Interaction of A^+ (D^-) centers in semiconductors with charged and neutral impurities

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An increase in the energy of the photodetachment of holes from A^+ centers with increasing acceptor concentration N_A was observed in p-Si at $N_A = 10^{15}$–10^{17} cm^{-3}. The effect is attributed to the influence of the field of the negatively charged acceptors on the A^+ centers and to hopping of the holes over the neutral impurities.

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There have been many recent reports (see, e.g., [1,2] and the references therein) of various effects produced in semiconductors by H^--like $D^-(A^+)$ centers. These centers are produced by attachment of an extra electron (hole) to a neutral donor D^0 (or acceptor A^0). In weakly-doped samples ($N^{1/3}a < 10^{-2}$, where a is the Bohr radius and N is the main-impurity concentration), the $D^-(A^+)$ centers can apparently be regarded as isolated[3]; under the condition of intrinsic or impurity excitation of the carriers, in semiconductors with low degree of compensation ($K \ll 1$), these centers are frequently decisive at helium temperatures in the scattering, recombination, etc. In samples with $0.1 < N^{1/2}a < 0.25$, conductivity with activation energy $\epsilon_2 \lesssim 0.5\epsilon_0$ is observed (ϵ_0 is the ionization energy of the ground state of the impurity); one of the mechanisms proposed to explain the ϵ_2-conductivity is the overlap of the wave functions of the $D^-(A^+)$ states.[4] It is of interest to study the D^- (A^+) centers at $N^{1/3}a > 10^{-2}$, when the average distance between impurities $R_c = (3/4\pi N)^{1/3}$ is only several times larger than the D^- (A^+) center radius1) a_{D^-} (a_{A^+}) and one can expect effects due to the influence of neighboring impurities on these centers.

We have investigated the photoconductivity (PC) of Si : B with $N_A = 3\times10^{14}$ to 10^{17} cm^{-3} ($N^{1/3}a = 0.02-0.1$)2) and $K = 0.01-0.005$ at helium temperatures under conditions of impurity excitation of carriers by a background of $T = 300$ °K. The experiments were performed at submillimeter wavelengths $\lambda = 50$ to 500 μ, where the value of $\delta\sigma/\sigma$ is governed entirely by photodetachment of holes from A^+ centers. The spectra of $\delta\sigma/\delta\sigma_{\max} = f(h\nu)$ (Fig. 1) were obtained with the aid of an echelette monochromator. It is seen that with increasing N_A the long-wave boundary of the PC shifts towards higher energies, while the short-wave boundary changes little at $N_A > 3\times10^{16}$ cm^{-3}. Raising the temperature decreases $\delta\sigma/\delta\sigma_{\max}$ in the long-wave part of the spectrum. The plot of $\delta\sigma/\sigma = f(T)$ (Fig. 2) at $\lambda = 450$ μ (which corresponds to a photodetachment energy $\epsilon_i = 2.5$ meV for the A^+ center) were obtained by using a high-sensitivity backward-wave tube spectrometer.[6] It follows from Fig. 2 that the exponential dependence of $\delta\sigma/\sigma = f(T)$ gives way to saturation at $T = T_c$, and T_c increases with increasing N_A.

The obtained regularities can be attributed, in our opinion, to the following:

1. The presence of isolated A^- and D^+ centers in p-type samples ($N_{A^-} \gtrsim N_D$; $N_{D^+} = N_D$) causes a change in the energy levels of the A^0 centers, owing to the Coulomb field, by an amount $\Delta(r) = \pm(e^2/\kappa r)$ (r is the distance between the $A^-((D^+)$ and A^0 centers). The attachment of the carrier to the A^0 center produces an A^+ center with photodetachment energy $\epsilon_{\rm pd}$ that is altered in first-order approximation by an amount $\Delta(\epsilon_{\rm pd} = \epsilon_i \pm \Delta)$.

2. With increasing N_A, the overlap of the wave functions of the A^+ states of the neighboring acceptors increases, as does the probability of the hopping of the hole ($W = 1/\tau_h \sim \exp(-2\alpha R_{\rm av}/a_{A^+})$, where $\alpha \approx 1$) to the nearest A^0 center. Under the experimental conditions, the difference between the energies of the neighboring centers is $\Delta_c = \Delta(r) - \Delta(R + R_{\rm av}) > kT$, while the value $W = 1/\tau_h$ calculated in analogy with[7] can become larger than the probability of the thermal emission of the hole, $1/\tau_e \sim \exp(-\epsilon_{\rm pd}/kT)$. Therefore the hole captured by the A^0 center hops over predominantly to the attracting center A^-, inasmuch as in this case the transitions are accompanied by energy loss (spontaneous emission of acoustic phonons). On approaching the A^- center, the value of $\epsilon_{\rm pd}$ of the hole increases (the A^+ center "sinks deeper") and can reach values of $\epsilon_{\rm pd} = \epsilon_i + e^2/\kappa R_{\rm av}$. We assume here, in essence, that the lifetime of the A^+–A^- complex (which is analogous to the ionic state of the H_2 molecule[8]), is not smaller than τ_h at $r \sim R_{\rm av}$.3)

The experimental values of $\epsilon_{\rm pd}$, which are determined at $T = 4.2$ °K as the values of $h\nu$ corresponding to $\delta\sigma = 0.2\delta\sigma_{\max}$, are superimposed in Fig. 3 on the calculated $\epsilon_{\rm pd}(R_{\rm av})$ curves and agree well with them. It follows therefore that in samples with $N_A > 10^{15}$ cm^{-3} most A^+ centers sink deeper. The change of the form of the spectrum with increasing T (Figs. 1a and 1b, samples 1–7) is due to the decrease of the number of A^+ centers that did not sink deeper because of thermal ejection of the holes. The weak dependence of the short-wave part of the spectrum on N_A (at $N_A > 10^{16}$ cm^{-3}) is apparently connected with the fact that when the A^+ and A^- centers come close enough together the carrier is detached from the A^+ to the A^- center. This occurs when the energy difference of the hole in the Coulomb field over the dimension of the A^+ center is close to ϵ_i.

The hops of the holes to the neighboring sunken A^0 center become the decisive mechanism of the destruction of the isolated A^+ centers at $1/\tau_h > 1/\tau_e$. This, in

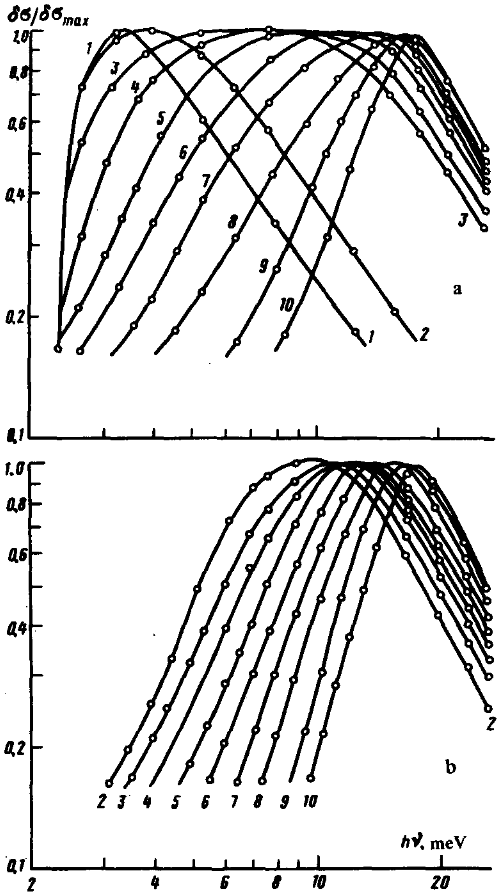

FIG. 1. Photoconductivity spectra $\delta\sigma/\delta\sigma_{\max} = f(h\nu)$ of Si : B samples with $K = 0.1$–0.005 and with values of N_A (in cm^{-3}): 1–3×10^{14}, 2–6×10^{14}, 3–1.5×10^{15}, 4–3×10^{15}, 5–5×10^{15}, 6–8×10^{15}, 7–1.2×10^{16}, 8–3×10^{16}, 9–6×10^{16}, 10–10^{17} at $T = 1.5$ °K (a) and $T = 4.2$ °K (b).

our opinion, is the cause of the increase of T_c with increasing N_A (see Fig. 2). In Fig. 3, the values of τ_e at $T = T_c$ are plotted as functions of R_{av}. It is seen that at $R_{av} < 700$ Å the $\tau_e(R_{av})$ dependence is exponential.

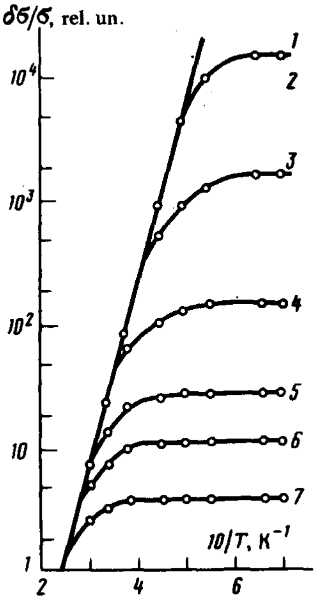

FIG. 2. Plot of $\delta\sigma/\sigma$ against T at $h\nu = 2.5$ meV for samples 1–7.

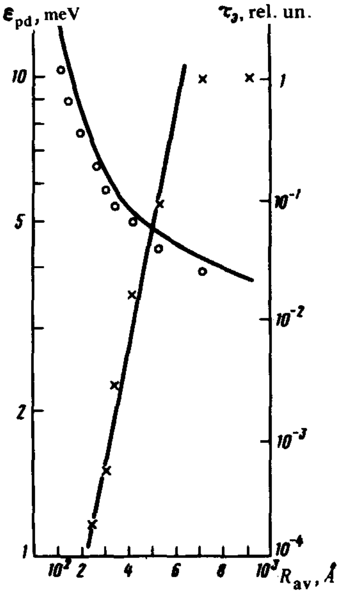

FIG. 3. Plots of ϵ_{pd} against R_{av} (circles); the solid line is calculated. The crosses mark the dependence of τ_e on R_{av} at $T = T_c$.

Knowing T_c for a number of samples and assuming $\tau_h = \tau_e$ at $T = T_c$, we can determine the value of a_{A^+}. It turns out to be 85 ± 10 Å (at $\alpha = 1$), in good agreement with the expected value $a_{A^+} = 4.2a \approx 95$ Å.[4]

When this paper was being readied for publication, we learned of Norton's paper,[9] where he reports, in particular, an increase of ϵ_{pd} of D^- centers in n-Si (Si : P or Si : As). Thus, for Si : P samples with $N_D = 4\times10^{16}$ cm^{-3} ($N^{1/3}a \approx 0.07$) and $K \approx 10^{-3}$ we have $\epsilon_{pd} = 6.8$ meV at $T = 4.2$ °K, whereas ϵ_i of isolated D^- centers in Si : P corresponds to 2.1 meV.[1] This effect is ascribed to the active role of the H_2^- complexes. According to our results, the change of ϵ_{pd} with increasing N up to $N \approx 10^{17}$ cm^{-3} is due to the influence of the attracting centers.

1) According to[4], $a_{D^-} = 4.2a$.

2) According to[5], the Bohr radius of the hole is $a = \hbar/\sqrt{2m_L\epsilon_0} \approx 22$ Å, where $m_L = 0.17m_0$ is the mass of the light hole and $\epsilon_0 = 45$ meV.

3) The mechanisms listed above, which lead to changes of ϵ_{pd} and T_c with increasing N_A, manifest themselves also in the temperature dependences of the holes in Si samples with $N_A \gtrsim 10^{15}$ cm^{-3}.

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