Hopping photoconductivity of doped silicon and germanium

E. M. Gershenzon, F. M. Ismagilova, L. B. Litvak-Gorskaya, and A. P. Mel'nikov

V. I. Lenin Pedagogical State University
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The photoconductivity has been studied for impurity and intraband excitation in Si and Ge over the doping range $0.08 \leqslant N^{1/3}a < 0.2$ and over the dopant compensation range $1 > K > 10^{-4}$ at temperatures $T = 1.6$–20 K (N is the concentration of the major dopant, and a is the first Bohr radius of the donor). A new type of photoconductivity has been observed in slightly compensated Si. This new photoconductivity is distinguished by the formation of two types of carriers — electrons and vacancies—during impurity photoexcitation. While the electrons are responsible for σ_c, the photoconductivity in the conduction band, the vacancies are related to a hopping photoconductivity through a band of impurity ground states, $\Delta\sigma_{dop}$. The conductivities σ_c and σ_{dop} were studied as functions of the temperature and dopant concentration N. The recombination of free carriers in Si with $10^{-2} > K > 10^{-4}$ is dominated by an indirect capture into the D^- band, just as for $K < 10^{-4}$ (Ref. 9). The new experimental results are used along with data from the literature to plot a diagram to illustrate the behavior of the photoconductivity mechanisms in the cases of impurity and interband excitation as functions of the dimensionless parameters $N^{1/3}a$ and K.

1. INTRODUCTION

Since its discovery,[1] hopping photoconductivity has been observed in several semiconductors at dopant concentrations N satisfying the condition $N^{1/3}a \geqslant 0.07$, where a is the carrier localization radius at the impurity center, and at degrees of compensation $K > 10^{-2}$ (Refs. 2–4).

The idea of a hopping motion of photocarriers in disordered semiconductors was raised in Refs. 5 and 6. The theoretical expression derived there for the photoconductivity signal $\Delta U_{ph}/U$ showed an exponential dependence on the temperature and the photon energy. This behavior was subsequently verified experimentally in Ref. 3. However, the uncertainties regarding the constants and the functions in the expressions for $\Delta U_{ph}/U$ in Refs. 5 and 6 complicate a quantitative comparison with experiment.

A theory of hopping photoconductivity with multiphonon processes for photons with $\hbar\omega \ll$ Ry was derived in Ref. 7; here Ry is the ionization energy of an isolated impurity center. Among the analytic expressions for $\Delta U_{ph}/U$ given in Ref. 7 for several particular cases, only the temperature dependence of the photoconductivity $\Delta\sigma$ at $\hbar\omega \ll kT$ has found experimental confirmation.[8] So far, that has been the only comparison of theory with experiment.

In the absence of a hopping-photoconductivity theory whose conclusions can be pursued to simple analytic expressions, a phenomenological model has been used.[3,8] According to that model, photoconductivity involving impurity particles is treated as a process analogous to static conductivity, with the one difference that it is the absorption of a photon, rather than a phonon, which is required to activate the electron. It should be noted that the hopping photoconductivity occurs in the same temperature range as the equilibrium hopping conductivity. The hopping photoconductivity is observed during interband illumination,[1,2] during impurity photoexcitation with a phonon energy $\hbar\omega >$ Ry (Refs. 3 and 4), and during intracenter excitation, $\hbar\omega <$ Ry, all the way to $\hbar\omega \approx 0.2$Ry (Ref. 3). Photoconductivity due to free electrons has not been observed in the first and second of these cases. The mechanism of a "descent" of photoelectrons from the conduction band into the band of impurity ground states (the ε_3 band) during interband or impurity photoexcitation was not discussed in Refs. 1 and 3. It was simply pointed out that the descent time would be much shorter than the photoconductivity relaxation time. (The entire discussion below is phrased in terms of a material with an n-type conductivity, although a hopping photoconductivity is also observed in a p-type material.)

The hopping photoconductivity is not the only mechanism for photoconductivity involving impurity centers in doped semiconductors. A study[9] of the photoconductivity of p-Si(B) over the acceptor concentration range $N = 3 \cdot 10^{16}$–$1.2 \cdot 10^{17}$ cm^{-3} ($0.06 \leqslant N^{1/3}a \leqslant 0.1$) at $K < 10^{-4}$ revealed an important contribution to the photoconductivity from conductivity in a band of delocalized impurity states: an upper Hubbard band (a D^- band). In addition, the photoconductivity due to free carriers (σ_c) and the photoconductivity corresponding to the D^- band (σ_g) are comparable in magnitude for $T \leqslant 15$ K. The equilibrium hopping conductivity in the band of impurity ground states (the ε_3 band) in studies[9,10] of p-Si at liquid-helium temperature was exceedingly low, because of the exceedingly low degree of compensation. An increase in the degree of compensation ($K > 10^{-4}$) in this p-Si, however, gives rise to a significant equilibrium ε_3 conductivity for $T \leqslant 15$ K. The mechanisms for the photoconductivity here are not clear.

Our purpose in the present study was to learn about the photoconductivity of Ge and Si during impurity excitation and intraband excitation in the dopant concentration range $0.08 \leqslant N^{1/3}a < 0.2$ and in the compensation range $10^{-4} < K \leqslant 10^{-2}$ in order to clarify the mechanisms for the photoconductivity at various temperatures and for various parameter values of the material ($N^{1/3}a$ and K).

We studied the temperature dependence of the photoconductivity corresponding to the free band and the impur-

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TABLE I.

Material	Sample	Dopant	N, 10^{16} cm^{-3}	K	$N^{1/3}a$	ε_3, meV	ε_2, meV	ε_1, meV
Ge	1	Sb	1,6	0,07	0,108	1,37	—	6,2
	2	Sb	3,8	0,7	0,144	1,6	—	11
	3	Sb	3,3	0,05	0,138	1,33	3	6
	4	Sb	5	0,05	0,158	1,25	2,4	5,8
	5	Sb	6,7	0,05	0,175	1,1	1,8	5,7
	6	As	2,9	0,03	0,098	1,6	—	—
	7	As	14	0,03	0,166	1,8	2,9	—
Si	8	P	26	0,2	0,109	4,9	—	44
	9	P	40	0,3	0,125	4,8	—	44
	10	P	50	0,5	0,134	4,7	—	45
	11	B	4,5	$2{,}2\cdot10^{-3}$	0,82	4,3	—	45
	12	B	5,2	$1{,}1\cdot10^{-3}$	0,086	4,4	—	45
	13	B	6	$7{,}8\cdot10^{-4}$	0,09	4,7	—	45
	14	B	7,8	$3\cdot10^{-4}$	0,098	5,2	—	45
	15	B	9	$2\cdot10^{-3}$	0,103	5,2	—	45
	16	B	12	$3\cdot10^{-4}$	0,113	6,2	—	45
	17	B	200	$<10^{-2}$	0,17	3,8	12,5	22
	18	Ga	21	$1{,}5\cdot10^{-4}$	0,083	11	—	73
	19	P	30	$3\cdot10^{-3}$	0,107	5,9	—	44

ity band ($\Delta\sigma_{dop}$) during impurity photoexcitation. We compared $\Delta\sigma_{dop}(T)$ with the corresponding property of a material with a greater degree of compensation ($K\leqslant 0.5$), during monochromatic photoexcitation in the ε_3 band. On the basis of the behavior $\Delta\sigma_{dop}(T,N)$ and $\sigma_c(T)$, it is shown that mechanisms for the impurity photoconductivity are different for $K<10^{-4}$ and $K>10^{-4}$, although the D^- band is present in both cases. On the basis of the new experimental results and data from the literature,[1,4] we construct a diagram which shows how the photoconductivity mechanisms depend on the dimensionless parameters $N^{1/3}a$ and K during impurity excitation and interband excitation.

2. TEST SAMPLES AND EXPERIMENTAL PROCEDURE

We studied the low-temperature photoconductivity of Si doped with B, P, Ga, and that of n-Ge doped with Sb and As. The parameter values of the samples are listed in Table I. All the samples exhibit an ε_3 hopping conductivity at liquid-helium temperature.[11] Table I shows values of the ε_3 energies. In the samples with the highest degree of compensation (samples 2 and 8–10) the ε_3 conductivity gives way, with decreasing temperature, to a conductivity with a variable hopping length, with $\ln\sigma\propto(T_0/T)^{1/4}$ (Ref. 12). The values found experimentally for T_0 and the temperatures of the transition to this type of conductivity, $T'\approx 12$ K for Si and $T'\approx 5$ K for Ge, agree well with the theory of Ref. 11. Also in agreement are the values of the energy ε_3 for silicon samples 8–16.

The samples with $N^{1/3}a\geqslant 0.13$ exhibit an ε_2-band conductivity along with the ε_3 conductivity.[1)] Exceptions to this rule are the highly compensated samples 2 and 10.

The photoconductivity was studied by several methods, with three different types of photoexcitation. In the first method, the photoexcitation of the charge carriers was carried out by background light (cold silicon filters were used[9]) in the wavelength interval $\lambda\approx 8$–$12\,\mu$m ($\hbar\omega>$ Ry) at low excitation levels, $W_{ph}=0.25$ and 1 s^{-1}. The temperature dependence of the electrical conductivity and of the Hall constant was measured over the temperature range $T=4.2$–20 K during background photoexcitation (σ, R_H) and in the absence of this excitation (σ_0, R_{H0}), at electric fields $E=10$–50 V/cm at a fixed magnetic field $H=4.4$ kOe. This method is used to study the photoconductivity of Si samples with $K\leqslant 10^{-2}$, except sample 17.

In the second photoexcitation method, we used a Fis-3 monochromator ($\lambda=25$–$300\,\mu$m). The light from the monochromator was modulated at a frequency of 400 Hz. The photoconductivity signal was measured directly by a Unipan 232-B tuned voltmeter in the current-source regime for $E\leqslant 10$ V/cm (Ohm's law). This method was used to study the photoconductivity of sample 17 at $\hbar\omega>\varepsilon_1$.

In the third method, we used monochromatic sources (backward-wave tubes) in the range $\lambda=1.2$–2.1 mm. The background illumination was eliminated completely with the help of filters 0.5 mm thick made of a fabric-based laminate. In other words, the carriers were photoexcited only in the ε_3 band. The radiation from the backward-wave tube was also modulated at 400 Hz, so it was possible to directly measure the photoconductivity signal at $T=1.6$–4.2 K in Ge and at $T=4.2$–14 K in Si. This method was used to study the photoconductivity of Ge and of silicon samples 8–10 and 17.

3. EXPERIMENTAL RESULTS

1. In Si and Ge, which we studied, it was not possible to study the photoconductivity during impurity illumination ($\hbar\omega>$ Ry) and during photoexcitation in the ε_3 band ($\hbar\omega\leqslant\varepsilon_3$) on the same sample (sample 17 was an exceptional case). Weakly compensated Si ($10^{-2}>K>10^{-4}$) has such a high resistivity that σ_c and $\Delta\sigma_{dop}$ can be determined only from measurements of R_H, σ and R_{H0}, σ_0. It is not possible to measure $\Delta\sigma_{dop}$ at $\hbar\omega\leqslant\varepsilon_3$ by the modulation technique described above. In Si with $K\approx 0.2$–0.5 and also in slightly compensated Ge, the significant equilibrium conductivity σ_0 essentially rules out a reliable calculation of σ_c and $\Delta\sigma_{dop}$ from R_H, σ and R_{H0}, σ_0. On the other hand, it is possible to study the photoconductivity at $\hbar\omega\sim\varepsilon_3$. A comparison of $\Delta\sigma_{dop}(T)$ for $\hbar\omega>$ Ry and at $\hbar\omega\leqslant\varepsilon_3$ is thus possible only if different samples are used. In practice, we were obliged to use two groups of samples: a first group consisting of Si samples with $10^{-2}>K>10^{-4}$ and a second group consisting of Ge and Si samples with $K>10^{-2}$. The studies of the photo-

conductivity in the two groups complemented each other. While we were able to learn about the behavior of σ_c and $\Delta\sigma_{dop}$ as functions of T, N, and H and also the photoconductivity relaxation mechanism by studying the samples of the first group, we were able to use the samples of the second group to analyze the features of the impurity photoconductivity as a function of the mechanisms for the equilibrium conductivity and the photon energy.

2. We begin our discussion of the experimental results with the photoconductivity during monochromatic excitation of carriers in the ε_3 band ($\hbar\omega \ll$ Ry). In this case (e.g., in sample 1) we have $\ln(\Delta\sigma_{dop}/\sigma_0) \propto T^{-1}$, while in samples 2, 8, and 9 we find $\ln(\Delta\sigma_{dop}/\sigma_0) \propto T^{-1/4}$. In other words, these results are in agreement with Ref. 3. The ratio σ_{dop}/σ_0 is determined primarily by the temperature dependence of the equilibrium conductivity. This result implies that the temperature dependence of $\Delta\sigma_{dop}$ is weaker than exponential.

The curves of $\Delta\sigma(T)$ of the group of Ge and Si samples in Fig. 1 are indeed similar: $\Delta\sigma_{dop}(T)$ has a maximum at $T \approx 8$–10 K in Si and one at $T \approx 4$ K in Ge. At low temperatures we find

$$\Delta\sigma_{dop}(T) \propto T^n. \qquad (1)$$

The value of n varies slightly, depending on the mechanism for the impurity conductivity. In the samples which exhibit only an ε_3 conductivity at low temperatures, for example, we find $n = 1.8 \pm 0.1$, regardless of whether the photon energy is sufficient to move an electron (or vacancy) to an impurity percolation level ($\hbar\omega \approx \varepsilon_3$) or the photoelectron moves among states near the Fermi level ($\hbar\omega < \varepsilon_3$). A significantly larger value, $n = 3.3 \pm 0.1$, is found in the samples in which there is an ε_2 band (samples 3, 4, and 17; Fig. 1), even if the photoexcitation is carried out within the ε_3 band. For example, in samples 2 and 3, with approximately the same parameter values ($N^{1/3}a = 0.144$ and 0.138), we find $n = 1.8$ and 3.3, respectively. These results are consistent with the understanding that sample 3 has an ε_2 band, while sample 2 does not, because of the substantial degree of compensation. From the curves of $\Delta\sigma_{dop}(T)$ for sample 17 we see that the behavior is the same at $\hbar\omega = 1.3$ meV ($\hbar\omega < \varepsilon_3 \ll \varepsilon_1$) and in the case of a monochromatic impurity photoexcitation, with $\hbar\omega = 40$ meV $> \varepsilon_1$. This comment also applies to sample 4, in which $\Delta\sigma_{dop}(T)$ is independent of $\hbar\omega$, although measurements were carried out at $\hbar\omega = 2$ meV $> \varepsilon_2 - \varepsilon_3$ and 0.4 meV $< \varepsilon_3$ (Fig. 1 and Table I). These examples show that the strengthening of the temperature dependence $\Delta\sigma_{dop}(T)$ is apparently not a consequence of photoconductivity involving any states outside the ε_3 band.

3. We turn now to a discussion of the photoconductivity during impurity illumination. Figure 2 shows curves of $\sigma(T)$, $\sigma_0(T)$, $R_H(T)$, $R_{H0}(T)$, and $\mu^*(T) = R_H\sigma$ for sample 14 at $W_{ph} = 1\ s^{-1}$. The shape of the $\sigma_0(T)$, $R_H(T)$, and $R_{H0}(T)$ curves is seen to be typical of hopping conductivity.[11] At $T \leqslant 16$ K we find differences between $\sigma(T)$, $R_H(T)$ and $\sigma_0(T)$, $R_{H0}(T)$; these differences increase with decreasing temperature. Similar $\sigma(T)$ and $R_H(T)$ curves were found for all samples of weakly compensated silicon. The existence of a temperature dependence $R_H(T)$ down to $T \leqslant 4.2$ K implies the presence of holes in the valence band,

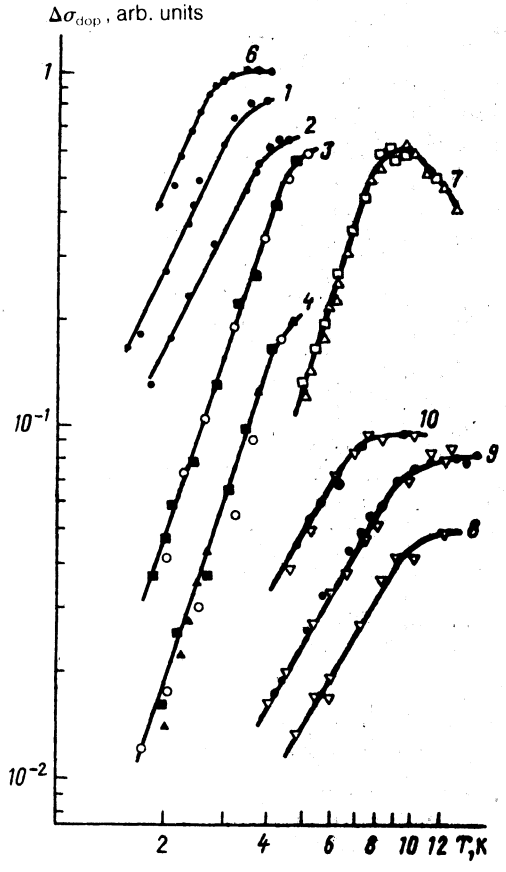

FIG. 1. Temperature dependence of $\Delta\sigma_{dop}$ for monochromatic excitation at various photon energies $\hbar\omega$ (meV): ●—1.4; △—1.3; ●—1.1; ▲—0.4; ○—2; ▽—4.7; □—40. The curve labels are the sample numbers in Table I.

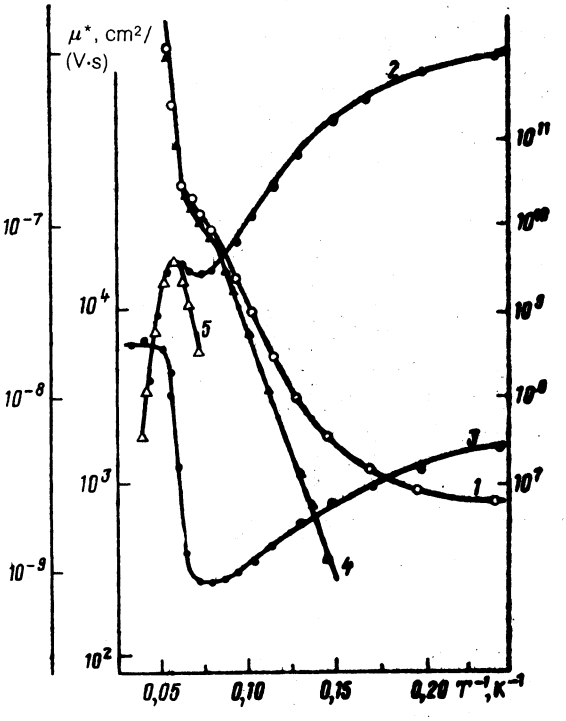

FIG. 2. The temperature dependence of $\sigma(T)$, $R_H(T)$, and $\mu^*(T) = R_H\sigma$ (curves 1–3, respectively) for sample 14 at $W_{ph} = 1\ s^{-1}$ and $E = 30$ V/cm. 4, 5—σ_0 and R_0, respectively, under equilibrium conditions.

but the minimum on the $\mu^* = R_H\sigma$ curve (as in Ref. 9) implies the existence of several equilibrium and nonequilibrium conductivity mechanisms. The tendency of $\mu^*(T)$ to approach the theoretical value of μ_c for scattering by neutral impurity centers[13] away from the minimum indicates that impurity conductivity and conductivity involving free carriers coexist.

The primary distinction between the $R_{H0}(T)$ and $\sigma_0(T)$ curves in Fig. 2, on the one hand, and the corresponding curves in Ref. 9, on the other, is a definite dark ε_3 hopping conductivity. We believe that this result is a consequence of an increase in the compensation from $K\sim 10^{-5}$ in Ref. 9 to $K\sim 10^{-4}$–10^{-3} (Table I), since the concentration of the major dopant was higher than that in Ref. 9 by a factor of less than 2.

To distinguish the contribution of charge carriers to the conductivity in the free band (σ_c) and that in the impurity band (σ_{dop}) during the impurity excitation, we followed Ref. 9 and used a two-band model of the conductivity. We assigned a mobility μ_{dop} to the impurity band. Since the magnetoresistance was negligible in the magnetic fields of our experiments, we will find σ_c and σ_{dop} from the very simple expressions for the two-band model. Under the assumption $\mu_c = \text{const}$, we have

$$\sigma=\sigma_c+\sigma_{\text{dop}}$$
$$R_H=(\sigma_c\mu_c+\sigma_{\text{dop}}\mu_{\text{dop}})/\sigma^2, \qquad (2)$$

where σ and R_H are found experimentally.

The number of unknowns in (2) is greater than the number of equations, so to find σ_c and σ_{dop} we introduce the quantity[2)] $b = (\mu_{\text{dop}}/\mu_c) < 10^{-3}$; we then have $\sigma_c = \sigma(R_H\sigma/\mu_c - b)(1-b)^{-1}$. If σ_c is the photoconductivity of the free carriers, then $\sigma_{\text{dop}} = \sigma_0 + \Delta\sigma_{\text{dop}}$. In other words, this conductivity is determined by the photoconductivity in the impurity band and by the equilibrium dark conductivity σ_0.

4. Let us examine a photoconductivity due to free carriers. Figure 3 shows curves of $\sigma_c(T)$ for samples 14 and 16 and also for two samples from Refs. 9 and 10 (their parameter values are given in the figure caption). These results demonstrate the effect of the degree of compensation on the value of σ_c (curves 1 and 2) and also the change in σ_c with increasing N at $K\geqslant 10^{-4}$ (curves 3 and 4). As was pointed out in Ref. 9, there are two regions of the $\sigma_c(T)$ curve in the case $K<10^{-4}$: a low-temperature region (σ_c'), associated with a population inversion in the conduction band, since we have $\hbar\omega > \text{Ry}$, and a high-temperature region associated with a thermal activation of electrons from the D^- band into the conduction band (σ_c''). There is accordingly an exponential dependence on T^{-1} in the latter case. In the samples with the higher degrees of compensation ($K>10^{-4}$), it appears at first glance that there is no region of exponential dependence $\sigma_c''(T)$ (Refs. 9 and 10). Actually, this σ_c'' region does exist, but it is smaller than for $K<10^{-4}$, because it is shunted on the low-temperature side by σ_c', while on the high-temperature side it is bounded by the conductivity due to equilibrium free carriers. The curves of $\sigma_c''(T) = \sigma_c(T) - \sigma_c'(T)$ in Fig. 3 show that we have $\ln\sigma_c'' \sim -\varepsilon_x/kT$, where ε_x is the energy gap between the maximum of the density of states of the D^- band and the bottom

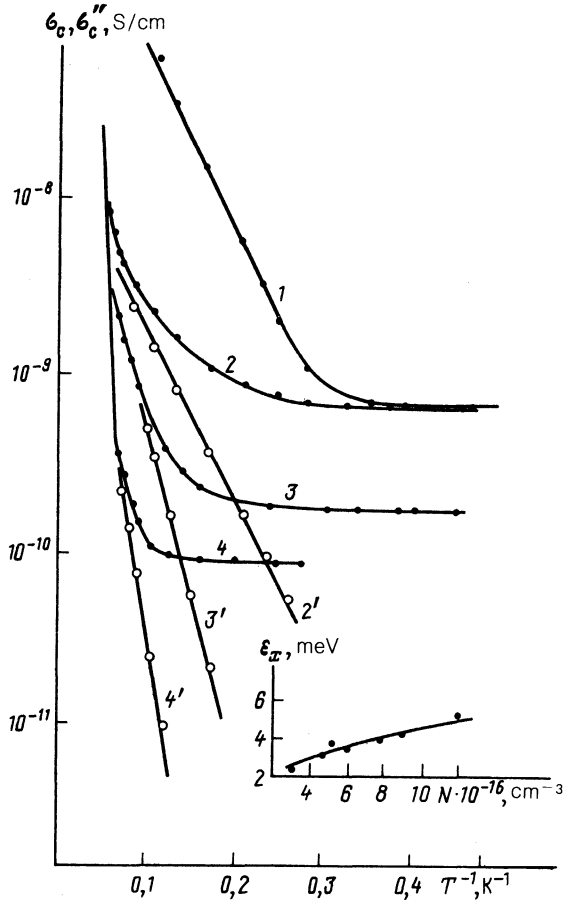

FIG. 3. Temperature dependence of σ_c and σ_c'' in p-Si⟨B⟩ at $W_{\text{ph}} = 0.25$ s^{-1}. 1—$N = 3\cdot 10^{16}$ cm^{-3}, $K = 4\cdot 10^{-5}$ (Ref. 9); 2—$N = 3\cdot 10^{16}$ cm^{-3}, $K = 4.5\cdot 10^{-3}$ (Ref. 10); 3, 4—samples 14 and 16, respectively (see Table I). The curves labeled with primed numbers correspond to σ_c'. The inset shows ε_x versus N. Solid line—Calculation of ε_x from Ref. 14.

of the conduction band. It follows from the curve of $\varepsilon_x(N)$ in the inset in Fig. 3 that ε_x increases with N. The solid curve corresponds to the theoretical value of ε_x calculated for Si(B) from Ref. 14. The agreement between the experimental and theoretical results can serve as indirect support for the validity of our method of analyzing the experimental results.

5. We turn now to the impurity photoconductivity. Figure 4 shows the temperature dependence $\Delta\sigma_{\text{dop}}(T)$ at $W_{\text{ph}} \approx 0.25$ and 1 s^{-1} for several silicon samples. We see that $\Delta\sigma_{\text{dop}} \propto T^{1.7\pm 0.1}$ reaches a maximum at $T_{\max} \approx 7$–8 K. This is not true of sample 18 [Si⟨Ga⟩], in which this maximum is reached at $T_{\max} = 14$ K. The apparent reason for this difference in $T_{\max}$ values is that the equilibrium hopping conductivity is observed at $T\leqslant 15$ K in Si doped with B and P, while it is observed at $T<25$ K in Si⟨Ga⟩. At $T>T_{\max}$ we see a tendency toward a decrease in $\Delta\sigma_{\text{dop}}$, but it is difficult to calculate $\Delta\sigma_{\text{dop}}$ because of the relation $\Delta\sigma_{\text{dop}} \ll \sigma_0$.

Let us examine the behavior of the photoconductivity of slightly compensated silicon as a function of the concentration of the major dopant at $T = 7$ K and $W_{\text{ph}} = 0.25$ s^{-1} (Fig. 5).[3] We see that the curves of $\sigma_g(N)$ (Ref. 9) and $\Delta\sigma_{\text{dop}}(N)$ behave oppositely: While σ_g falls off with increasing N, $\Delta\sigma_{\text{dop}}$ increases in proportion to N. Also shown in this

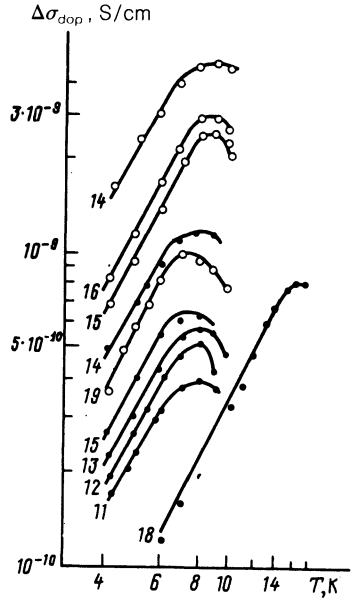

FIG. 4. Temperature dependence of $\Delta\sigma_{dop}$ at two photoexcitation levels. ○—$W_{ph} = 0.25$ s^{-1}; ●—1 s^{-1}. The curve labels are the sample numbers in Table I.

figure are curves of $\sigma_c(N)$ at $T = 7$ K. However, as can be seen from Fig. 3 and Ref. 9, at $K < 10^{-4}$ we are dealing with $\sigma_c''(N)$, while at $K > 10^{-4}$ we are dealing with $\sigma_c'(N)$. The nature of the changes as a function of N is the same for $\sigma_c''(N)$ and $\sigma_g(N)$, but the curves of $\Delta\sigma_{dop}(N)$ and $\Delta\sigma_c'(N)$ are very different. With increasing N, there is an increase in the difference between $\Delta\sigma_{dop}$ and σ_c': While at $N \approx 6\cdot10^{16}$ cm^{-3} we find $\Delta\sigma_{dop} \approx \sigma_c'$, at $N \approx 10^{17}$ cm^{-3} we find $\Delta\sigma_{dop}/\sigma_c' \approx 6$, and at $N \approx 10^{18}$ cm^{-3} we find $\Delta\sigma_{dop}/\sigma_c' \sim 10^3$. We thus see the reason for the complete agreement of the $\Delta\sigma_{dop}(T)$ curves for sample 17 during monochromatic excitation in the conduction band and in the ε_3 band (Fig. 1). The dashed line in this figure shows the possible magnitude of a D^--band conductivity in a material with $K > 10^{-4}$ (σ_g'), which we will discuss below.

6. The difference in the nature of the impurity photoconductivity for $K < 10^{-4}$ and $K > 10^{-4}$ is manifested in differences in the behavior of σ_g and $\Delta\sigma_{dop}$ as functions of the magnetic field strength H. For $\sigma_g(H)$ in the range $H = 0$–12 kOe, a negative magnetoresistance has been observed; this magnetoresistance was studied in Ref. 15 and was linked with quantum corrections to the conductivity involving delocalized impurity states. At $K > 10^{-4}$ the magnetoresistance is positive, with $\ln[\Delta\sigma_{dop}(H)/\Delta\sigma_{dop}(0)] \propto H^2$, and the magnetoresistance can be described quantitatively by the theory of a magnetoresistance with a hopping conductivity.[11]

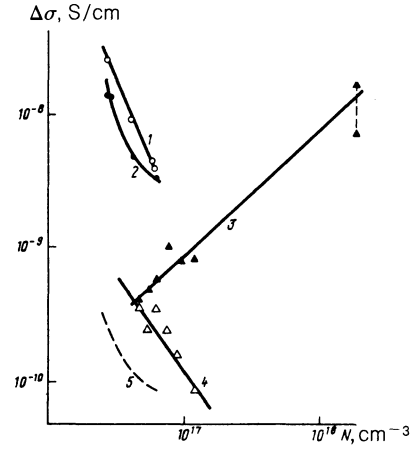

FIG. 5. Dependence of the various types of photoconductivity in p-Si on the dopant concentration at $W_{ph} = 0.25$ s^{-1} and $T = 7$ K. 1, 2—σ_c'' and σ_g according to the data of Ref. 9; 3—$\Delta\sigma_{dop}(N)$; 4—$\sigma_c'(N)$; 5—estimate of σ_g' at $K > 10^{-4}$.

4. DISCUSSION OF EXPERIMENTAL RESULTS

1. The agreement of the temperature dependence of the photoconductivity in the case of impurity photoexcitation with the corresponding temperature dependence for excitation in the ε_3 band (Figs. 1 and 3), combined with the nature of the dependence $\Delta\sigma_{dop}(N,H)$, suggests that hopping photoconductivity involving the ε_3 band plays a governing role for the impurity photoconductivity for $N^{1/3}a \geqslant 0.08$ and $K > 10^{-4}$. We will find some corresponding estimates, under the assumption that for $10^{-2} > K > 10^{-4}$ each absorbed photon liberates a vacancy for motion in the impurity band. In this case we have[13]

$$\Delta\sigma_{dop} = eW_{ph}N\mu_{ph}\tau, \tag{3}$$

where τ is the relaxation time of the hopping photoconductivity, and μ_{ph} is the mobility of the photocarriers, which we will equate to the equilibrium mobility: $\mu_{ph} = \mu$.

To determine μ we make use of the idea that the equilibrium conductivity is determined by the number of vacancies in percolation level n (since $K \ll 1$; Ref. 11). Working from some simple statistical relations, assuming that the number of states at the percolation level is N, and assuming $n \ll N_K$ (the right side here is the concentration of the compensating dopant), we find

$$n \simeq N\exp(-\varepsilon_3/kT), \tag{4}$$

$$\mu \approx \sigma_0/eN\exp(-\varepsilon_3/kT).$$

The mobility can also be found from the saturation region for the hopping conductivity (Fig. 2), since we have[11]

$$\sigma_{sat} \approx e\mu NK. \tag{5}$$

Values found for μ from expressions (4) and (5) are given in Fig. 6. We see that the mobilities found by the two methods depend on the dopant concentration in the same way: $\ln\mu \sim (N^{1/3}a)^{-1}$. In magnitude, however, the values differ by a factor of nearly 10. We have more faith in the values of μ found from expression (4), since the measurements of $\sigma_0(T)$ showed that the values of σ_{sat} are higher than the calculated values[11] for $K \leqslant 10^{-3}$ (this situation is not found for $K \sim 10^{-2}$).

A dependence of μ on the dopant concentration similar to that in Fig. 6 would be expected on the basis of the diffusion relation[11,16]

$$\mu = \frac{er^2\nu_0}{3kT}\exp\left(\frac{2r}{a}\right) \approx \frac{eN^{-2/3}\nu_0}{3kT}\exp\left(\frac{\alpha}{N^{1/3}a}\right), \tag{6}$$

where $r \sim N^{-1/3}$ is the average distance between impurity centers, $\nu_0 \sim 10^{12}$–10^{13} s^{-1} is the characteristic phonon fre-

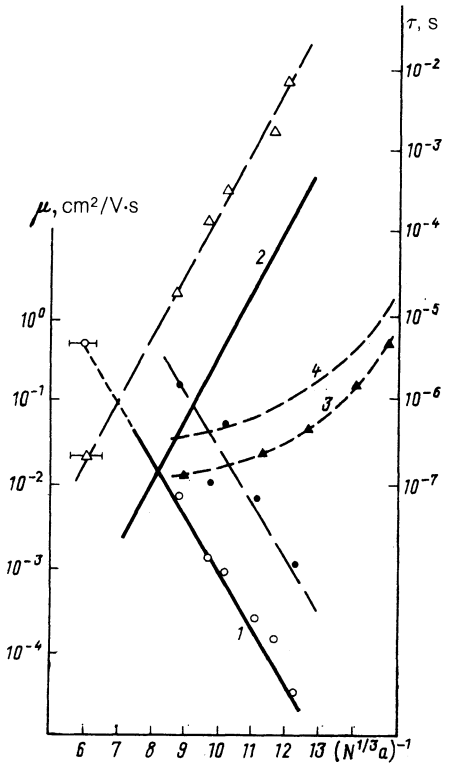

FIG. 6. Mobility and relaxation time of the photoconductivity versus the dopant concentration in p-Si⟨B⟩ at $W_{ph} = 0.25\ s^{-1}$ and $T = 7$ K. 1—Calculation of μ from (6); 2—calculation of τ from (7); 3—relaxation time of the photoconductivity in the D^- band in p-Si with $K < 10^{-4}$ (Ref. 9) at $T = 4.2$ K; 4—approximation of τ_g near $T = 7$ K according to the data of Ref. 9. Experimental values of μ found by different methods: ○) From Ref. 4; ●) from Ref. 5; △) experimental values of τ found from (3) and (4).

quency,[12] and $\alpha = 1.25$–2. To calculate μ from (6), we need to refine the values of two parameters: ν_0 and α. These parameters determine not only the absolute values of μ but also the slope of the $\ln[\mu(N^{-1/3}a^{-1})]$ curve. If we adopt $\nu_0 = 10^{13}\ s^{-1}$ and $\alpha = 1.73$, we find that the theoretical values of μ agree with the experimental values.

To determine τ, we substitute the value found for μ into (3). It can be seen from the curve of $\tau(N)$ in Fig. 6 that we have $\ln \tau \sim (N^{1/3}a)^{-1}$. Solid line (curve 2) in this figure shows results calculated on the time for a single hop, $\tau_0(N)$, in the case of a hopping photoconductivity, with the parameter values of the material from Refs. 11 and 12:

$$\tau_0 = \nu_0^{-1} \exp\left(\frac{1{,}73}{N^{1/3}a}\right). \qquad (7)$$

We see that τ is larger than τ_0 by a factor of about 70. The ratio τ/τ_0 cannot be taken to be the number of hops (Q) which a vacancy undergoes before recombination, but it does show that Q in this material is considerably smaller than that in amorphous Si (Ref. 17). It is apparently for this reason that we see differences in the behavior $\tau(N)$ for the hopping photoconductivity in these materials. The curve of the relaxation time of the D^--band photoconductivity, $\tau_g(N)$, shown for comparison in this figure,[9] exhibits not only a different concentration dependence but also much smaller values of τ_g in samples with $K < 10^{-4}$.

2. Can we determine the role played by the D^- band in the photoconductivity and in recombination processes at $K > 10^{-4}$? There can be no doubt that this band does play a role here, since the experimental dependence of σ_c'' corresponds to an "inverse" transition of electrons from the D^- band into the conduction band. The steady-state electron density in the D^- band, however, is considerably lower than for $K < 10^{-4}$; otherwise, we could not explain the pronounced difference in the values of σ_c'' for $K < 10^{-4}$ and $K > 10^{-4}$. Let us estimate an expected value of the photoconductivity corresponding to the D^- band, σ_g', in a material with $K > 10^{-4}$ with the understanding[9] $\sigma_g K \approx$ const and under the assumption that the average degree of compensation in the samples with $K < 10^{-4}$ is $\approx 3 \cdot 10^{-5}$, while that in samples with $K > 10^{-4}$ is $\approx 1 \cdot 10^{-3}$. We thus have $\sigma_g' \approx 0.03\sigma_g$. The plot of $\sigma_g'(N)$ shown by the dashed curve in Fig. 5 reveals that σ_g' in the most lightly doped samples is smaller than $\Delta\sigma_{dop}$ by a factor of only 3, while that at $N \approx 10^{17}\ cm^{-3}$ is smaller by a factor of more than 10. Despite this extremely crude estimate of σ_g', we see that the contribution of σ_g' to the total photoconductivity can be ignored starting at $N > 5 \cdot 10^{16}\ cm^{-3}$, but at $N \approx 3 \cdot 10^{16}\ cm^{-3}$ the values of σ_g' and $\Delta\sigma_{dop}$ are comparable.

We thus assume that during impurity excitation, and when the predominant contribution of hopping motion of a vacancy in the ε_3 band to the photoconductivity dominates, indirect trapping of free electrons continues to occur in a material with $K < 10^{-2}$, and the electrons subsequently move through the D^- band to an attractive center.

3. On the basis of the experimental results and these estimates we can propose the following model for the recombination of photoexcited carriers in p-Si with $N^{1/3}a > 0.06$ and $10^{-4} < K < 10^{-2}$. During impurity photoexcitation, an electron is produced in the conduction band, and a vacancy is produced in the ε_3 band, apparently near the maximum of the density of states. The recombination of the electron with "its own" vacancy does not contribute to the photoconductivity, so we will not discuss it here. The entire discussion of Ref. 9 regarding electrons in the conduction band and the D^- band holds here.[9] In contrast with Ref. 9, on the other hand, we are assuming that the recombination occurs primarily not at attractive D^+ centers but at $D^+ - A^-$ complexes near the Fermi level. The electron which is the first to "land on" the complex converts it into a $D^0 - A^-$ complex; then a vacancy recombines there. The time taken by the electron from the D^- band to "land on" the $D^+ - A^-$ complex is short, since it converts into excited states of a $D^+ - A^-$ complex, with energies lying in the delocalization band of D^- states (a pseudocrossing[16]). The situation apparently does not change as ε_x increases with increasing N. The hopping photoconductivity itself is related to the motion of a vacancy from states near the maximum of the density of states of the ε_3 band toward the Fermi level.

We have thus observed a new type of photoconductivity in doped and weakly compensated Si. A distinctive feature of this new photoconductivity is the formation of charge carriers of two types (electrons and vacancies) during impurity excitation. The photoconductivities which they cause, in the conduction band (σ_c) and in the ε_3 band ($\Delta\sigma_{dop}$), respectively, exist in Si⟨B⟩ for $T < 15$ K and $N > 3 \cdot 10^{16}\ cm^{-3}$ (if $K > 10^{-4}$). Only at these values of N and K does $\Delta\sigma_{dop}$ begin

to outweigh the σ_g', due to motion of photoelectrons through the D^- band, in the impurity photoconductivity (Fig. 5). The relation between σ_c and $\delta\sigma_{dop}$ depends on the dopant concentration: $\sigma_c \approx \sigma_{dop}$ at $N \approx 6\cdot 10^{16}$ cm^{-3} and $\Delta\sigma_{dop}/\sigma_c \approx 10$ at $N \approx 2\cdot 10^{17}$ cm^{-3}. All the theoretical results of Ref. 9 apply to σ_c. It is not possible at this point, in the absence of a theory, to discuss in detail the process by which a vacancy moves in the ε_3 band. Recent theoretical papers on hopping photoconductivity have dealt with only amorphous semiconductors.[17-19] The different energy dependence of the density of localized impurity states, $g(\varepsilon)$, in crystalline semiconductors and the mobility gaps in amorphous semiconductors rule out an extension of the theoretical results derived for the latter to hopping photoconductivity in crystalline semiconductors.

It is possible that a change in $g(\varepsilon)$ near the Fermi level in a presence of an ε_2 band in a semiconductor is associated with enhancement of the temperature dependence of $\Delta\sigma_{dop}$ [see (1) and Fig. 1].

4. Comparison of the behavior $\Delta\sigma_{dop}(T)$ which has been found with the data in the literature[3,4] reveals complete agreement, with the one exception that the value of n in (1) in n-InSb and boron-doped diamond is slightly smaller and varies from 1.3 to 1.5. On the basis of the results found here and the data in the literature, we have attempted to draw a picture of the mechanisms for the photoconductivity in semiconductors as a function of the dimensionless parameters $N^{1/3}a$ and K, for low levels of impurity or interband photoexcitation. The results are shown in Fig. 7. We see that in the overall range of the parameters $0.03 \leqslant N^{1/3}a \leqslant 0.3$ and $10^{-5} \leqslant K \leqslant 1$ we can distinguish four regions, in which different photoconductivity mechanisms operate. Each of these regions is the result of a generalization of experimental data, since we know of no theoretical work on this question. There has been no study of the condition for the occurrence of hopping conductivity as a function of $N^{1/3}a$ and K, even for the equilibrium case. This condition should apparently determine the condition for the transitions to hopping photoconductivity from other types of photoconductivity involving impurities.

Let us characterize the regions which we have distinguished in Fig. 7. In region I the photoconductivity is of a band nature. For $K > 10^{-2}$, the ordinary cascade-recombination mechanism is observed,[20] while for $K < 10^{-2}$ the predominant recombination process is the indirect capture of photoelectrons to D^- states of isolated donors, with a subsequent hopping motion among these donors toward a D^+–D^- complex and a recombination there.[16] In region II, where there is a D^- band, the photoconductivity is caused by free electrons and D^--band electrons.[9] In region III, the free-electron photoconductivity is accompanied by hopping photoconductivity in the band of donor ground states. This conductivity is determined by the motion of a vacancy from a maximum of the density of states toward the Fermi level. For $K < 10^{-2}$, however, the D^- band apparently continues to dominate in the recombination of free electrons. The contribution of the D^--band photoconductivity to the overall photoconductivity varies with the dopant concentration (Fig. 5), being generally small.

In region IV, only hopping photoconductivity is observed, regardless of the photoexcitation method. The significant fluctuation potential, characteristic of the degree of doping and compensation in region IV, apparently facilitates and accelerates the "landing" of a free electron in the ε_3 band, so that the photoconductivity is determined by hopping of electrons through the ε_3 band if $K \leqslant 1$, or of vacancies if $K \leqslant 10^{-2}$. The nature of the motion of the nonequilibrium electrons, the mechanism for the relaxation of the photoelectrons, and the corresponding relaxation time all await theoretical attention.

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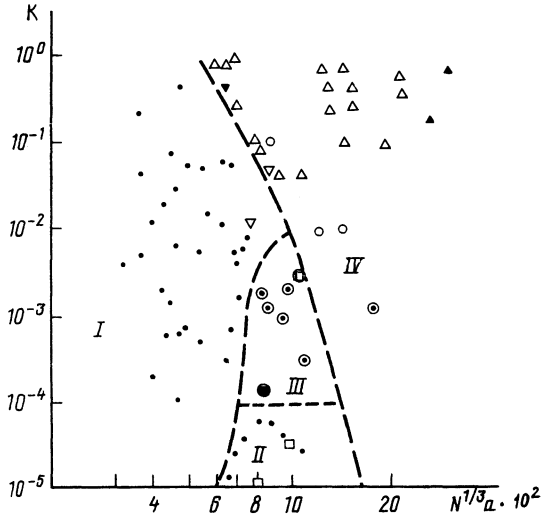

FIG. 7. Photoconductivity mechanisms during impurity photoexcitation as a function of the degree of compensation and the dimensionless parameter $N^{1/3}$ in various semiconductors. ●—Si⟨B⟩ (Ref. 9); □ Si⟨P⟩; ■—Si⟨Ga⟩; ▲—n-InSb (Ref. 3); ▼—p-Ge (Refs. 1 and 2); △—n-Si (Refs. 1 and 2); ○—n-Ge (Refs. 1 and 2); △—diamond.[4] The circled symbols represent samples 11–19 in Table I.

[1)]The upper Hubbard band (the D^- band) is usually called the "ε_3 band" at values of N and K such that on the temperature dependence of the resistivity one sees, between the regions with energies ε_1 and ε_3, yet another region of an exponential dependence $\sigma(T^{-1})$ (Ref. 12).

[2)]The choice of b is discussed in Ref. 9.

[3)]In sample 17, we measured $\Delta\sigma_{dop}$ at $W_{ph} = (2\text{–}6)\cdot 10^{-4}$ s^{-1} and then converted the results to $W_{ph} = 0.25$ s^{-1}, using $\Delta\sigma_{dop} \propto W_{ph}$ (Fig. 4).

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