Free carrier recombination in doped silicon at low compensations

L. A. Vorozhtsova, E. M. Gershenzon, Yu. A. Gurvich, F. M. Ismagilova, and A. P. Mel'nikov

V. I. Lenin State Pedagogic Institute, Moscow

Free carrier recombination in silicon is studied for principal impurity concentrations $N = 10^{15}$–10^{17} cm^{-3}, compensations $K = 10^{-5}$–10^{-1}, and optical excitation levels $W_{ph} N = (10^{-3}$–$10^3) \cdot N$ s^{-1} cm^{-3}. Several recombination mechanisms can occur, depending on the values of these parameters and the temperature: 1) direct (cascade) trapping at the attracting centers (AC); 2) trapping by D$^-$D$^+$ complexes; 3) indirect recombination at the attracting centers, i.e., capture into the D$^-$ state with subsequent hopping (along neutral centers) or drifting (along the D$^-$ band), with a flow of carriers to the AC's. Indirect recombination dominates for large N and small K, T, and W_{ph}, and the corresponding lifetime τ is several orders of magnitude shorter than for cascade trapping at the attracting centers. The observed dependence of τ on N and T is explained qualitatively, and the estimated lifetimes τ agree in order of magnitude with the experimental values. Values of τ shorter than the energy relaxation time were observed for $N > 3 \cdot 10^{16}$ cm^{-3} indicating that the photocarrier distribution function was inverted.

1. INTRODUCTION

The lifetime τ of electrons (or holes) excited from neutral centers is generally thought to be determined by cascade trapping by attracting centers[1]:

$$\tau = \tau^+ = (\alpha^+ N^+)^{-1},$$

where α^+ and N^+ are the trapping coefficient and the concentration of the attracting centers. At low photoexcitations $W_{ph} N$ we have $N^+ \approx KN$, so that

$$\tau^+ = \tau_0^+ = (\alpha^+ KN)^{-1}$$

(here K is the compensation, N is the concentration of neutral centers, and we assume $K \ll 1$).

At low temperatures ($kT < \varepsilon_i \approx \varepsilon_0/20$, where ε_0 is the ionization energy for the neutral centers), D$^-$ (A$^+$)-centers[2] are generated in the semiconductor with binding energy ε_i and effective radius $a_i \approx 4.2 a_0$, where a_0 is the Bohr radius for the ground state. These D$^-$ centers (we will assume throughout that the material is n-type) result in the formation of an equal number of attracting centers: $N^+ = KN + N^-$, where N^- is the number of D$^-$ centers. For materials with $K < 5 \cdot 10^{-2}$, there is a temperature T_1 depending on W_{ph} below which N^- exceeds KN and τ^+ decreases.[3-5] For $N^{1/3} a_0 > 5 \cdot 10^{-2}$, the overlapping among the D$^-$ states becomes large enough to permit the trapped electrons to hop along the neutral centers and approach the attracting centers to within a distance $R \approx R_c$, where $R_c \approx 0.6 N^{-1/3}$ is the mean distance between the impurities. This leads to the formation of D$^-$–D$^+$ complexes which are analogous to ionized hydrogen molecules with binding energy $\varepsilon(R) \approx \varepsilon_i + e^2/\varkappa R$ (Refs. 6, 7). The generation of these complexes causes T_1 to increase.

In the above situation the neutral centers act as attachment centers; the steady-state lifetime τ is equal to τ^+, and for $T > T_1$, $\tau^+ = \tau_0^+$. However, our previous measurements[8] showed that this is not always the case—the influence of the neutral centers on the carrier lifetime in Si may be more complicated. For very small K, there is a wide range of temperatures T for which τ is appreciably less than τ_0^+ even

when $T > T_1$ holds, and the ratio τ_0^+/τ may be as large as 10^4. Moreover, τ is N-dependent (and may in fact be determined by N alone), which indicates that some other recombination mechanism is dominant. It has been shown that one such mechanism involves trapping at the neutral centers followed by migration to the attracting centers (indirect recombination). This is the dominant mechanism in materials with low K and sufficiently high doping concentrations, where overlapping of the D$^-$ states allows the electrons to move toward the attracting centers, either by hopping along the neutral centers or by drifting along the D$^-$ band. Materials were classified into groups I and II, depending on which type of transport occurs.

These results suggested that photoconduction along the D$^-$ band should be observed in group-II materials, and indeed in Ref. 9 it was found that for $N^{1/3} a_0 > 6 \cdot 10^{-2}$, $K < 10^{-4}$, and small $W_{ph} = 10^{-3}$–10^{-1} s^{-1}, the D$^-$-band photoconductivity σ_D is nonzero and may be several tens of times larger than the photoconductivity σ_c along the free c-band.

In the present paper, which is a continuation of Ref. 8, we discuss the results of an investigation of the role of the D$^-$ states in free carrier recombination in silicon for a wide range of N, K, and W_{ph} (10^{15}–10^{17} cm^{-3}, 10^{-5}–10^{-1}, and 10^{-3}–10^3 s^{-1}, respectively). We show that under our experimental conditions, the following trapping mechanisms occur in silicon. 1) Ordinary cascade trapping at attracting centers; 2) trapping by D$^-$–D$^+$ complexes; 3) trapping into D$^-$ states, with subsequent hopping toward an attracting center (indirect "hopping" recombination); 4) trapping into D$^-$ states, after which the carriers move along the D$^-$-band toward the attracting centers (indirect D$^-$-band recombination). As N increases and K decreases, the indirect recombination mechanisms 3) and 4) determine τ over a wider range of T and W_{ph}.

The external conditions determine the dominant mechanism. The dependence of τ on N^+ and T is found to be highly unusual: τ may increase substantially as N^+ increases and T decreases. Since the first step in indirect recombination involves trapping at a neutral center, the properties of

TABLE I.

Specimen No.	N_A, 10^{16}cm^{-3}	N_D, 10^{12} cm^{-3}	K, 10^{-4}	Specimen No.	N_A, 10^{16}cm^{-3}	N_D, 10^{12} cm^{-3}	K, 10^{-4}
1	0.004	6	1500	21	3	9	3
2	0.30	12	40	22	3.1	140	45
3	0.38	163	429	23	3.5	4.7	1.3
4	0.5	1	2	24	4	12	3
5	0.5	70	140	25	4	1200	300
6	0.62	12.4	20	26	4.2	2.1	0.5
7	0.67	9.4	14	27	4.3	172	40
8	0.7	3.2	4.6	28	4.5	27	6
9	0.8	4.8	6	29	5	175	35
10	0.8	48	60	30	5.3	1590	300
11	0.89	5.8	6.5	31	5.9	2.2	0.37
12	1.3	74	57	32	6.8	136	20
13	1.35	6.75	5	33	7.3	43.8	6
14	1.6	7.3	4.6	34	7.8	26	3.3
15	2.2	6.6	3	35	8	2.4	0.3
16	2.4	1400	583	36	8	4000	500
17	2.5	0.31	0.125	37	9.4	188	20
18	2.6	19	7.3	38	12	2.4	0.2
19	2.8	0.7	0.25	39	12	36	3
20	3	1.2	0.4				

the latter influence the measurements. For example, the trapping coefficient α^0 increases tenfold as the carrier energy ε increases. The photoelectron distribution function is inverted under certain conditions, so that τ becomes less than the energy relaxation time.

In Sec. 2 below we describe the experimental method and the results of the measurements, while in Sec. 3 we use a model for the electron transitions to analayze the experimental results. The main conclusions are discussed at the end.

2. EXPERIMENTAL METHOD AND RESULTS

The free carriers were excited by background radiation at room temperature in the wavelength range $\lambda = 8$–$12\,\mu$m (we used an interference filter). This ensured that the carriers were uniformly generated inside the doped Si crystals, which in most cases had a Hall geometry with dimension $d = 0.1$ cm along the direction of the radiation. The excitation intensity $W_{ph} N$cm^{-3}s^{-1} was varied by using light from a CO_2 laser at $\lambda = 10.6\,\mu$m ($W_{ph} \approx 10^{-1} \approx 10^4$ s^{-1}) and was calibrated by measuring the conductivity σ of a Si : B reference specimen for which $N_A \approx 4\cdot10^{13}$ cm^{-3} and $K = 0.15$ were known. In many cases we used radiation from an InAs diode, $\lambda \approx 3\,\mu$m, $W_{ph} \approx 0$–0.25 s^{-1}; both the specimen and the emitter were positioned precisely. In all cases, the values of σ for the specimens were thus obtained at a constant W_{ph} with $T = $ const ($T = 4.2$ or 1.5 K).

We measured σ and R_H. In the case when the product $R_H\sigma = \mu^*$ was equal to the value μ_c calculated for scattering by neutral impurities, σ was equal to the conductivity σ_c along the c-band. In contrast, the two-band model[9–10] was used to calculate σ_c and σ_D when μ^* was less than the calculated values and depended on T and W_{ph} (indicating that conduction occurred along both the c- and the D^--bands).[9]

We studied the dependence of τ on the energy difference $\varepsilon^* = \hbar\omega - \varepsilon_0$, $\hbar\omega = 45$–60 meV, by inserting an Si : Ga filter ahead of the specimen. The specimen thickness was $d \approx 0.02$ cm. The radiation spectrum of the IKS-31 (Fis-3) monochromators used as the emitter was calibrated using a Ge bolometer. The Si specimens were doped with B, Ga, As, or P to $N = 10^{15}$–10^{17} cm^{-3}, and K ranged from 10^{-5} to 10^{-1}. For given values of K and $N^{1/3}a_0$, the results were

similar[9] regardless of whether the silicon was doped with B, Ga, P, or As; they will be illustrated here for the case of Si : B. The properties of the specimens were found by standard equilibrium galvanomagnetic measurements and are shown in Table I. We used the approximation $N_V \approx 2\cdot10^{15}$ $T^{3/2}$ cm^{-3} (Ref. 11) to calculate K and N, and the Hall factor was taken equal to 1.

Figure 1 shows $\tau(T)$ for three Si : B specimens Nos. 1, 11, 15 with the same amount of compensating impurity $KN \approx 6\cdot10^{12}$ cm^{-3} but with unequal principal impurity concentrations N. The dependence $\tau(T)$ evidently changes as N increases. Thus for specimen 1, $\tau(T) \propto T^{1.3-1.4}$ for $T > 3$ K, while $\tau(T) \approx$ const for $T < 3$ K and $\tau \approx \tau^+$ is independent of
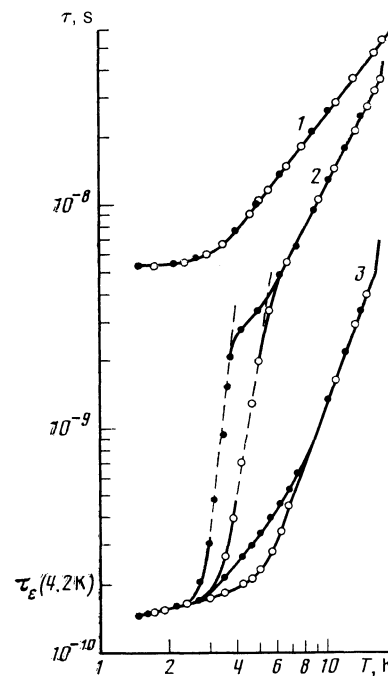

FIG. 1. Dependence $\tau(T)$ for specimens No. 1, 11, and 15 with equal $KN \approx 6\cdot10^{12}$ cm^{-3} but different N, cm^{-3}: 1) $4\cdot10^{13}$; 2) $8.9\cdot10^{15}$; 3) $2.2\cdot10^{16}$ for $W_{ph} \approx 0.25$ s^{-1} ($\bullet$) and $W_{ph} = 30$ s^{-1} (O). The dashed curves show $\tau(T)$ calculated by Eq. (7).
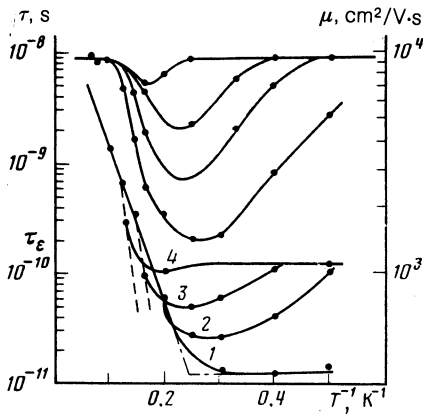
FIG. 2. Curves $\tau(T)$ and $\mu^* = \sigma R_H(T)$ for specimen No. 26, $W_{ph} = 1)$ 0.25; 2) ≈ 3; 3) ≈ 30; 4) $\approx 3 \cdot 10^2 \, \text{s}^{-1}$. The dashed curves give $\tau(T)$ calculated by Eq. (7).

W_{ph}. For specimen 2, $\tau \propto T^{2-2.2}$ at high temperatures, but τ is appreciably less than τ^+; as T decreases, the power-law dependence $\tau(T)$ is replaced by a stronger exponential dependence with activation energy $\approx \varepsilon(R_c)/2$, where $\varepsilon(R_c) \approx 5.8$ meV. The temperature T_1 at which this transition occurs decreases with decreasing W_{ph}. At still lower temperatures $T \lesssim T_2$ the dependence $\tau(T)$ becomes less pronounced. For all the specimens with $N = 3 \cdot 10^{15} - 2 \cdot 10^{16}$ cm^{-3} we have $\tau \approx \tau_\varepsilon$ for $T \lesssim T_2$, and T_2 also depends on W_{ph}. Finally, for the more heavily doped specimens 3, $\tau(T) \propto T^{2.5}$ for $T = 4$–20 K, and τ is substantially less than τ^+ for all T and depends only weakly on W_{ph}.

Figure 2 plots $\tau(T)$ and $\mu^* = R_H \sigma(T)$ for Si : B specimen No. 26 for $E = 10$ V/cm and several values of W_{ph}. The curve $\mu^*(T)$ is nonmonotonic and the dependence changes with W_{ph}. As W_{ph} increases, the minimum of $\mu^*(T)$ becomes shallower and eventually disappears, so that $\mu^*(T) = \text{const} = \mu_c$.

For low T the lifetime τ may be shorter than the energy relaxation time τ_ε for small W_{ph} and equal to τ_ε for large W_{ph}. This is typical for specimens with $K \approx 10^{-5} - 10^{-3}$ in a narrow range of concentrations $N \approx 2.5 \cdot 10^{16} - 5 \cdot 10^{16}$ cm^{-3}.
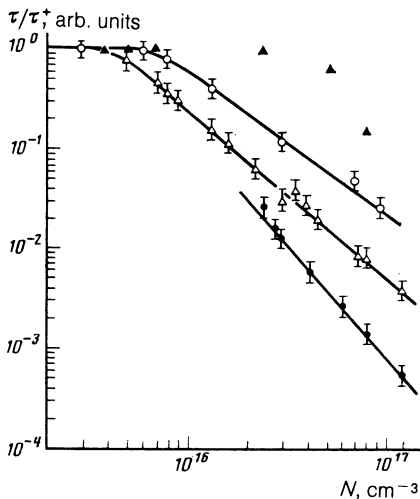

FIG. 3. The ratio $\tau/\tau^+(N)$ for $W_{ph} \approx 0.25$ s^{-1}, $T = 7$ K, for $K = (2$–$6) \cdot 10^{-5}$ (●); (2–16)$\cdot 10^{-4}$ ($\triangle$); (2–6)$\cdot 10^{-3}$ (○); (2–6)$\cdot 10^{-2}$ (▲).
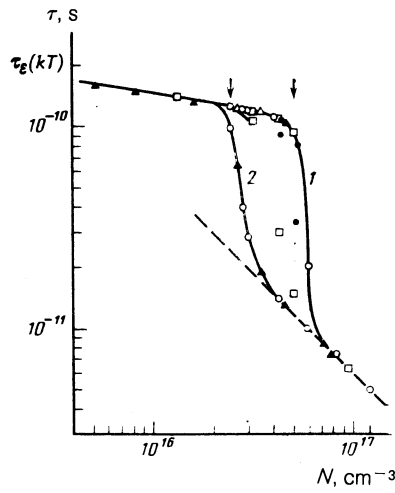

FIG. 4. Dependence $\tau(N)$ for $T = 1.5$ K and $W_{ph} = 300$ (1) and 0.25 s^{-1} (2) for specimens with $K = (2$–$6) \cdot 10^{-5}$ (○); (2–6)$\cdot 10^{-4}$ (▲); (2–6)$\cdot 10^{-3}$ ($\square$); (2–6)$\cdot 10^{-2}$ (●).

We note that there is a range of W_{ph} in which the dependence $\tau(T)$ for these specimens is "anomalous": τ increases with $1/T$ to values $\tau \approx \tau_\varepsilon$. For $T > 3.5$ K

$$\tau(T) \infty \exp(-\delta\varepsilon/kT),$$

and for small W_{ph}, $\delta\varepsilon = \varepsilon_x \approx 2.8$ meV (Ref. 9), while for large W_{ph} the curve has a region characterized by a large activation energy $\delta\varepsilon \approx \varepsilon(R_c/2)$, $\varepsilon(R_c) \approx 8$ meV. As W_{ph} increases, the transition from one activation energy to the other occurs at higher T.

Figure 3 plots $\tau/\tau^+(N)$ for $W_{ph} = 0.25$ s^{-1} and $T = 7$ K. For our values of T and W_{ph}, τ is independent of W_{ph} for all of the specimens (at least for $W_{ph} = 0.1$–1 s^{-1}). We see that as N increases above $5 \cdot 10^{15}$ cm^{-3}, the ratio τ/τ^+ decreases faster as K decreases. For small $K = 10^{-4} - 10^{-5}$, it satisfies $\tau^+/\tau \propto N^{-(2-3)}$ and reaches $\approx 10^3$. For larger $K = 10^{-2} - 10^{-1}$, τ/τ^+ approaches the value 1.

Figure 4 shows the curves $\tau(N)$. For small $N \tau \approx \tau_\varepsilon$, but when N increases above a critical value N^* (indicated by the arrow) depending on W_{ph}, τ drops abruptly to $\tau \lesssim 10^{-11}$ s. For $W_{ph} \approx 3 \cdot 10^2$ s^{-1} (curves 1) τ is independent of K, and $N^* \approx 5 \cdot 10^{16}$ cm^{-3}. When W_{ph} drops to ≈ 0.25 s^{-1}, for $N \approx 2.5$–$5 \cdot 10^{16}$ cm^{-3}, τ decreases more rapidly as K becomes smaller. For $K < 10^{-3}$, $N^* \approx 2.5 \cdot 10^{16}$ cm^{-3} (curve
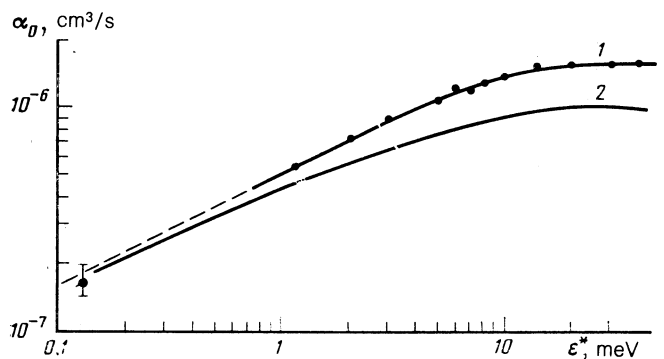

FIG. 5. Dependence $\alpha^0(\varepsilon^*)$ for specimen No. 28, $T = 1.5$ K, $W_{ph} \approx 0.5$ s^{-1} (curve 1). Curve 2 gives the calculated dependence $\alpha^0(\varepsilon^*)$.

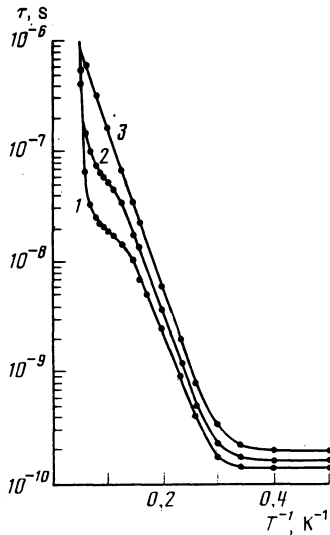FIG. 6. The dependence $\tau(1/T)$ for specimen No. 17, $W_{ph} = 0.25$ s^{-1}, electric field $E = 10$ (1), 30 (2), 70 V/cm (3).
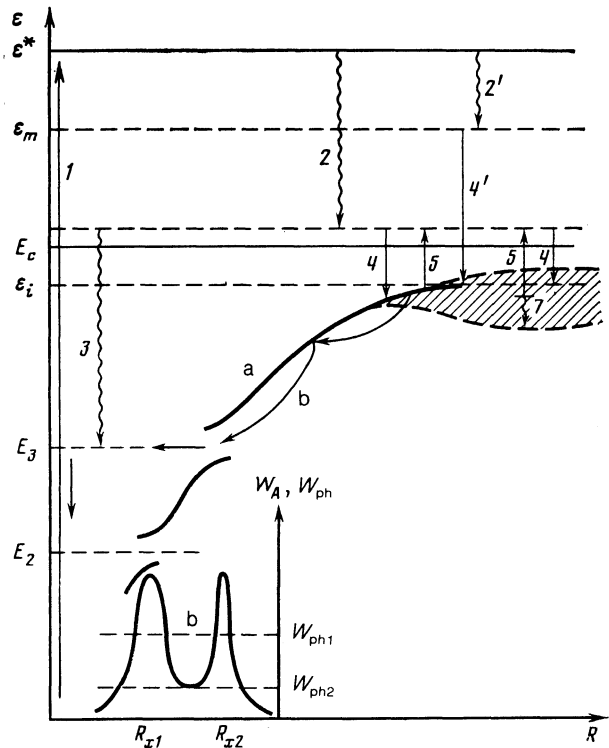

FIG. 7. Diagram of the electron transitions: a) energy $\varepsilon(R)$ of the ionic term; b) the dependence W_A (R) for levels E_2, E_3.

2). Under these conditions τ clearly increases with K (i.e., with N^+). We note that for still smaller $W_{ph} \approx 3 \cdot 10^{-2}$ s^{-1}, the lifetimes τ for specimens with $K > 10^{-3}$ approach those for curve 2.

Figure 5 shows how the trapping coefficient α^0 depends on the transition energy of the electron for specimen No. 28:

$$\alpha^0(\varepsilon^*) \infty \frac{\delta\sigma}{\sigma}(\varepsilon^*) \infty \tau^{-1}(\varepsilon^*),$$

where $\varepsilon^* = \hbar\omega - \varepsilon_0$. We see that for $T \approx 2$ K and $W_{ph} \approx 0.5$ s^{-1}, $\tau^{-1}(\varepsilon^*)$ increases with $\varepsilon^* \approx 1$–10 meV, while for $\varepsilon^* > 10$ meV we have $\tau^{-1}(\varepsilon^*) \approx$ const. For higher $T \approx 10$ K or $W_{ph} \approx 300$ s^{-1},

$$\tau^{-1}(\varepsilon^*) \approx \tau_\varepsilon (kT) = \text{const}.$$

Figure 6 shows $\tau(T)$ for specimen No. 17. For $T = 3$–10 K we see that $\sigma_c \propto \exp(-\delta\varepsilon/kT)$, where $\delta\varepsilon \approx \varepsilon_x \approx 2.5$ meV; for $T \gtrsim 10$ K, $\sigma_c \propto T^2$. The dependence $\tau \propto \exp(-\varepsilon_x/kT)$ holds for all T when the electric field E is increased from 10 V/cm (curve 1) to 70 V/cm (curve 3). For $T < 3$, $\tau \approx \tau_\varepsilon$.

3. DISCUSSION

We divide the specimens into groups, according as the trapped carriers reach the attracting centers by hopping (group I) or along the D^- band (group II).

1. For $N \approx 5 \cdot 10^{15}$–$8 \cdot 10^{16}$ cm^{-3} the first group contains the specimens with $K > 10^{-4}$. Estimates show that delocalization of the D^- states is not important in this case (if present at all, the delocalization does not extend over many neutral centers). The separation of the specimens into groups depending on the values of N and K is of course somewhat arbitrary in that the mode of carrier transport may change with the external conditions (T, W_{ph}, E) (see 5. below). The following experimental findings are characteristic for the specimens in group I. For large T there is a power-law dependence $\tau \propto T^{2-2.5}$ (Fig. 1, curves 2, 3); $R_H\sigma = \mu^* = \mu_c$ = const. In addition, there is a characteristic drop in τ/τ^+ as N increases (Fig. 3) and T decreases (Fig. 1); for $N \approx$ const, τ/τ^+ decreases with K (Fig. 3); for $T < 3$–5 K

$N < 3 \cdot 10^{16}$ cm^{-3}, $\tau \approx \tau_\varepsilon$; for $N > (3$–6$) \cdot 10^{16}$ cm^{-3}, $\tau < \tau_\varepsilon$ and $\tau \propto N^{-1}$ (Fig. 4). The electron transitions for the impurities excited in the Group-I specimens can be described as follows (Fig. 7). Absorption of a photon with $\hbar\omega > \varepsilon_0$ generates a free electron of energy $\varepsilon^* = \hbar\omega - \varepsilon_0$ and an attracting center AC (transition 1). The subsequent fate of the electron depends on the relative magnitudes of $\tau_\varepsilon (kT)$ and $\alpha^0(kT)N$, the inverse lifetime for trapping by neutral centers.[12] If $\alpha^0(kT)N < \tau_\varepsilon^{-1}(kT)$, the electron cools down to the bottom of the c-band during a time $\sim \tau_\varepsilon (kT)$ (transition 2) and is trapped either directly by an attracting center (transition 3) or else by a neutral center NC [transition 4, trapping coefficient $\alpha^0(kT)$]. If $\alpha^0(kT)N > \tau_\varepsilon^{-1}(kT)$ the electron cools down to an energy $\sim \varepsilon_m$ satisfying the equation $\alpha^0(\varepsilon_m)N = 2\tau_\varepsilon^{-1}(\varepsilon_m)$ if $\varepsilon_m < \varepsilon^*$ (transition 2'), followed by trapping at a neutral center (transition 4'), trapping coefficient $\alpha^0(\varepsilon_m)$]. If $\varepsilon^* < \varepsilon_m$, the ε_m must be replaced by ε^* in these results. The trapped electron may be ejected into the c-band (transition 5); the corresponding probability is

$$W_T[\varepsilon(R), T] = \alpha^0(kT)N_c \exp(-\varepsilon(R)/kT)$$

where N_c is the state density in the c-band; or it may hop along the neutral centers and approach an attracting center to within a distance $R \approx R_c$, giving up energy in the process (transition 6).

The rate of energy loss is characterized by W_L, the reciprocal of the time required for the electron energy to drop by an amount $\sim kT$ (Ref. 7); W_L depends primarily on the amount of overlap among the D^- states:

$$W_L \propto \exp(-\beta R_c/a_i), \quad \beta \approx 2,$$

but it also depends on the energy difference Δ for the initial and final D^- states for a typical hop, as well as on T. For $R > R_c$, W_L increases with decreasing R (Δ increases, and with it the phase-space volume of the phonons emitted during the hops), while W_T drops due to the increase in $\varepsilon(R)$. There is a value $R = R_{\rm eff}(N, T)$ at which $W_T(R_{\rm eff}T) = W_L(R_{\rm eff}, N, T)$. For $R > R_{\rm eff}$ the electrons may be assumed to be ejected primarily into the c-band; for $R < R_{\rm eff}$, the electrons approach the attracting centers to within $R \approx R_c$ and form complexes $D^- - D^+$ with binding energy

$$\varepsilon(R) \approx \varepsilon_i + e^2/\varkappa R,$$

where the fluctuations of R about R_c obey Poisson statistics.

For the group-I specimens, the D^- states far from the attracting centers ($R > R_{\rm eff}$) may be delocalized (hatched region in Fig. 7). However, these states do not participate significantly in the recombination. An electron in a complex can hop from a neutral center to an attracting one (this is accompanied by breakup of the complex). The lifetime $\tau_A = W_A^{-1}$ of the complex relative to this process is sensitive to R. For $R \approx R_x$, the energies $\varepsilon(R_x) = \varepsilon_i + e^2/\varkappa R_x$ and ε_n of the ionic and homeopolar terms are nearly equal, pseudo-crossing of terms is important,[7] and τ_A is small and comparable to the intracenter transition time (short-lived or recombination complexes). If R is not close to R_x, the complexes are long-lived and permit photoconduction at submillimeter wavelengths.[7] These complexes can break up due to thermal (W_T) or phonon ($W_{\rm ph}^*$) re-emission into the c-band, or when they trap an electron [$D^- - D^+$ dipole]. One must bear in mind that in addition to direct photodetachment, impact neutralization of D^- centers by electrons cooling in the c-band may also influence $W_{\rm ph}^*$. Estimates show that for silicon doped to $N \gtrsim 10^{16}$ cm^{-3}, this process is as important as photodetachment. As a result, an electron remains near the bottom of the c-band for a time $\tau \approx \tau_\varepsilon(kT)$.

Depending on the ratio $W_A(R)/(W_T(R) + W_{\rm ph}^*)$, the complexes can thus act either as recombination or attachment centers. Analysis of the submillimeter photoconduction spectra for Si : B specimens[7] shows that the pseudocrossings are important for the deep excited states $E_2 = -14.5$ meV and $E_3 = -10.5$ meV; for $T = 1.5$ K and $W_{\rm ph} \approx 300$ s^{-1}, the estimates in Ref. 7 give 13 meV $\lesssim E_2 \lesssim 16$ meV and 9.5 meV $\lesssim E_3 \lesssim 11.5$ meV for the bands corresponding to the pseudocrossings. If the distances between the centers in the complexes are assumed to obey Poisson statistics, the relative number ξ of recombination complexes for Si : B increases from 0.03 to 0.3 as N increases from $5 \cdot 10^{15}$ cm^{-3} to $5 \cdot 10^{16}$ cm^{-3}.

Indirect three-stage recombination is thus possible in sufficiently doped materials: electrons are trapped by neutral centers, after which they approach an attracting center through a series of hops and undergo a transition to deep excited states of the AC. For this type of recombination one can write $\tau = (\alpha_{\rm eff} N^+)^{-1}$, where

$$\alpha_{\rm eff} = \alpha^+ + \xi \alpha^0(T) \cdot {}^4/_3 \pi R_{\rm eff}^3 N. \qquad (1)$$

For small N, ξ and $R_{\rm eff}^3 N$ are small and $\alpha_{\rm eff} \approx \alpha^+$ (see Fig. 3, $N < 5 \cdot 10^{15}$ cm^{-3} and Fig. 1, curve 1). In this case we have $\tau \propto T^{1.3-1.5}$ for $T > 3$ K; for $kT \lesssim mS^2 \approx 2.8$ K, we have $\tau(T) = {\rm const}$ (m is the effective mass and S is the speed of sound). Both ξ and $R_{\rm eff} N$ increase with N, and indirect re-

combination becomes dominant. In this case τ/τ^+ decreases (Fig. 3 and Fig. 1, curves 2, 3), and the dependence $\tau(T)$ is more pronounced (Fig. 1 curve 3, and curve 2 for $T > 5$ K). The quantity $\alpha_{\rm eff}$ increases with $1/T$, primarily due to $R_{\rm eff}$; however, $R_{\rm eff}$ cannot exceed the mean distance $R_c^+ \approx 0.62(N^+)^{-1/3}$ between the charged centers. When $R_{\rm eff} \approx R_c^+$, the trapping regions (spheres) overlap and $\alpha_{\rm eff}(T)$ is constant (Fig. 1, curve 3, $T < 6$ K). As R_c^+ decreases (i.e., as K increases) $\alpha_{\rm eff} \to \alpha^+$ (Fig. 3). Since for large N ($N > N^*$)$\alpha^0/\alpha^+ \to 10^{-1}$ (see 4. below), for small K $\alpha_{\rm eff}$ may become very large as T decreases, $\alpha_{\rm eff}/\alpha^+ \approx \alpha^0/\alpha^+ K$; thus for $K \approx 10^{-5}$, $\alpha_{\rm eff}/\alpha^+ = \tau^+/\tau \to 10^4$.

The calculation of $\alpha_{\rm eff}$ is a difficult self-consistent problem. The migration of an "excess" electron by hopping toward an attracting center is analogous to the freezing-out of vacancies in a $D^+ - A^-$ dipole as they hop along the ground states, and it differs from a flow of carriers (vacancies) hopping from contact to contact. We will give a rough estimate for the dependences $\alpha_{\rm eff}(T)$, $\alpha_{\rm eff}(N)$, and obtain an approximate value for $R_{\rm eff}$. The equation

$$\frac{1}{4}\left(\frac{\varepsilon_i}{mS^2}\right)^2 \frac{\Delta}{mS^2}\left(\frac{a_i}{R_c}\right)^2 \frac{S}{l_0} \exp\left(-\frac{2R_c}{a_i}\right)$$
$$= \alpha^0(T)\exp\left(-\frac{\varepsilon_i + e^2/\varkappa R_{\rm eff}}{kT}\right)N_c(T) \qquad (2)$$

will be used to find $R_{\rm eff}$. Here l_0 is the characteristic distance for energy loss by a free electron. The power loss W_h appears on the left, while the right-hand side contains the probability for ejection into the band per second. We found W_h by using the method in Ref. 13 to calculate the probability of a hop between two neutral centers[1] located a distance R_c apart and at a distance R from an attracting center (the wave function of the isolated centers were of the form $\psi \propto r^{-1} \exp(-r/a_i)$; $\Delta \approx e^2 R_c/\varkappa R^2$). To estimate W_h we must multiply the hopping probability by $N_q + 1$ (where N_q is the number of phonons) and divide by the number of jumps $\sim kT/\Delta$ required for the energy to decrease by $\sim kT$. Under our conditions (for $T \sim 10$ K), $\Delta > kT$. Therefore $(N_q + 1)\Delta/kT \approx N_q\Delta/kT \approx 1$ and the hopping probability coincides with W_h.

This estimate for W_h is of course very crude. All the hopping distances are assumed equal to R_c, and only hops along the line joining the neutral and attracting centers are considered. Under these conditions, a correct order-of-magnitude value for the factor multiplying the exponential on the left is the most that can be hoped for (it is clear that this value will be an underestimate).

We use the following parameter values in (2): $mS^2 = 2.8$ K, $l_0 = 3 \cdot 10^{-4}$ cm (Ref. 1), $\varkappa = 12$. The value $\alpha^0 \times (2$ K$) \approx 2 \cdot 10^{-7}$ cm^3/s was found experimentally[14]; correcting for the temperature dependence (see below), we obtain $\alpha^0(10$ K$) \sim 10^{-6}$ cm^3/s. The remaining values were given above.

Substituting these values into (2), we find that for $T \sim 10$ K and $N \sim 10^{16}$ cm^{-3} (this corresponds to the high-temperature portion of curve 2, Fig. 1), the factors multiplying the exponentials on the left and right in Eq. (2) differ by less than an order of magnitude. Because their dependence on N and T is much weaker than exponential, we will simplify by taking them equal. Equation (2) then reduces to an equality of the exponential arguments:

$$\frac{2R_c}{a_i} = \frac{\varepsilon_i}{kT} + \frac{e^2}{\varkappa R_{\text{eff}} kT} .$$ (3)

For this range of N and T, the left-hand side of (3) is nearly three times larger than the first term on the right. Neglecting the latter, we obtain $R_{\text{eff}} T \simeq$ const as T varies. For indirect hopping capture we thus have $[\alpha(T) \propto T^{-0.5}$, see below]

$$\alpha_{\text{eff}} \approx \xi \cdot {}^{4}\!/_{3}\pi R_{\text{eff}} \alpha_0{}^{'}(T) \infty T^{-2.5}$$ (4)

and hence $\tau \propto T^{2.5}$. Curves 2, 3 in Fig. 1 show that indeed $\tau \propto T^{2-2.5}$ for 6 K $< T <$ 18 K.

Turning now to the dependence $\tau(N)$, we again neglect the first term in (3) and obtain $R_c R_{\text{eff}} =$ const. Therefore, for $\alpha_{\text{eff}} \gg \alpha^+$ and $\xi =$ const,

$$\alpha_{\text{eff}} \infty R_c{}^{-3} N \infty N^2.$$ (5)

Consequently $\tau \propto N^{-2}$, which is very close to the dependence shown in Fig. 3. Our simplified model thus predicts $\tau(T)$ and $\tau(N)$ in good agreement with the experimental findings. It should be noted that we are assuming that ξ is independent of T and N, which while not strictly true is a good approximation for T and N in the interval considered.

We now derive a numerical estimate for τ. For $T = 10$ K and $N = (4\pi R_c{}^3/3)^{-1} = 10^{16}\,\text{cm}^{-3}$, Eq. (3) yields $R_{\text{eff}} = 2.3 R_c$. Omitting α^+, we find from (1) that $\alpha_{\text{eff}} \simeq 5 \cdot 10^{-5} \xi\,\text{cm}^3/\text{s}$. For $N^+ = 6 \cdot 10^{12}\,\text{cm}^{-3}$ (Fig. 1) we obtain $\tau \sim 3 \cdot 10^{-9} \xi^{-1}$ s. Taking $\xi = 0.1$, this gives $\tau \simeq 3 \cdot 10^{-8}$ s. According to curve 2, Fig. 1, the experimental lifetime is $\tau = 1.2 \cdot 10^{-8}$ s. Considering the crudeness of our assumptions, this agreement is quite satisfactory.

We now consider $D^- - D^+$ complexes whose separation R does not correspond to the pseudocrossing bands. The relative number of these complexes is $1 - \xi$. With decreasing T or increasing W_{ph}, it is clear that their concentration will increase, and for $T < T_1$ recombination proceeds by direct trapping of electrons at the complexes: $N_c \alpha_c > N^+ \alpha_{\text{eff}}$. In finding $N_c (N, W_{\text{ph}}, T)$ we encounter the same difficulties as in calculating α_{eff}. However, the dependence of τ on T, N, K, W_{ph}, and E can be understood qualitatively by using the recombination model in Ref. 5 for the case of isolated D^- centers (i.e., small N, for which $W_h \approx 0$ and $\varepsilon \approx \varepsilon_i$) with ε_i replaced by $\varepsilon(R_0) = \varepsilon_i + e^2/\varkappa R_c$ and α^+ by α_c. For $N_c \alpha_c > N^+ \alpha_{\text{eff}}$ and $\xi = 0$, the kinetic equations[5] for n and τ give

$$n \simeq \left[\frac{W_{\text{ph}}(W_{\text{ph}}^* + W_T)}{\alpha_c \alpha^0}\right]^{1/2}, \quad \frac{N^+}{N} \simeq \left[\frac{W_{\text{ph}} \alpha^0 (kT)}{\alpha_c (W_{\text{ph}}^* + W_T)}\right]^{1/2},$$ (6)

where W_{ph}^* is the probability for the complex to break up and emit phonons. Taking $W_{\text{ph}}^* \approx W_{\text{ph}}$ (Ref. 5), we have

$$\tau \simeq \frac{1}{N}\left[\frac{(1 + W_T/W_{\text{ph}})}{\alpha_c \alpha^0}\right]^{1/2},$$ (7)

i.e., for $W_T > W_{\text{ph}}$

$$\tau \propto W_{\text{ph}}^{-1/2} \exp[-\varepsilon(R_c)/2kT].$$ (8)

Figure 1 shows the curves calculated for specimen No. 2 together with the experimental results; we see that the agreement is good even when the values $\varepsilon(R_c)$ are not fitted to the experimental data. We note that, as in the case of trapping by

attracting centers, τ cannot be less than τ_ε for trapping by $D^- - D^+$ complexes. For specimen 3, the trapping does not appreciably influence the $D^- - D^+$ complexes when W_{ph} is increased; this is because the indirect recombination ensures that τ is already nearly equal to τ_ε.

We note that for $N \gtrsim 10^{16}\,\text{cm}^{-3}$ and small W_{ph}, the dependence $\tau(T)$ for low T is less pronounced (see, e.g., curves 2, 3 in Fig. 1 for $T < 5$–7 K). We attribute this to freezing-out of the charged centers in the $D^+ - A^-$ dipole (Ref. 1). As N increases, the formation of $D^+ - A^-$ dipoles becomes important even for large T and W_{ph}, as evidenced by the nonzero hopping conductivity σ_3 in unirradiated specimens with $N \gtrsim 5 \cdot 10^{16}\,\text{cm}^{-3}$, $\sigma_3 \propto \exp(-\varepsilon_3/kT)$ (Ref. 15). The dark hopping conductivity becomes comparable to the photoconductivity in a wider range of W_{ph} and T as N increases.

2. We now consider the group-II specimens with $N \gtrsim 2.5 \cdot 10^{16}\,\text{cm}^{-3}$, $K < 10^{-4}$; estimates indicate that for these materials the D^- states are delocalized in most of the neutral centers. The following results are typical for small $W_{\text{ph}} : \mu^*$ depends on W_{ph} and T (see Fig. 2), which indicates that there are two photoconduction mechanisms, involving the c- and the D^--bands, respectively[9]; for $T > T^* \approx 3.5$ K, we have $\tau \propto \exp(-\varepsilon_x/kT)$ (Fig. 2), so that we may assume that the electrons in the c-band are in equilibrium with those in the D^--band.

We will assume that far from the attracting centers, the width of the D^--band is at least a few kT. The transition diagram in Ref. 9 can be obtained from the one in Fig. 7 by eliminating the transitions 3 and adding transitions 7 (cooling in the D^--band). The cooling electrons may enhance the conductivity. According to Ref. 9, the c-band contains two types of electrons—n_1 electrons with energy $\approx \varepsilon_m$, and n_2 electrons with energy $\approx kT$. These electrons are generated by thermal re-emission from the D^- states (transitions 5):

$$n_c = n_1 + n_2 \simeq W_{\text{ph}}/\alpha^0(\varepsilon_m) + W_{\text{ph}} W_T/\alpha^0(kT)W_h .$$ (9)

When $T > T^*$, so that $W_T/\alpha^0(kT)W_h \gg 1/\alpha^0(\varepsilon_m)$, the electrons are thermalized (Fig. 2):

$$n_c \approx n_2 \infty \exp(-\varepsilon_x/kT).$$

For $T < T^*$, we have $n_0 \approx n_1 = W_{\text{ph}}/\alpha^0(\varepsilon)$ and $\tau = (\alpha^0(\varepsilon)N)^{-1}$ (photoinduced heating). For large W_{ph} (curve 4, Fig. 2), trapping by $D^- - D^+$ complexes becomes significant with decreasing $T < T_1$. The dashed curves in Fig. 2 were calculated using Eq. (7); they agree closely with the experimental curve $\tau(T)$ for $\tau > \tau_c$. For $\tau < \tau_c$, the lifetimes τ increase to $\tau \approx \tau_\varepsilon$ as W_{ph} increases. We note that the switching on of an additional recombination mechanism ordinarily decreases the lifetime τ:

$$\tau^{-1} = \tau_1{}^{-1} + \tau_2{}^{-1}.$$

In the present case, the trapping by the complexes eliminates the recombination channel involving the D^- band (see 4. below for a fuller discussion).

3. For N large enough so that $\tau \ll \tau_\varepsilon$, it is meaningful to consider the lifetime for electrons with energy $\varepsilon - \tau(\varepsilon)$. In this case, the experimentally measured lifetime is equal to the average of $\tau(\varepsilon)$ over the electron distribution function, $\tau \equiv \langle \tau(\varepsilon) \rangle$. The spectral measurements show (Fig. 5) that for $T < 2$ K, τ depends on the energy difference $\varepsilon^* = \hbar\omega - \varepsilon_0 : \tau = \tau(\varepsilon^*)$; τ decreases with increasing $\varepsilon^* < 10$ meV and saturates at $\varepsilon^* \gtrsim 10$ meV.

The dependence $\alpha^0(\varepsilon)$ was calculated in Ref. 15; however, the final expression for $\alpha^0(\varepsilon)$ should be corrected to read ($\varepsilon \ll \varepsilon_0$)

$$\alpha^0(\varepsilon) = \frac{\pi^2}{8} \left(\frac{\hbar}{mS^2} \right)^3 \frac{S}{l_0} \frac{1}{\beta} \frac{(1-\beta)^2 + \varepsilon/\varepsilon_i}{1 + \varepsilon/\varepsilon_i}, \tag{10}$$

where $\beta = 4\pi^{-1}(2mS^2/\varepsilon_i)^{1/2}$ (≈ 0.64 for holes in silicon). Equation (10) shows in particular that $\alpha^0(kT) \propto T^{0.5}$ for $T \sim 10$ K.

According to Ref. 12, for $\varepsilon > kT$ the photoelectron distribution function can be expressed as

$$F(\varepsilon) \propto \varepsilon^{-2} \exp\left[-\int_\varepsilon^{\varepsilon^*} \frac{\tau_\varepsilon(\varepsilon')d\varepsilon'}{\tilde{\tau}(\varepsilon')\varepsilon'} \right], \tag{11}$$

in terms of the "partial" lifetime $\tilde{\tau}(\varepsilon)$, where

$$[\tilde{\tau}(\varepsilon)]^{-1} = \alpha^0(\varepsilon)N$$

and $\tau_\varepsilon(\varepsilon) \propto \varepsilon^{-1/2}$ (acoustic phonons). The integrand $N\alpha^0(\varepsilon)\tau_\varepsilon(\varepsilon)\varepsilon^{-1}$ decreases with increasing ε. For $N < N^*$, where $N^*\alpha^0(kT)\tau_\varepsilon(kT) = 2$, we have $\exp \approx 1$ and $F(\varepsilon) \propto \varepsilon^{-2}$; there is no photoinduced heating, although this does occur when $N > N^*$. In the latter case the dependence $F(\varepsilon)$ changes with increasing ε^*, as follows. For $\varepsilon^* < \varepsilon_m$, $F(\varepsilon)$ has a maximum at the point $\varepsilon = \varepsilon^*$, while for $\varepsilon^* > \varepsilon_m$ it peaks at $\varepsilon = \varepsilon_m$. When $\varepsilon^* < \varepsilon_m$, most of the electrons have energies close to $\varepsilon = \varepsilon^*$:

$$\tau^{-1}(\varepsilon^*) \approx \langle \tilde{\tau}(\varepsilon) \rangle^{-1} = N\langle \alpha^0(\varepsilon) \rangle \approx N\alpha^0(\varepsilon^*) \tag{12}$$

and the dependence of $\langle \alpha^0(\varepsilon) \rangle$ on ε^* should be similar to $\alpha^0(\varepsilon^*)$.

Curve 2 in Fig. 5 shows $\alpha^0(\varepsilon^*)$ found from Eq. (10) by replacing ε by ε^*; we see that the curve lies close to the experimental result (curve 1). The value of α^0 found by extrapolating the experimental dependence $\alpha^0(\varepsilon^*)$ to $\varepsilon \approx kT$ coincides with the value $\alpha^0(kT) \approx (1.5-2)\cdot10^{-7}$ cm^3/s measured in Ref. 14 for materials with $N \approx 10^{14}$ cm^{-3} and $K < 10^{-2}$ for $T \approx 1.5$ K.

Let us now consider the dependence $\langle \alpha^0 \rangle(N)$ under the assumption that ε^* is large. For $N > N^*$, $F(\varepsilon)$ has a maximum at $\varepsilon = \varepsilon_m(N) > kT$, and we therefore have $\langle \alpha^0 \rangle(N) \approx \alpha^0[\varepsilon_m(N)]$. Thus as $N \lesssim N^*$ increases, the coefficient $\langle \alpha^0 \rangle$ must also increase. Since by (10) the function $\alpha^0(\varepsilon)$ saturates for $\varepsilon \approx 8$–10 meV, as N increases further the dependence $\langle \alpha^0 \rangle(N)$ becomes less pronounced and eventually disappears altogether. In this region we have $\tau \propto N^{-1}$ (Fig. 4). Using the experimental value $\alpha^0(kT) = (1.5-2)\cdot10^{-7}$ cm^3/s, we calculated $N^* = (2 - 2.6)\cdot10^{16}$ cm^{-3}. This is very close to the result $2.4\cdot10^{16}$ cm^{-3} at which $\tau(N)$ drops abruptly (curve 2, Fig. 4, for which $\xi = 1$, see below).

4. It is plain from Fig. 4 that as N increases, τ drops rapidly from $\tau \approx \tau_\varepsilon$ to $\tau \approx 0.1\tau_\varepsilon$ The critical value N^* depends on KN and W_{ph} and may vary in the interval $N \approx (2.5$–$5)\cdot10^{16}$ cm^{-3}. The dependence of τ on T and N^+ (see Fig. 2) is also unusual from the standpoint of ordinary trapping by attracting centers. We note that since trapping by the neutral centers is the intermediate step in three-stage recombination, in order for τ to be less than τ_ε and for the distribution function $F(\varepsilon)$ to be inverted at $N = N^*$, it is necessary that all the trapped carriers recombine at the attracting centers without any emission back into the c-band (i.e., we must

have $\xi \approx 1$). Indeed, at higher $T > 4.2$ K for which $n_2 > n_1$, the dependence $\tau(\varepsilon^*)$ disappears and $\tau \gtrsim \tau_\varepsilon$. There are two situations when ejection into the c-band does not occur for low T and $R_c \approx R_x$:

a) When W_{ph}^* is small enough so that $W_A(R) > W_{ph}^*$ holds for a wide range of R. The data show that for specimens with $N \approx (3$–$5)\cdot10^{16}$ cm^{-3} and $K > 10^{-3}$, $\tau \approx 1/\alpha^0(\varepsilon_m)N$ only when $W_{ph} < 10^{-1}$ s^{-1}; this implies that for complexes with $R \neq R_x$, W_A is quite small, $W_A \lesssim 10^{-1}$ s^{-1}.

b) When there is an extended D$^-$-band, along which an electron from a long-lived complex can migrate to another attracting center and form a complex with R such that $W_A > W_{ph} + W_T$.

Indeed, the energy δE separating the state in the complex from the bottom of the D$^-$ band is considerably less than $\varepsilon(R_c)$ (Ref. 16), and a transition to the D$^-$ band is more likely.[16] The D$^-$ band thus enables all of the electrons trapped at the attracting centers to recombine without emission into the C-band. The D$^-$ band retains this property even when there is no appreciable conduction along it, as is the case when $K \approx 10^{-4}$–10^{-3}. In this case, for small N the delocalization, although not extensive, nevertheless suffices for electrons with $W_T + W_{ph} \neq 0$ to migrate from one attracting center to another and recombine. As $N(\Delta)$ increases, the energy band of the delocalized states becomes narrower, the gap δE becomes larger, and complexes with $R \neq R_x$ can break up either through phonon emission or thermal ejection into the c-band, or by free carrier trapping at a complex. We ascribe the unusual increase in τ with N^+, observed for a narrow interval of N and W_{ph} ($N = (2.5$–$5)\cdot10^{16}$ cm^{-3}, Fig. 4), to cutoff of the rapid transport channel due to cluster breakup.

The influence of the fluctuating energy difference Δ on the delocalization can be modeled for a single specimen by increasing the illumination intensity W_{ph} (Fig. 2, curves 2–4). As W_{ph} and $1/T$ increase, so does the number of D$^-$–D$^+$ complexes. This increases the relative contribution from trapping by these complexes (Fig. 2), while at the same time narrowing the band of delocalized states.[16] For some values W_{ph} (Fig. 2) τ actually increases with $1/T$ from $\tau \approx (\alpha^0(\varepsilon)_{max}N)^{-1}$ to $\tau \approx \tau_\varepsilon$. At still higher W_{ph}, $\tau \approx \tau_\varepsilon$ continues to hold. Delocalization sets in when the ratio I/Δ becomes large (Ref. 17). The energy overlap integral I is proportional to $\exp(-\alpha R_c/a_i)$, and Δ increases slowly with K (Ref. 13). Therefore, as N increases delocalization begins even in specimens with large K, and this causes τ to drop abruptly for large N. The specimens with $N = 3\cdot10^{16}$ cm^{-3}, $K \approx 10^{-4}$ and $N \approx 6\cdot10^{16}$ cm^{-3}, $K \approx 10^{-2}$ are identical with regard to estimated ratios I/Δ. On the other hand, unless the inequality

$$\alpha^0(kT)N > 2\tau_\varepsilon^{-1}(kT)$$

is satisfied the D$^-$ band cannot invert $F(\varepsilon)$ and make $\tau < \tau_\varepsilon$ (Fig. 6).

5. We note that for specimen No. 17 (Fig. 6), the exponential dependence $\sigma_c(T)$ for $T > 7$ K and $E \approx 10$ V/cm is replaced by a power law $\tau \propto T^{2.5}$, which is typical for the specimens in group I, i.e., for which the trapped carriers migrate to the attracting centers by hopping along neutral centers. Specimen No. 17 is transitional in the sense that the trapped carriers can migrate either by hopping or by flowing along the D$^-$ band, depending on the external conditions

422   Sov. Phys. JETP 67 (2), February 1988

Vorozhtsova et al.   422

(T, E, W_{ph}). The lifetime is given by the expression

$$\tau^{-1} = \alpha_{eff} N^+ + \alpha^0 N \frac{W_h}{W_h + W_T}. \tag{13}$$

The second term becomes more important as N increases and N^+ decreases; on the other hand, the first term dominates as T (and hence W_T) increases. Finally, the drop in α_{eff} with increasing E means that recombination via the D^- band determines the free carrier lifetime from low ($T \approx 1.5$ K) to high temperatures ($T \approx 15$-17 K), for which thermal ionization of the impurities becomes important.

All the experimental findings are thus readily explained by the above recombination model in which the neutral centers play an active role. We stress once again that several different recombination mechanisms may dominate in a relatively narrow range of primary impurity concentrations, depending on N, K, and the external conditions. The processes which we have studied are of course not limited to silicon and should occur in other semiconductors such as germanium with comparable values of $N^{1/3}a$ and K. Our results are directly relevant to the problem of maximizing the photosensitivity of IR radiation receivers and may also be useful in clarifying the conditions under which H^--like states become delocalized in disordered systems of neutral atoms interacting by long-range Coulomb forces.

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