Observation of the delocalization threshold of the H$^-$-like states of impurity centers in doped semiconductors

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The concentration threshold N_c of delocalization of excess carriers is determined from the qualitative variation of the photoconductivity (PC) spectra, and its dependence on the temperature T is investigated. It was determined that N_c is almost two orders of magnitude lower than the concentration N_M corresponding to the Mott transition.

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At present, there is a great deal of interest in questions relating to delocalization of electrons in disordered systems. One example of such a system is a weakly compensated semiconductor that has been doped with shallow impurities. Either one electron (neutral hydrogen-like center) or two electrons –a "ground" electron with a binding energy $E_0 = \hbar^2/2ma^2{}_0$ and with a wave-function decay length a_0 and an "excess" electron with a binding energy $E_i \approx 0.55E_0$ and a decay length $a_i = (1/\hbar)\sqrt{2mE_i} \approx 4.2\ a_0$ (H$^-$-like center)[1]–can be in the impurity center. In this case two types of delocalization are possible. According to theoretical and experimental data, the delocalization of ground electrons occurs at $N = N_M$, where $N_M = (8–15) \times 10^{-3}\, a_0^{-3}$ (Mott transition).[2] Delocalization of "excess" electrons should lead to the formation of a conducting impurity band [upper Hubbard band (UHB) or D^- band] in the disordered system. The so-called σ_2 conductivity, which is characterized by an activation energy ϵ_2, occurs along this band.[2] In the absence of charged centers, this delocalization should occur at $N = N_x$, where $N_x = \lambda a_i^{-3}$.[3] The exact value of the parameter λ is unknown. The delocalization threshold N_x is difficult to experimentally determine from the static σ_2 conductivity under equilibrium conditions: it must compete with other conduction mechanisms.[2]

Spectral measurements of the photoconductivity are more suitable for determining N_x: the conditions can be chosen in such a way that the photoconductivity, which is not associated with the phototransitions of "excess" carriers would be almost absent in the spectral interval of interest, and the H$^-$-like states would be populated as a result of capture by neutral impurities which are produced by the impurity (background) light.

We have determined the concentration threshold of delocalization of the H$^-$-like states; the spectral measurements of the photoconductivity $\sigma/\sigma(h\nu)$ of the doped ($N = 3 \times 10^{16}–10^{18}\text{cm}^3$) and weakly compensated ($k < 0.01$) Si:B and Si:P samples were made using a Fourier spectrometer ($h\nu = 1–30$ meV) at $T = 1.5–15$ K and an impurity illumination. The photoconductivity spectra of Si:B for different N and $T = 4.2$ K are

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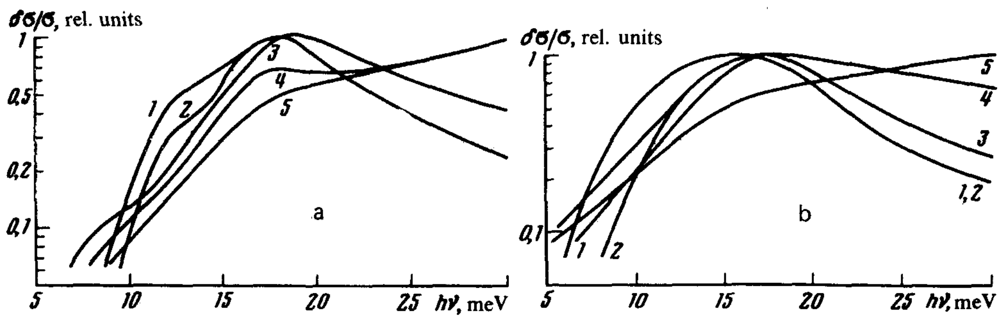

FIG. 1 (a) PC spectra of SI : B for $T = 4.2$ K and $N(\times 10^{17}$ cm^{-3}): 1–0.1, 2–0.5 -0.9, 4–2.5, 5–4.5; (b) PC spectra of Si : P for $N = 3\times 10^{17}$cm^{-3} and T(K): 1–2,3–4.2, 3–5.5, 4–6.2, 5–7.

shown in Fig. 1a. The spectrum changes as N increases--for $N = N_c^{pc} \approx 2.5\times 10^{17}$ cm^{-3} the slope of the short-wave decay decreases, and then the photoconductivity begins to increase monotonically with frequency. Similar changes were observed for Si-P N_c^{pc} 5×10^{17}cm^{-3} and $T = 4.2$ K) and for Ge:Sb ($N_c^{pc} \approx 2.6\times 10^{16}$ cm^{-3} and $T = 1.46$ K].[4] An analogous transformation of the spectrum can be obtained with some samples by increasing the temperature (Fig. 1b). Figure 2 shows the $T_c(N)$ values for Si:B and Si:P, where T_c is the temperature at which the slope of the short-wave decay decreases by 10–15%. Figure 3 shows the $\delta\sigma(T)$ dependences for several Si:P samples; the T_c values are indicated by the arrows. We can see that for $N > 10^{17}$ cm^{-3} $\delta\sigma$ begins to increase with T at $T \approx T_c$.

A monotonic increase of absorption with frequency is characteristic of band-to-band transitions. Under experimental conditions the surface recombination is unimportant because of the small absorption, and the absorption spectrum should be similar to the photoconductivity spectum. Therefore, a qualitative change in the PC spectrum (Fig. 1) indicates that the "excess" carriers are delocalized. The degree of delocalization increases with N and T. We note that at sufficiently high T the N_c^{pc} values are much lower than the N_c^{σ} values obtained from measurements of the σ_2 conductivity (Si:P $- N_c^{\sigma} \approx 1.2\times 10^{18}$cm^{-3} and $\epsilon_2 \approx 10$meV[5];Ge:Sb $- N_c^{\sigma}$

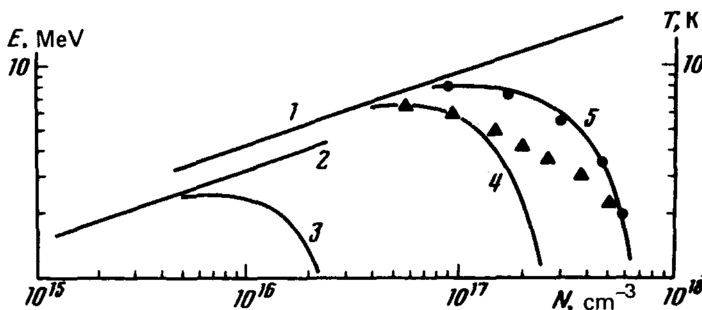

FIG. 2. $T_c(N)$ dependence for Si:B (Δ) and for Si:P (●), calculated Δ values for Si (1) and for Ge (2), and δE for Ge:Sb (3), for Si:B (4), and for Si:P(5).

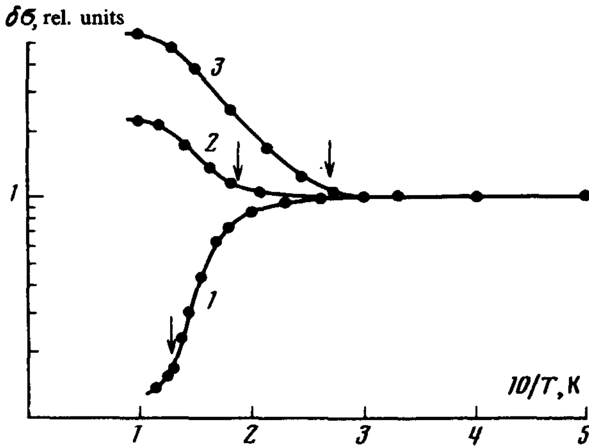

FIG. 3. $\delta\sigma(T)$ dependences for Si: P with $N(x\,10^{17}$ $\text{cm}^{-3})$ equal to: 1–0.9, 2–3, and 3–5.

$\approx 2.9\times10^{16}\text{cm}^{-3}$ and $\epsilon_2\approx 3.9\text{meV}$[6];Si:B $- N_c^\sigma\approx 6\times10^{17}\text{cm}^{-3}$and $\epsilon_2\approx 16\text{meV}$). To obtain more detailed knowledge of the examined care, we must determine the nature of the localized states. We assume that they are molecular-type $(H^- H^+)$ ionic states produced by the trapping centers $(D^+$ or $A^-)$.[7] The binding energy of an "excess" carrier in these states is $E = E_i + (e^2/\kappa R)$, is the dielectric constant and R is the distance to the trapping center. The energy gap between the filled localized states and the bottom of the UHB in this case is $\delta E = \Delta - J$, where $\Delta = (e^2/\kappa)(\frac{4}{3}\pi N)^{1/3}$ and J is the exchange-interaction energy. The value of J depends of the fluctuational spread Δ_{ij} of the levels of adjacent centers, due to the presence of charged impurities.[6] If the influence of Δ_{ij} on J is disregarded, the dependence of J on N, is taken into account, i.e.,$J(N)\sim\exp(-2N/a_i)^{1/3}$, for a known a_i, and the ϵ_2 values are used at N_c^σ as tie-points, then we can estimate δE (curves 3–5 in Fig. 2). We note that the $\delta E(N)$ and T_c (N) dependences are qualitatively similar. The divergence of $\delta E(N)$ and $T_c(N)$ for Si:B at $N > 3\times10^{17}$ cm^{-3} may be due to a decrease of the effective Bohr radius of the ground state[8], and , hence a decrease of a_i. For sufficiently heavily doped samples $(\Delta\approx J)\delta E \ll \Delta$, which primarily determines the value of T_c. The carriers are ejected from the localized states into the UHB; in this case the total number of "excess" carriers is not reduced (Fig. 3). For smaller N the value of $\delta\sigma$ decreases with increasing T (Fig. 3) and , consequently, the total number of "excess" carriers and charged centers is reduced. In this case a decrease of δE, which is caused by a decrease of Δ_{ij} and an increase of J, contributes to a relative overpopulation of the localized and delocalized states as T increases. It follows from this that the optimum temperature $T\gtrsim T_c$ must be chosen to determine N_x. Thus, according to the estimates of Ge:Sb, N_x must be equal to $\approx 5\times10^{15}\text{cm}^{-3}$ and $T_c\gtrsim 2.5$ K. Therefore, the value $N_x = 2.6\times10^{16}\text{cm}^{-3}$ obtained in Ref. 4 is too large because of the small value of $T = 1.46\text{ K} < T_c$.

Thus, the results of our work show that the critical impurity concentration for delocalization of the "excess" carriers is $N_x < 0.05\, a_i^{-3}\approx 7\times10^{-4}\, a_0^{-3}$, i.e., it is almost two orders of magnitude lower than the concentration characteristic of the Mott transition.

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