\mathrm{H}}^{(++)}$ is the equilibrium occupation probability of the doubly ionized state of the H configuration.

However, at relatively small concentration of equilibrium carriers ($n_0 \lesseqqgtr 10^{14}$ to 10^{15} cm^{-3}) one can easily "freeze" BTD in the H configuration by quenching the n-Si crystals in liquid nitrogen from the temperatures at which $F_0 < E(0/++)$. In this case the H^0 and H^+ states could be realized and one can observe the well-known hydrogen-like series of absorption bands in the region 400 to 1100 cm^{-1} [6, 7]. Besides, the $E_\mathrm{H}(0/+)$ and $E_\mathrm{H}(+/++)$ levels can be determined from the measured temperature dependences of the Hall coefficient for such crystals [4, 5]. Fig. 1a represents the BTD occupancy level scheme. The $E(0/+)$ and $E(0/++)$ levels characterize BTD as a system of B and H configurations. The $E(+/++)$ level is practically determined only by the properties of the H configuration and coincides with the $E_\mathrm{H}(+/++)$ level.

Under external illumination BTD may change both charge state and configuration. As shown in [4] the trapping of non-equilibrium holes created by extrinsic illumination of the crystals leads to a rearrangement of BTD from B to H configuration. When the quasi-equilibrium electron Fermi level F_n is below $E_\mathrm{H}(+/++)$, the final state of the centre will be H^{++} and the summary reaction is

$$\mathrm{B}^0 + \mathrm{h} \rightarrow \mathrm{H}^{++} + \mathrm{e}\,. \tag{1}$$

If $F_\mathrm{n} > E_\mathrm{H}(+/++)$, then the final centre charge state will be H^+. After turning off the illumination a long-time decay of PC is observed due to the BTD rearrangement to the initial state. The summary reaction for this process at $F_\mathrm{n} < E_\mathrm{H}(+/++)$ will be

$$\mathrm{H}^{++} + 2\mathrm{e} \rightarrow \mathrm{B}^0\,. \tag{2}$$

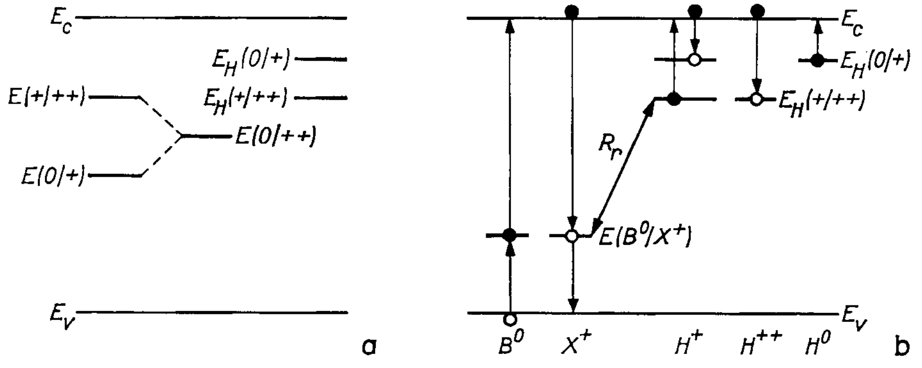

Fig. 1. a) The BTD level occupancy diagram. For the thermal equilibrium the $E(0/+)$ and $E(+/++)$ levels could be changed on the mean level $E(0/++)$ introduced in [11]. The $E_\mathrm{H}(0/+)$ and $E_\mathrm{H}(+/++)$ levels determine the BTD occupany in "freezed" H configuration. b) Scheme of electron (●) and hole (○) transitions between the conduction and valence bands and the levels of the charge-configurational states of BTD represented below the diagram. R_r is the configurational rearrangement. In case it proceeds from left to right ($\mathrm{X}^+ \rightarrow \mathrm{H}^+$) the empty $E(\mathrm{B}^0/\mathrm{X}^+)$ level disappears and the filled $E_\mathrm{H}(+/++)$ and empty $E_\mathrm{H}(0/+)$ levels appear simultaneously. According to [10] one can introduce the $E(\mathrm{B}^0/\mathrm{X}^+)$ level as $E(\mathrm{B}^0/\mathrm{X}^+) = E_\mathrm{c} + kT \ln (e_{\mathrm{nB}}^0/c_{\mathrm{nX}}^+ N_\mathrm{c})$

Before proceeding to the description of the trapping scheme it should be noted that (2) does not yield a detailed description of the PC relaxation process (at $n_0 \leqq 10^{15}$ cm^{-3} the probability of triple collisions is small). The return of BTD to the initial state should involve several stages. At the first stage the capture of an electron by the H^{++} state and the BTD transition to the H^+ state are, evidently, most likely. When the second electron has been captured from the c-band (or the hole has been emitted to the v-band) the direct transition to the B^0 state becomes possible. However, the possibility of the latter process involving several stages cannot be ruled out. First, the rearrangement of BTD from the H^+ state to some other singly ionized one (later on referred to as X^+) with configuration slightly different from that of B_0 occurs. Only then the transition from the X^+ state to the B^0 one takes place due to the capture (emission) of free carriers by BTD. A similar model of the U^--centre with bistable, singly ionized state was used when analyzing PC in amorphous silicon [8] and the field effect in chalcogenide glasses [9].

Thus we shall regard BTD as a centre with five different states: B^0, X^+, H^0, H^+, and H^{++}.

3. Scheme of Electron Transitions and Kinetic Equations

In such a model of the centre several paths of transformation from H to B configuration are possible. Let us consider in detail only one of them which, in our opinion, is the main channel of decay of the BTD metastable occupancy.

We assume that the rate of the configuration rearrangement $X^+ \to H^+$ is the largest one compared to those for other possible processes, which also lead to the transition from X to H configuration. Then the variation of the BTD occupancy with the concentration of excess carriers can be described by the following scheme of transitions between different states of this centre:

$$\begin{tikzcd}
 & & & H^{++} \arrow[dl, shift left] \\
B^0 \arrow[r, shift left, "a"] & X^+ \arrow[l, shift left] \arrow[r, shift left, "b"] & H^+ \arrow[l, shift left] \arrow[ur, shift left, "c"] \arrow[dr, shift left, "d"] & \\
 & & & H^0 \arrow[ul, shift left]
\end{tikzcd} \tag{3}$$

Reactions (3a), (3c), and (3d) occur due to the capture and emission of charge carriers by different BTD states. The rates of these processes have been defined as in [10]. Thus for the reaction (3a) the rates of the direct v_1 and reverse w_1 processes will be

$$B^0 \to X^+, \qquad v_1 = c_{pB}^0 p + e_{nB}^0, \tag{4a}$$

$$X^+ \to B^0, \qquad w_1 = c_{nX}^+ n + e_{pX}^+, \tag{4b}$$

where n and p are the concentrations of electrons in the c-band and holes in the v-band, n_0 and p_0 are the corresponding equilibrium values; c_{pB}^0 and e_{nB}^0 are the coefficients of the hole capture and electron emission by the B^0 state, c_{nX}^+ and e_{pX}^+ the coefficients of the electron capture and hole emission by the X^+ state, which are independent of the free carrier concentration. The rates of the direct v_2 and v_3 and reverse w_2 and w_3 transitions for reactions (3c) and (3d) are determined in the same way.

The rates of the structural rearrangement (3b) are determined as

$$X^+ \to H^+, \qquad \omega_1 = \omega_{10} \exp\left(-\frac{E_{aX}}{kT}\right), \tag{5a}$$

$$H^+ \to X^+, \qquad \omega_2 = \omega_{20} \exp\left(-\frac{E_{aH}}{kT}\right). \tag{5b}$$

According to [4] the transition from the X$^+$ to H$^+$ state occurs spontaneously, i.e. the X$^+$ state has higher energy and, consequently, the barrier height for the direct reaction (3b) E_{aX} will be lower than the same value for the reverse reaction E_{aH}. Therefore, we assume in further analysis that

$$\omega_1 \gg \omega_2 \,. \tag{6}$$

The examined transition scheme can be simplified if the coefficients of hole capture and the rate of hole emission by positively charged H$^+$ and H^{++} states are regarded to be small. That is, $v_2 \approx e^+_{\mathrm{nH}}$, $w_2 \approx c^{++}_{\mathrm{nH}} n$, $v_3 \approx c^+_{\mathrm{nH}} n$, and $w_3 \approx e^0_{\mathrm{nH}}$, i.e. $E_{\mathrm{H}}(0/+)$ and $E_{\mathrm{H}}(+/++)$ are trapping levels for electrons. The conventional energy-level diagram illustrating the reaction kinetics for BTD is shown in Fig. 1b.

In order to describe the PC we consider the model of a homogeneous n-type semiconductor, which contains both recombination centres which determine the lifetime of holes τ_{r} and bistable double donors which are ineffective in terms of recombination processes. If the volume rate of the electron–hole pair photogeneration G does not depend on coordinates, the system of kinetic equations describing the nonequilibrium processes will be as follows:

$$\frac{\mathrm{d}p}{\mathrm{d}t} = G - \frac{\delta p}{\tau_{\mathrm{r}}} - N(c^0_{\mathrm{pB}}\, \delta p\, f^{(0)}_{\mathrm{B}} - e^+_{\mathrm{pX}} f^{(+)}_{\mathrm{X}}) \,, \tag{7}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} f^{(0)}_{\mathrm{B}} = -v_1 f^{(0)}_{\mathrm{B}} + w_1 f^{(+)}_{\mathrm{X}} \,, \tag{8}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} f^{(+)}_{\mathrm{X}} = v_1 f^{(0)}_{\mathrm{B}} - (\omega_1 + w_1)\, f^{(+)}_{\mathrm{X}} + \omega_2 f^{(+)}_{\mathrm{H}} \,, \tag{9}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} f^{(+)}_{\mathrm{H}} = \omega_1 f^{(+)}_{\mathrm{X}} - (\omega_2 + v_2 + v_3)\, f^{(+)}_{\mathrm{H}} + w_2 f^{(++)}_{\mathrm{H}} + w_3 f^{(0)}_{\mathrm{H}} \,, \tag{10}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} f^{(++)}_{\mathrm{H}} = v_2 f^{(+)}_{\mathrm{H}} - w_2 f^{(++)}_{\mathrm{H}} \,, \tag{11}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} f^{(0)}_{\mathrm{H}} = v_3 f^{(+)}_{\mathrm{H}} - w_3 f^{(0)}_{\mathrm{H}} \,. \tag{12}$$

It is suggested that the recombination rate of excess free holes is proportional to their concentration $\delta p = p - p_0$, where p_0 and p are equilibrium and nonequilibrium values of the free hole concentration. The probabilities of occupying different BTD states are related by

$$f^{(0)}_{\mathrm{B}} + f^{(+)}_{\mathrm{X}} + f_{\mathrm{H}} = 1 \,, \tag{13}$$

where $f_{\mathrm{H}} = f^{(0)}_{\mathrm{H}} + f^{(+)}_{\mathrm{H}} + f^{(++)}_{\mathrm{H}}$ is the summary fraction of BTD in the H configuration. Besides, the charge balance condition is fulfilled,

$$n = p + (N_{\mathrm{d}} - N_{\mathrm{a}}) + N(f^{(+)}_{\mathrm{X}} + f^{(+)}_{\mathrm{H}} + 2 f^{(++)}_{\mathrm{H}}) \,. \tag{14}$$

Using (14) the PC value can be represented as a sum of two components,

$$\delta\sigma = \delta\sigma_{\mathrm{p}} + \delta\sigma_{\mathrm{t}} \,,$$

where

$$\delta\sigma_\mathrm{p} = e(\mu_\mathrm{n} + \mu_\mathrm{p})\,\delta p\,, \tag{15}$$

$$\delta\sigma_\mathrm{t} = e\mu_\mathrm{n}(\delta N_\mathrm{X}^{(+)} + \delta N_\mathrm{H}^{(+)} + 2\,\delta N_\mathrm{H}^{(++)}) \equiv e\mu_\mathrm{n}\,\delta p_\mathrm{t}\,. \tag{16}$$

In (16) δp_t is the total concentration of excess holes in all levels of BTD.

4. Steady-State Condition

The occupancy numbers of different BTD states under nonequilibrium steady-state conditions, $f_\mathrm{Bs}^{(0)}$, $f_\mathrm{Xs}^{(+)}$, $f_\mathrm{Hs}^{(++)}$, etc., can easily be determined assuming that the right-hand side of (8) to (12) are equal to zero. It is evident that the ratio of the occupancy numbers of either two states will be equal to the ratio of the rates of direct and reverse transitions between them. For instance, the ratio between the occupancy numbers $f_\mathrm{X}^{(+)}$ and $f_\mathrm{H}^{(+)}$ will be the same as that under thermal equilibrium conditions,

$$\frac{f_\mathrm{Xs}^{(+)}}{f_\mathrm{Hs}^{(+)}} = \frac{\omega_2}{\omega_1}\,. \tag{17}$$

As follows from (6) and (17) the BTD fraction in the X$^+$ state under steady-state conditions is always small and its effect on the value of stationary photoconductivity is negligible. Besides, in accordance with the above transition scheme,

$$\frac{f_\mathrm{Hs}^{(0)}}{f_\mathrm{Hs}^{(+)}} = \frac{v_\mathrm{3s}}{w_\mathrm{3s}} = \frac{n_\mathrm{s}}{n_\mathrm{H}(0/+)}\,, \tag{18}$$

$$\frac{f_\mathrm{Hs}^{(+)}}{f_\mathrm{Hs}^{(++)}} = \frac{w_\mathrm{2s}}{v_\mathrm{2s}} = \frac{n_\mathrm{s}}{n_\mathrm{H}(+/++)}\,, \tag{19}$$

where $n_\mathrm{H}(0/+) = e_\mathrm{nH}^{+}/c_\mathrm{nH}^{++}$, $n(+/++) = e_\mathrm{nH}^{0}/c_\mathrm{nH}^{+}$.

Thus the levels $E_\mathrm{H}(0/+)$ and $E_\mathrm{H}(+/++)$ are also in thermal equilibrium with the c-band. This allows one to write down the stationary concentration of additional carriers, associated with the BTD rearrangement, as follows:

$$\delta p_\mathrm{ts} = \left[\frac{f_\mathrm{Hs}^{(+)}}{f_\mathrm{Hs}} + 2\,\frac{f_\mathrm{Hs}^{(++)}}{f_\mathrm{Hs}}\right]\delta N_\mathrm{Hs}\,. \tag{20}$$

It is apparent that at $F_\mathrm{n} > E_\mathrm{H}(0/+)$ $f_\mathrm{Hs}^{(+)} = f_\mathrm{Hs}^{(++)} \approx 0$ and PC associated with BTD is absent. Therefore, we shall deal later on with the case where F_n is below $E_\mathrm{H}(0/+)$. In this case the excess stationary concentration of BTD in the H configuration is determined by the relation between the hole capture rate by the B^0 state and the BTD relaxation rate to the equilibrium state. When the BTD concentration is small ($N \ll n_0$),

$$\delta N_\mathrm{Hs} = \frac{c_\mathrm{pB}^0\,\delta p_\mathrm{s}}{\tau_{00}^{-1} + c_\mathrm{pB}^0\,\delta p_\mathrm{s}}\,f_\mathrm{B}^{(0)} N\,, \tag{21}$$

where τ_{00}^{-1} is the PC relaxation rate, to be determined in the next section.

As follows from (20) and (21) the maximum value δp_ts attained at $c_\mathrm{pB}^0\,\delta p \gg \tau_{00}^{-1}$ depends only on F_n. This dependence is given in Fig. 2.

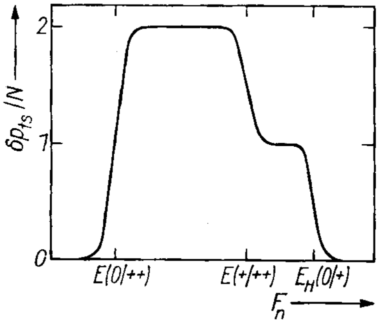

Fig. 2. Maximum stationary concentration of excess trapped holes δp_{ts} as a function of electron Fermi level F_n

5. Relaxation Processes

The transient processes will be analyzed in the approximation of small BTD concentration $N \ll n_0$. We shall confine our attention to the case of absence of multiple trapping of minority carriers, which is realized in n-Si crystals [1]. This will be the case when recombination centre concentration is sufficiently high and accordingly the hole lifetime is small, i.e. $\tau_r^{-1} \gg N c_{pB}^0$.

Then one can neglect the right-hand terms of (7), which are related to transitions between the v-band and BTD, under the assumption that the rate of hole emission by the X^+ state will be low at not very high temperatures. In this case a certain stationary hole concentration independent of the BTD state in the crystal is attained during the time τ_r when the external conditions are changed. As τ_r is small it can be considered that on turning on or off the external excitation source at $t = 0$ the hole concentration changes instantly from some stationary value p_{s1} at $t < 0$ to another stationary value p_{s2} at $t \geqq 0$. If there is an external excitation at $t < 0$ and at $t \geqq 0$ p_{s1} and p_{s2} differ from their equilibrium value p_0.

When the above-mentioned conditions are fulfilled, (8) to (12) are a set of linear differential equations with constant coefficients.

As in Section 4 we consider the case $F_n < E_H(0/+)$. In this case the excess carrier behaviour can be described by a simpler set of equations as compared with (8) to (12),

$$\frac{d}{dt} f_B^{(0)} = w_1 - (v_1 + w_1) f_B^{(0)} - w_1 f_H , \tag{22}$$

$$\frac{d}{dt} f_H = \omega_1 - \omega_1 f_B^{(0)} - (\omega_1 + \omega_2) f_H + \omega_2 f_H^{(++)} , \tag{23}$$

$$\frac{d}{dt} f_H^{(++)} = v_2 f_H - (v_2 + w_2) f_H^{(++)} . \tag{24}$$

The expression for δp_t obtained by solving this set is

$$\delta p_t = \delta p_{ts} + N \left(\frac{v_2}{v_2 + w_2} \delta f_{Bs}^{(0)} + \delta f_{Hs}^{(++)} \right) \exp(-\lambda_H t) - \\ - N \frac{2 v_2 + w_2}{v_2 + w_2} \delta f_{Bs}^{(0)} \exp(-\lambda_{s0} t) , \tag{25}$$

where $\delta f_{Bs}^{(0)}$ and $\delta f_{Hs}^{(++)}$ are the initial deviations of the occupancy numbers $f_B^{(0)}$ and $f_H^{(++)}$ from their stationary values attained at $t \to \infty$; δp_{ts} is the stationary value of

δp_t at $p = p_{s2}$. While solving (22) to (24) we have taken into account that the ω_1 and $v_2 + w_2$ values substantially exceed ω_2, v_1, and w_1. Then λ_{s0} will be

$$\lambda_{s0} = c^0_{pB} p_{s2} + e^0_{nB} + \frac{f^{(+)}_{Hs}}{f_{Hs}} \frac{\omega_2}{\omega_1} (c^+_{nX} n_{s2} + e^+_{pX}) \tag{26}$$

and assuming $\omega_1 \gg v_2 + w_2$, then

$$\lambda_H = v_2 + w_2 \,. \tag{27}$$

First consider the growth of PC. The semiconductor is in equilibrium at $t < 0$ and at $t = 0$ the external illumination is turned on, the corresponding hole concentrations being $p_{s1} = p_0$ and $p_{s2} = p_0 + \delta p_s$ (supposing that $\delta p_s \ll n_0$). In this case $\delta f^{(0)}_{Bs}$ and $\delta f^{(++)}_{Hs}$ are related in such a way that the second term on the right-hand side of (25) is reduced to zero and the change of δp_t is determined only by the long-time component of PC. At $\delta p_s = 0$[2]) the PC growth rate τ_g^{-1} has the minimum value $\tau_{00}^{-1} = \lambda_{s0}(n_0, p_0)$.

With increasing excess hole concentration the time constant of PC growth reduces. If the hole concentration is such that under steady-state conditions the part of BTD in the B^0 state is very small, then τ_g^{-1} will be determined only by the rate of the hole capture by the B^0 state.

Let us consider now the decay of PC ($p_{s1} = p_0 + \delta p_s$ and $p_{s2} = p_0$). If the semiconductor were at $t < 0$ in the stationary state, i.e. (17) to (19) were fulfilled then as in the case of the PC growth, the second term on the right-hand side of (25) would be equal to zero and the time constant of the decay would be τ_{00}. On the other hand, if we assume $\delta f^{(0)}_{Bs}$ and $\delta f^{(++)}_{Hs}$ to be arbitrary values at $t > 0$ (certainly, (14) should be fulfilled in this case), then the distribution of BTD among the X^+, H^+, and H^{++} states will be, after the period of time $\Delta t > \max\{\omega_1, v_2 + w_2\}$, the same as that under stationary conditions. This distribution is maintained during the whole process of relaxation that allows one to simplify the calculation of relaxation kinetics. Employing (17) to (19) one can easily pass from the set (8) to (12) to an ordinary differential equation of first order. This method of analysis of relaxation kinetics is used in the Appendix in the case of arbitrary BTD concentration.

6. Analysis of Temperature Dependences of Relaxation Rate

First consider the special features of the charge carrier capture and emission processes associated with the configurational bistability of the singly ionized state. According to the principle of detailed balance the relation between the electron emission rate from the B^0 state and the cross-section of its capture by the X^+ state should be determined by the energy level differing from the occupancy level $E(0/+)$ (see Fig. 1b). However, in order to describe the slow processes characterized by the time constant exceeding greatly ω_1^{-1} it is reasonable to use the concept of the electron capture from the c-band at the $E(0/+)$ level and the hole emission from the $E(0/+)$ level to the v-band. Actually, the X^+ state can be regarded as an excited state of singly ionized BTD (the H^+ state obviously will be the ground state). According to [10] and assuming the time of the centre thermalization after its transition to the singly ionized state to be small when compared to its average time of existence in this state,

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[2]) This condition can be realized when the sample is rapidly heated in darkness from temperature T_i, when the equilibrium concentration of H^{++} is small, to temperature T_f, when the equilibrium concentration of H^{++} is large.

the following relation is satisfied:

$$e_{nB}^0 = c_n^+ n(0/+) , \tag{28}$$

where $n(0/+) = N_c \exp\left[\left(E(0/+) - E_c\right)/kT\right]$. In this case the coefficient of electron capture at the $E(0/+)$ level c_n^+ is by a factor of ω_1/ω_2 less than the capture coefficient c_{nX}^+. This relation reveals that only a fraction of the centres being in the positively charged state captures electrons with transformation to the B configuration. Similarly, the hole emission rate from the $E(0/+)$ level is

$$e_p^+ = c_{pX}^+ p(0/+) . \tag{29}$$

Thus if (17) is satisfied under nonequilibrium conditions, then the two-step process (3a) and (3b) occurs as if it were a single-step transition $B^0 \rightarrow H^+$. If the time constant of any investigated process is smaller than ω_1^{-1}, this approach is not applicable.

To analyze (26) further it is more convenient to represent it as

$$\tau_{00}^{-1} = c_{pB}^0 p_0 + e_{nB}^0 + \frac{f_{0H}^{(+)}}{f_{0H}} \frac{\omega_2}{\omega_1} c_{nX}^+ n_0 + \frac{f_{0H}^{(+)}}{f_{0H}} \frac{\omega_2}{\omega_1} e_{pX}^+ \equiv \tau_{\pi1}^{-1} + \tau_{v1}^{-1} + \tau_{v2}^{-1} + \tau_{\pi2}^{-1} , \tag{26a}$$

where $\tau_{\pi1}^{-1}$ is the first term, τ_{v1}^{-1} is the second term, etc.

These terms are associated with four different processes, which contribute to the PC relaxation rate. Two of them τ_{v1}^{-1} and τ_{v2}^{-1} are related to the emission by the B^0 state and the capture of free electrons by the X^+ state. Another pair of terms $\tau_{\pi1}^{-1}$ and $\tau_{\pi2}^{-1}$ characterizes the PC relaxation processes due to the capture and emission of free holes by the B^0 and X^+ states, respectively. Accordingly, one can distinguish BTD of the r-type, which exchange charge carriers mainly with c-band and BTD of the t-type for which the hole exchange processes with the v-band are more intensive. In the first case the level corresponding to the transition of BTD from the B^0 state to the X^+ state is the recombination level and in the second case the trapping level. According to the principle of detailed balance,

$$\frac{\tau_{v2}}{\tau_{v1}} = \frac{\tau_{\pi2}}{\tau_{\pi1}} = \frac{f_{0H}^{(++)}}{f_{0B}^{(0)}} . \tag{30}$$

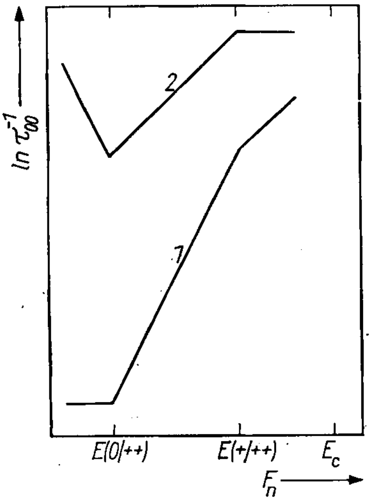

Fig. 3. Relaxation rate of δp_t vs. Fermi level position (1) for BTD of r-type and (2) for BTD of t-type

Making use of (30) one can easily determine the interval of the Fermi level change, where a certain term in the right-hand side of (26a) will dominate.

For BTD of the r-type the term associated with the majority carrier capture by the X^+ state prevails at $F_0 > E(0/++)$ and τ_{00}^{-1} should be proportional to n_0 at $F_0 > E(+/++)$ and to n_0^2 at $F_0 < E(+/++)$. When F_0 is below the $E(0/++)$ level the term associated with electron emission to the c-band by B^0 state becomes dominant and τ_{00}^{-1} does not depend on the electron concentration (Fig. 3).

As to BTD of the t-type τ_{00}^{-1} does not depend on the electron concentration at $F_0 > E(+/++)$ and is proportional to n_0 at $E(0/++) < F_0 < E(+/++)$ ($\tau_{\pi 2}^{-1}$-term). When the Fermi level shifts below $E(0/++)$, the free hole capture dominates and τ_{00}^{-1} is inversely proportional to n_0 (Fig. 3).

If the cross-section of hole capture S_p by the B^0 state and that of electron capture S_n by the X^+ state can reveal the activation dependence on temperature,

$$S_{n(p)} = \tilde{S}_{n(p)} \exp\left(-\frac{\Delta_{n(p)}}{kT}\right), \tag{31}$$

where $\tilde{S}_{n(p)}$ is the frequency factor, $\Delta_{n(p)}$ the activation energy of electron (hole) capture, then the cross-section of electron capture on the $E(0/+)$ level can be defined as

$$S_n^* = \frac{\omega_2}{\omega_1} S_n = \tilde{S}_n^* \exp\left(-\frac{\Delta_n^*}{kT}\right), \tag{32}$$

where $\tilde{S}_n^* = (\omega_{20}/\omega_{10}) \tilde{S}_n$, $\Delta_n^* = \Delta_n - E_{aX} + E_{aH}$.

When the doping impurity is completely ionized in the investigated temperature range, the temperature dependence of free carriers is as represented in Fig. 4a [3] and that of τ_{00}^{-1} as in Fig. 4b. At $T < T_h$ the condition $F_0 > E(0/++)$ is fulfilled and the dependence $\tau_{00}^{-1}(1/T)$ is determined by the term $\tau_{\nu 2}^{-1}$ for BTD of r-type and the term $\tau_{\pi 2}^{-1}$ for BTD of t-type. At $T < T_l$ the activation energy E_a for $\tau_{\nu 2}^{-1}(\tau_{\pi 2}^{-1})$ is changed due to the variation of the H configuration stationary charge state. For BTD of r-type $E_{al} = \Delta_n^*$ at $F_0 > E(+/++)$ $(T < T_l)$ and $E_{am} = \Delta_n^* - \Delta E_2$ at $E(0/++) < F_0 < E(+/++)$ $(T_h > T > T_l)$ and for BTD of t-type in the same positions of the

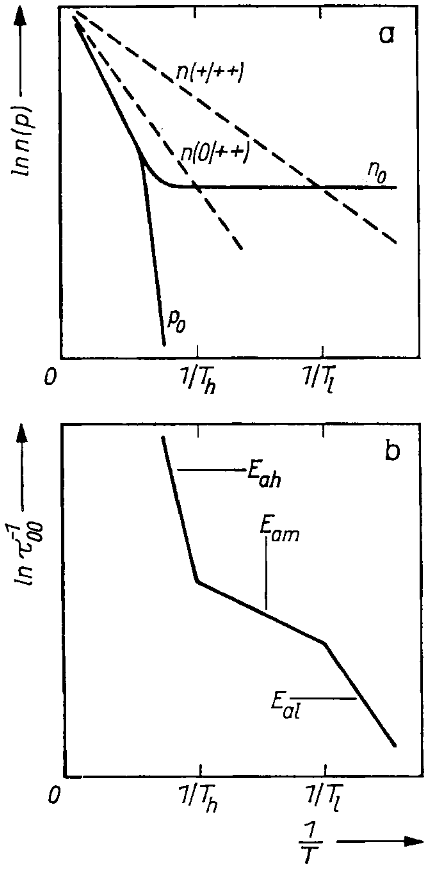

Fig. 4. Temperature dependence a) of equilibrium carrier concentrations and b) of relaxation rate τ_{00}^{-1} in the same semiconductor

Fermi level $E_{\mathrm{al}} = \Delta_{\mathrm{p}} + E_{\mathrm{G}} - \Delta E_1$ and $E_{\mathrm{am}} = \Delta_{\mathrm{p}} + E_{\mathrm{G}} - \Delta E_1 - \Delta E_2$ where E_{G} is the energy band gap and $\Delta E_1 = E_{\mathrm{c}} - E(0/+)$, $\Delta E_2 = E_{\mathrm{c}} - E(+/++)$. At $T > T_{\mathrm{h}}$, where $F_0 < E(0/++)$, the rate of the BTD rearrangement is determined either by the $\tau_{\nu 1}^{-1}$ term with activation energy $E_{\mathrm{ah}} = \Delta_{\mathrm{n}}^* + \Delta E_1$ or by the $\tau_{\pi 1}^{-1}$ term with $E_{\mathrm{ah}} = E_{\mathrm{G}} + \Delta_{\mathrm{p}}$.

Thus the dependence $\tau_{00}^{-1}(1/T)$ for the BTD both of r- and t-type in a limited temperature range can be given as

$$\tau_{00}^{-1} = n_0^{b_i} A_i(T) \exp\left(-\frac{E_{\mathrm{ai}}}{kT}\right), \tag{33}$$

where $b_i = -1, 0, 1, 2$ and the pre-exponential factor $A_i(T)$ has a power law temperature dependence.

For b_i and E_{ai} the following relations specified by the inverse ordering of the $E(0/+)$ and $E(+/++)$ levels should be fulfilled:

(i) while passing from the temperature range $T < T_1$ to that of $T > T_1$ (at $T_1: F_0 = E(+/++)$) the activation energy E_{ai} should decrease by the value of ΔE_2 and the exponent b_i should be increased by 1;

(ii) if the investigated temperature region includes T_{h} (at T_{h}: $F_0 = E(0/++)$), then the E_{ai} value at $T > T_{\mathrm{h}}$ exceeds E_{ai} at $T < T_{\mathrm{h}}$ by $\Delta E_1 + \Delta E_2$, while the corresponding b_i value diminishes by 2.

7. Comparison of Theory with Experiments and Concluding Remarks

As an experimental check-up of the analysis performed we consider the temperature dependence of the relaxation time of the slow component of PC for n-Si⟨O⟩ crystals ($\varrho = 2$ to $200\ \Omega$ cm) with BTD of two types: α-traps and β-traps (Fig. 5 a and b). First consider the β-trap which has been investigated in more detail earlier [1, 4].

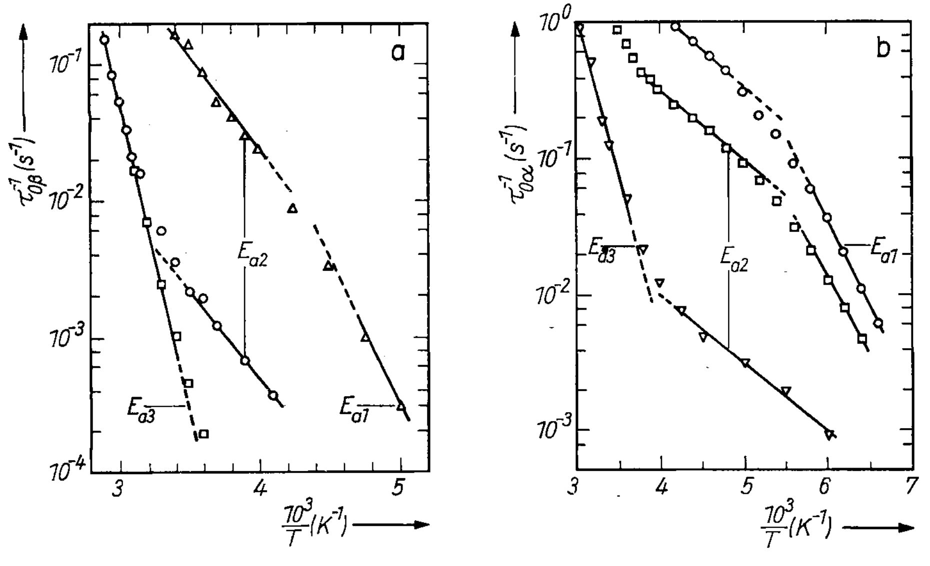

Fig. 5. Temperature dependences of relaxation rate of slow photoconductivity related with a) β-BTD: ϱ = □ 60, ○ 20, △ 2 Ω cm and b) α-BTD: ϱ = ▽ 200, □ 60, ○ 20 Ω cm

It should be noted that in both [1] and [4] the ratio of the concentration of the traps to the concentration of free electrons has not been taken into account and the relaxation time τ_0 has been measured only under the condition of small deviation from equilibrium, i.e. $n_0 \gg \delta n$ (while for determining τ_{00} two conditions should be fulfilled, $n_0 \gg \delta n$ and $n_0 \gg N$). As shown in the Appendix τ_0 is somewhat different from τ_{00} when the Fermi level is near $E(0/{+}{+})$.

According to [4, 5] the $E(0/{+}{+})$ level of the β-trap is near $E_c - 0.32$ eV and the relaxation rate of PC associated with their rearrangement can be represented as a sum of two terms. The first term $\hat{\tau}_{0\beta}^{-1}$ depends only on temperature, the second term $\check{\tau}_{0\beta}^{-1}$ which dominates at lower temperatures is proportional to the square of the carrier concentration in the moderately low temperature range [1, 4]. The difference in activation energies for $\hat{\tau}_{0\beta}^{-1}$ ($E_{a3} \approx 0.91$ eV) and $\check{\tau}_{0\beta}^{-1}$ ($E_{a2} \approx 0.27$ eV) in accordance with the present model is $E_{a3} - E_{a2} = 2(E_c - E_\beta(0/{+}{+}))$. Besides we have established that in crystals with $\varrho \approx 2\ \Omega$ cm the activation energy of $\check{\tau}_{0\beta}^{-1}$ increases at the Fermi level $\geqq E_c - 0.15$ eV. Thus the β-centre in the investigated temperature and carrier concentration ranges behave as BTD of r-type, which makes clear the absence of hole retrapping even at high concentrations of β-traps.

Let us consider the experimental evidence for the α-trap [12]. The Fermi level is above the $E_\alpha(0/{+}{+})$ level in the investigated temperature range, nevertheless the $\tau_{0\alpha}^{-1}(1/T)$ dependence is characterized by three activation energies (Fig. 5b) as in the case of the β-trap. The low temperature part of the $\tau_{0\alpha}^{-1}(1/T)$ dependence is determined by the $\tau_{\nu2}^{-1}$-term, as follows from $\tau_{0\alpha}^{-1} \sim n_0$ ($E_{a1} \approx 0.28$ eV), if $F_0 \geqq E_c - 0.15$ eV ($T \leqq 200$ K) and $\tau_{0\alpha}^{-1} \sim n_0^2$ ($E_{a2} \approx 0.1$ eV), if $E_c - 0.4\ \text{eV} \leqq F_0 \leqq E_c - 0.15$ eV ($200\ \text{K} \leqq T \leqq 330$ K). However, the interpretation of E_{a3} for the α-trap is different from that for the β-BTD. The high temperature part of the $\tau_{0\alpha}^{-1}(1/T)$ dependence can be related to the $\tau_{\pi2}^{-1}$ term, which also follows the law $\tau_{\pi2}^{-1} \sim n_0$ at $F_0 < E(+/{+}{+})$. This discrepancy between α- and β-traps is due to the fact that $E_\alpha(0/+) < E_\beta(0/+)$. Thus the α-traps behave as BTD of r-type at low and of t-type at high temperatures.

Earlier in [6] an attempt was made to reveal the infrared absorption bands of the electronic transitions on α-traps. However, it failed, as the stationary concentration of these centres in our crystals was lower than the detection limit of the infrared absorption spectroscopy. So small a concentration value of the α-trap reflects the trend of the change of the stationary concentration of first thermal donor species successively formed [13, 14].

The PC relaxation kinetics has been treated under the assumption that the configurational rearrangement in singly charged state is the main channel determining the rate of the decay of metastable occupancy of BTD. However, another path of transformation is possible, when the configurational rearrangement $H^0 \rightarrow B^0$ has its greatest rate. For this rearrangement a barrier ΔE_{HB} must be overcome. Considering this channel to be the main one, it is possible to account for the observed peculiarity of the experimental dependence of the β-trap related slow PC relaxation time versus temperature and majority carrier concentration.

However, the value of ΔE_{HB} obtained from the experimental data (see [4]) is much greater than the bound energy of the electron in the H^0 state. This fact allows one to suggest that the transition to the B^0 state through the H^0 state by decay of BTD metastable occupancy can be neglegible.

Another fact, confirming the possibility of the configurational rearrangement through the H^+ state, is the revealing of the part of the $\tau_{0\alpha}^{-1}(1/T)$ dependence which is connected with the hole emission from the singly charged state of BTD.

Appendix

Let us consider the effect of a moderately large BTD density on the slow PC behaviour under the assumption that τ_1 is very small. Then at the long-time stage of PC decay $\delta p \ll \delta p_t \approx \delta n$ is fulfilled. We shall also regard the $E_H(0/+)$ and $E_H(+/++)$ levels to be in equilibrium with the conduction band at this stage of the photoconductivity decay, i.e. (18), (19) are valid where the stationary concentration n_s is substituted by its instant value $n(t)$. Assuming that the rates of direct and reverse reactions (3b) are mutually balanced ((17) is fulfilled) we obtain from (8) the following equation describing the decay kinetics of the slow component of excess concentration under the condition of large BTD concentration:

$$\frac{\mathrm{d}\delta n}{\mathrm{d}t} = -\frac{\delta n}{\tau_{\text{inst}}}, \tag{A1}$$

where

$$\begin{aligned}\tau_{\text{inst}}^{1-} = \Bigg\{&(c_{\text{pB}}^0 p + e_{\text{pB}}^0)\left[1 + \frac{N_0^{++}}{n + n(+/++)}\right] + \\ &+ (c_{\text{nX}}^+ n + e_{\text{pX}}^+)\,\frac{\omega_2}{\omega_1}\,\frac{n}{n + n(+/++)} + \\ &+ \frac{N_0^{++}}{n + n(+/++)}\,\frac{\omega_2}{\omega_1}\left[c_{\text{nX}}^+ n_0\,\frac{n + 2n(+/++)}{n(+/++)} + 2c_{\text{nX}}^+ n_0 + 2e_{\text{pX}}^+\right]\Bigg\} \times \\ &\times \left[1 + \frac{N^{++}}{n + n(+/++)}\right]^{-1}.\end{aligned} \tag{A2}$$

In (A2) N_0^{++} and N^{++} are equilibrium and nonequilibrium concentrations of doubly ionized U$^-$-centres, and $n(+/++) = n_H(+/++)\,(1 + \omega_2/\omega_1)$ is the density of free electrons when the Fermi level is at the level $E(+/++)$. It is not necessary to fulfil the requirement (6), as it has been proposed when analyzing relaxation processes in Section 5, where $n_H(+/++)$ has been used as $n(+/++)$.

The relaxation time for small deviations from the thermal equilibrium ($n \approx n_0$) designed as τ_0, is of practical interest. From (A2) it follows that τ_0 differs from τ_{00} only if F_0 is near $E(0/++)$. In this case τ_0 becomes

$$\tau_0^{-1} = \tau_{00}^{-1} + 2\,\frac{\omega_2}{\omega_1}\,\frac{N_0^{++}}{n(+/++)}\,(2c_{\text{nX}}^+ n_0 + e_{\text{pX}}^+)\,. \tag{A3}$$

As follows from (A3) the temperature dependence of relaxation time at large concentration of thermal U$^-$-donors differs from that considered in Section 6. The difference is caused not only by the varying concentration of majority carriers but also by the change in the equilibrium BTD density in doubly ionized state.

References

[1] J. R. Haynes and J. A. Hornbeck, Phys. Rev. **100**, 606 (1955).

[2] J. A. Hornbeck and J. R. Haynes, Phys. Rev. **97**, 311 (1955).

[3] J. S. Blakemore, Semiconductor Statistics, Pergamon Press, 1962.

[4] V. D. Tkachev, L. F. Makarenko, V. P. Markevich, and L. I. Murin, Fiz. Tekh. Poluprov. 17, 526 (1984).

[5] L. F. MAKARENKO, V. P. MARKEVICH, and L. I. MURIN, Fiz. Tekhn. Poluprov. 18, 1936 (1985).
[6] YA. I. LATUSHKO, L. F. MAKARENKO, V. P. MARKEVICH, and L. I. MURIN, Extended Abstr. 10th All-Union Conf. Phys. Semicond., Vol. 3, Beloruss. STI Inst. Press, Minsk 1985 (p. 64).
[7] YA. I. LATUSHKO, L. F. MAKARENKO, V. P. MARKEVICH, and L. I. MURIN, phys. stat. sol. (a) **93**, K181 (1986).
[8] C. R. FRYE and D. ADLER, Phys. Rev. B **24**, 5485 (1981).
[9] C. R. FRYE and D. ADLER, Phys. Rev. B **24**, 5812 (1981).
[10] C. T. SAH and W. SHOCKLEY, Phys. Rev. **109**, 1103 (1958).
[11] G. A. BARAFF, E. O. KANE, and M. SCHLÜTER, Phys. Rev. B **21**, 5662 (1980).
[12] L. F. MAKARENKO and L. I. MURIN, Fiz. Tekh. Poluprov. **19**, 1530 (1986).
[13] B. PAJOT, H. COMPAIN, J. LEROUILLE, and B. CLERJAUD, Physica (Utrecht) **B 117/118**, 110 (1983).
[14] R. ÖDER and P. WAGNER, Defects in Semiconductors, Ed. S. MAHAJAN and J. W. CORBETT, Vol. II, North-Holland Publ. Co., New York 1983 (p. 171).

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