Radio-frequency hopping photoconductivity involving excited states of dopant boron in silicon

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The extrinsic photoconductivity of silicon doped with boron to a concentration $N_B = 10^{15}–10^{17}\,\mathrm{cm}^{-3}$ and with phosphorus to a concentration $N_P = 2\cdot 10^{12}–2\cdot 10^{14}\,\mathrm{cm}^{-3}$ with a microwave (8 mm) bias voltage has been studied. This photoconductivity was studied as a function of the modulation frequency and intensity of the exciting light (at 10.6 μm), the temperature (over the range 5–50 K), and the concentrations of the major and compensating dopants. The quasisteady photoconductivity is found to be proportional to N_P and to the excitation intensity I, provided that the latter is below a threshold I_{thr} which depends on N_B and N_P. At higher values of I the change in the photoconductivity is slower than linear. The time constant of the photoconductivity for $N_B > 2\cdot 10^{16}\,\mathrm{cm}^{-3}$, $T \leqslant 15$ K, and $I < I_{\mathrm{thr}}$ is $\tau^* = 4\cdot 10^{-4}$ s. For $I > I_{\mathrm{thr}}$ the relaxation is not exponential. The N_B dependence of the photoconductivity is extremely sharp. As a function of the average distance between boron atoms, $r_{\mathrm{av}} = (\frac{4}{3}\pi N_B)^{-1/3}$, the photoconductivity is proportional to $\exp(-r_{\mathrm{av}}/r_0)$ in the interval $r_{\mathrm{av}} = (2–3)\cdot 10^{-6}$ cm, where $r_0 = 2\cdot 10^{-7}$ cm. The quantity r_0 is close to the first Bohr radius of the major dopant. The behavior found is explained in terms of a relaxation hopping conductivity involving metastable excited states of the dopant boron. The lifetime of these states determines τ^*. The process by which the ionized and excited boron atoms localize at a minimum distance from one another includes the hopping transport of charge or excitation by the set of atoms of the major dopant. A possible physical reason for the metastable state of the dopant boron in the silicon is discussed.

1. INTRODUCTION

Preliminary results on the extrinsic photoconductivity of silicon doped with group-III and -V elements in concentrations of $10^{16}–10^{17}\,\mathrm{cm}^{-3}$ with microwave and static bias voltages were reported in Refs. 1 and 2. It was found that with a static bias voltage the temperature dependence of the quasisteady photoconductivity and its relaxation time agree with the theory of cascade trapping of free carriers by ionized atoms of group-III and -V dopants in the silicon.[3] In the case of the microwave bias voltage, however, a slow ($\sim 10^{-5}$ s) relaxation of the photoconductivity was observed at low temperatures ($\lesssim 10$ K), for dopants of boron, indium, and arsenic. As the temperature was lowered, this slow relaxation increased the quasisteady photoconductivity to a level nearly three orders of magntidue higher than that at a static voltage. The slow relaxation of the microwave photoconductivity was attributed to the long lifetime of deep excited states of these dopants. The absence of a slow relaxation in the cases of Ga and Bi under similar conditiosn seemed natural, since the energies of the optical phonons are in resonance with the $2P_0$ state of the Bi and with the second excited state of the Ga in silicon, and the emission of a single phonon results in a rapid relaxation of an excitation of these dopants.[4] The spectra of excited states of the B, In, and As dopants do not have any energy levels which are in resonance with optical phonons, and relaxation of an excitation is possible only through radiative or multiphonon transitions. The reason is that the energies of their deep excited states are many times the average thermal energy kT at low temperatures. We might add that the lowest-lying states in the spectra of excited states of group-V donors in silicon are the $1S(\Gamma_5,\Gamma_3)$ states, and optical transitions between these states and the $1S(\Gamma_1)$ ground state are forbidden.[4] The metastable states of the group-III acceptors are $1S(P_{1/2})$ states formed from states of a valence band which are split off by a spin–orbit interaction.[4] An excitation may remain localized at these states for a fairly long time. This conclusion is supported by the slow (10^{-3}-s) relaxation of the extrinsic absorption which has been observed for dopant In in silicon.[5]

It was also shown in Ref. 2 that the photoconductivity results from an increase in the active component of the conductivity and cannot be linked with the photodielectric effect. Hopping photoconductivity involving long-lived excited states of the group-III and -V dopants in silicon looks like the most probable mechanism for the appearance of a high photoconductivity in the case of a microwave bias voltage. The hopping photoconductivity in an rf electric field may be many orders of magnitude greater than the dc photoconductivity, like the hopping photoconductivity involving ground states of dopants in silicon.[6]

In the present study we use the example of a boron dopant in silicon to determine the basic behavior of the microwave extrinsic photoconductivity. We find that this behavior agrees with the polarization model of hopping conductivity.

2. EXPERIMENTAL PROCEDURE

We studied silicon samples doped with boron to a concentration $N_B = 10^{15}–10^{17}\,\mathrm{cm}^{-3}$, with a low concentration of background impurities. The compensating phosphorus

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dopant, in a concentration $N_P = 2\cdot10^{14}$–$2\cdot10^{12}$ cm^{-3}, was introduced by bombarding the samples with thermal neutrons and then annealing them. The phosphorous concentration was monitored on the basis of the resistivity of "witnesses," i.e., samples of high-resistivity silicon which underwent an identical bombardment and an identical heat treatment.

Boron in silicon is an excellent dopant for our purposes. A random distribtion of the boron is achieved by virtue of the high distribution coefficient of boron (0.9). The fact that silicon absorbs neutrons only slightly also promotes the random distribution of the phosphorus. Boron is furthermore the shallowest acceptor in silicon, so the concentration of compensated boron atoms corresponds to the phosphorus concentration N_P.

We studied the photoconductivity of samples with dimensions of $10\times3.5\times1$ mm^3. The samples were placed at the closed end of an 8-mm waveguide, into which the radiation from a Gunn diode (at 37 GHz) and the exciting light (at 10.6 μm), modulated at a frequency between 30 Hz–10 MHz, were injected. The change in the conductivity of the sample during photoexcitation resulted in modulation of the microwave power. This modulated component of the microwave signal, U, was studied as a function of the temperature T (over the range 5–50 K), the excitation modulation frequency f, and the excitation intensity I. Relaxation times down to 10^{-8} s were determined from the plot of U versus f, and relaxation times of up to 10^9 s were determined from the phase delay of the photoconductivity signal (Ref. 7). A disadvantage of the microwave apparatus, which stems from its broad-band nature, is that the sensitivity is relatively low. This low sensitivity is a limitation in measurements at the lowest photoexcitation levels. Samples in which current contacts has been implanted were studied simultaneously at the microwave and static bias voltages.

3. EXPERIMENTAL RESULTS

Figure 1 shows the microwave photoconductivity signal U as a function of the frequency f at which the exciting light is modulated for several silicon samples doped with phosphorus to a concentration $N_P = 10^{14}$ cm^{-3}, for various boron concentrations N_B. Figure 2 shows the results for various temperatures T, and Fig. 3 shows results for various photoexcitation intensities I. We see from these figures that a frequency dependence arises at $N_B \geqslant 5\cdot10^{15}$ cm^{-3}. At $N_B \geqslant 1.2\times10^{16}$ cm^{-3} and 5 K, this dependence is bascially the same for all the samples and corresponds to a relaxation time $\tau^* \approx 4\cdot10^{-4}$ s of the photoconductivity. As the temperature is raised to 15 K, the nature of the frequency dependence does not change, but the amplitude of the photoconductivity decreases. At 30 K, the frequency dependence disappears. At sufficiently low photoexcitation levels, the frequency dependence is independent of the intensity I, while the photoconductivity increases in proportion to I (Fig. 4). When a threshold intensity, which depends on the boron concentration N_B, is reached, however, the relaxation of U becomes nonexponential (Fig. 3), and the amplitude of this photoconductivity signal increases more slowly than linearly (Fig. 4). With these points in mind, we continued the study of the quasisteady photoconductivity at a fairly low intensity I and at a fairly low modulation freqency f.

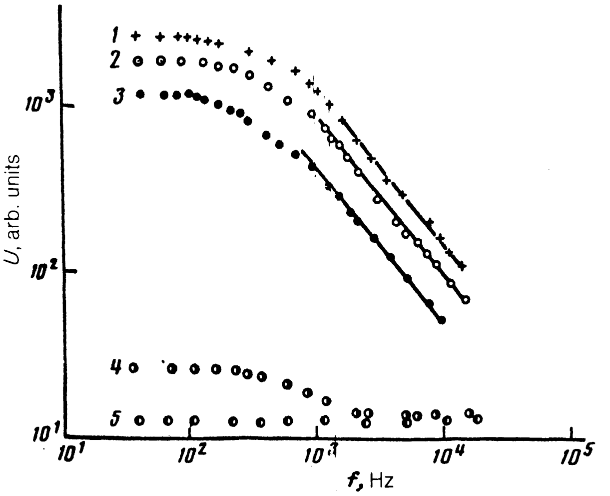

FIG. 1. The microwave photoconductivity signal U versus the modulation frequency f of the exciting light at 5 K for silicon samples with a phosphorus concentration $N_P = 10^{14}$ cm^{-3} and several boron concentrations N_B (in units of 10^{16} cm^{-3}): 1—2.7; 2—2.1; 3—1.8; 4—0.5; 5—0.3.

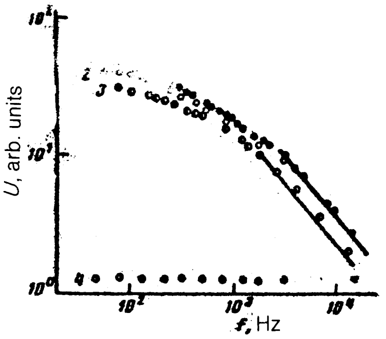

FIG. 2. The microwave photoconductivity signal U versus the modulation frequency f for a sample with $N_B = 3.5\cdot10^{16}$ cm^{-3} and $N_P = 10^{14}$ cm^{-3} at several temperatures T: 1—5 K; 2—11 K; 3—15 K; 4—30 K.

Figure 5 shows the temperature dependence of the quasisteady photoconductivity U(LF) for several samples with $N_P = 10^{14}$ cm^{-3}. The curves of the microwave photoconductivity at a high excitation modulation frequency, U(HF), are essentially identical for all the samples of this lot, and they are the same as the curves of U(LF) for the

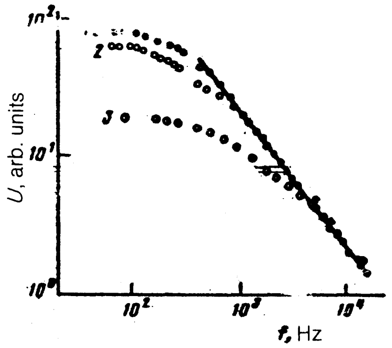

FIG. 3. The microwave photoconductivity signal U versus the modulation frequency f at 5 K for a sample with $N_B = 1.8\cdot10^{16}$ cm^{-3} and $N_P = 10^{14}$ cm^{-3} at various excitation intensities I: $I_1 < I_2 < I_3$.

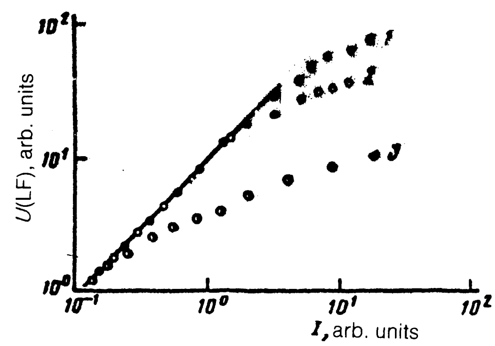

FIG. 4. The quasisteady microwave photoconductivity signal U(LF) versus the excitation intensity I at 5 K for samples with $N_P = 10^{14}\,\mathrm{cm}^{-3}$ and several concentrations N_B ($10^{16}\,\mathrm{cm}^{-3}$): *1*—1.5; *2*—1.8; *3*—3.5.

lightly doped samples (1 and 2 in Fig. 5). They are also similar to the photoconductivity curves for a static bias voltage. It can be seen from Fig. 5 that the difference between U(LF) and U(HF) appears at a boron concentration $N_B \approx 4\cdot 10^{15}\,\mathrm{cm}^{-3}$. It increases rapidly with increasing N_B, to a value nearly three orders higher at $N_B = 2.7\cdot 10^{16}\,\mathrm{cm}^{-3}$ and 5 K.

Figure 6 shows the temperature dependence of the microwave photoconductivity signal for several silicon samples doped with boron to a concentration $N_B = 3.5\cdot 10^{16}\,\mathrm{cm}^{-3}$ and with phosphorus to various concentrations. These results are shown for low and high modulation frequencies of the exciting light [U(LF) and U(HF), respectively]. The difference between the low- and high-frequency photoconductivities increases sharply with increasing concentration of the compensating dopant.

Note that the temperature dependence of the photoconductivity signal at low and high modulation frequencies f is the same in the interval 30–40 K, and it agrees with the dependence at a static bias voltage. The photoconductivity relaxation times measured for the microwave and static bias voltages are the same, to within the experimental errors. Figure 7 shows the lifetime τ_p versus the boron concentration N_P at 30 K. We see that τ_p is inversely proportional to the

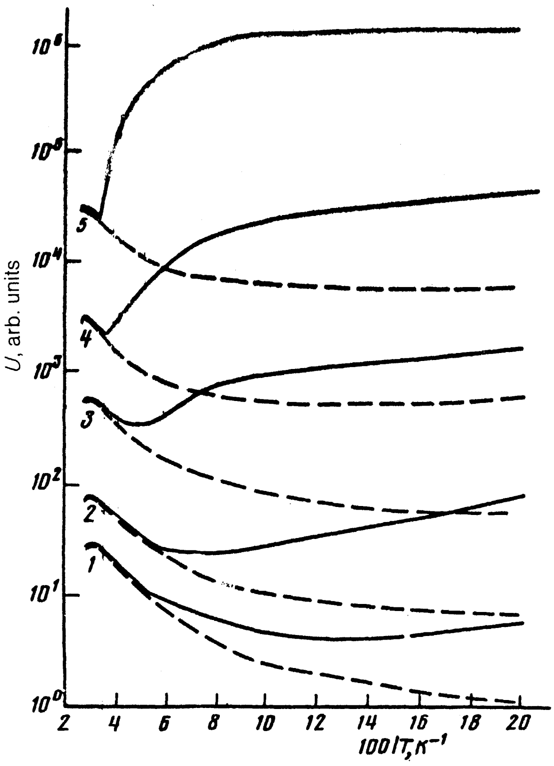

FIG. 6. Temperature dependence of the microwave photoconductivity signal at a low modulation frequency, U(LF) (solid lines), and at a high modulation frequency U(HF), for samples with $N_B = 3.5\cdot 10^{16}\,\mathrm{cm}^{-3}$ and several values of N_P: *1*—$5\cdot 10^{12}$; *2*—$1\cdot 10^{13}$; *3*—$2\cdot 10^{13}$; *4*—$4\cdot 10^{13}$; *5*—$10^{14}\,\mathrm{cm}^{-3}$.

concentration of the compensating dopant. This result is natural for recombination of free photocarriers at comparatively high temperatures.[3] It follows that the ordinary extrinsic photoconductivity due to free holes dominates at high temperatures. It can thus be concluded that in this region the photoconductivity is quasisteady at both low and high modulation frequencies ($f = 10^5$–10^6 Hz). It is on this basis that the high-temperature parts of the curves in Fig. 6 have been brought into coincidence for each of the samples, although

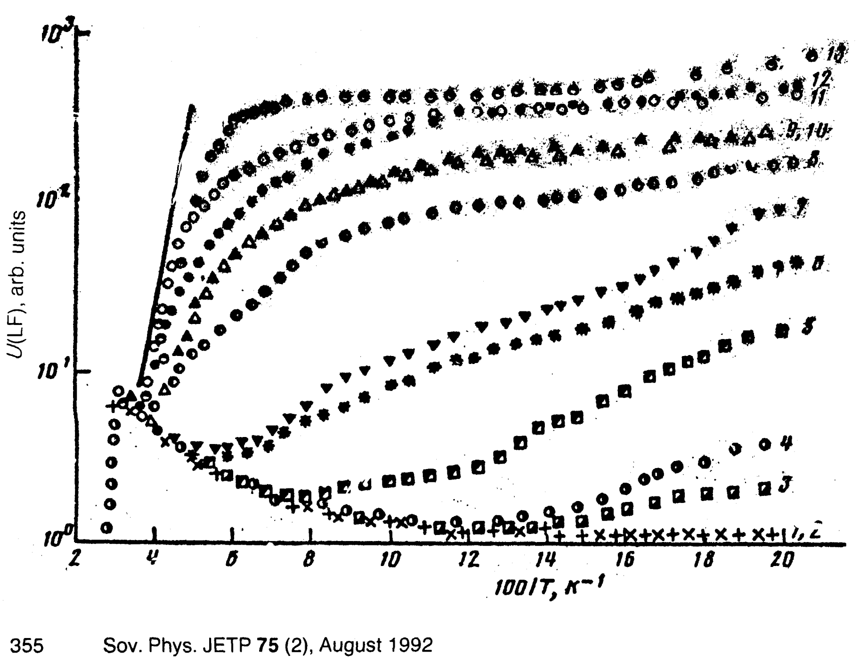

FIG. 5. Temperature dependence of the quasisteady microwave photoconductivity signal U(LF) for samples with $N_P = 10^{14}\,\mathrm{cm}^{-3}$ and several values of N_B ($10^{16}\,\mathrm{cm}^{-3}$): *1*—0.31; *2*—0.4; *3*—0.52; *4*—0.88; *5*—1.15; *6*—1.25; *7*—1.5; *8*—1.8; *9*—2.1; *10*—2.3; *11*—3.5; *12*—2.8; *13*—4. The curves of the microwave photoconductivity signal for $f = 10^5$–10^6 Hz, for all samples, coincide with those for samples *1* and *2*. The straight line corresponds to an activation energy of 23 meV.

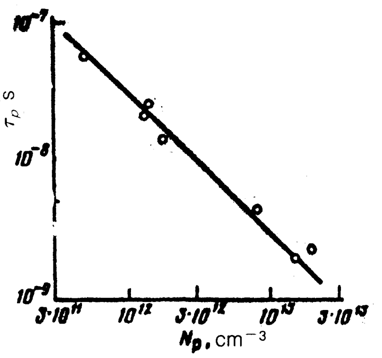

FIG. 7. The hole lifetime τ_p at 30 K versus the phosphorus concentration N_P [$N_B = (3\text{–}4)\cdot10^{16}$ cm^{-3}].

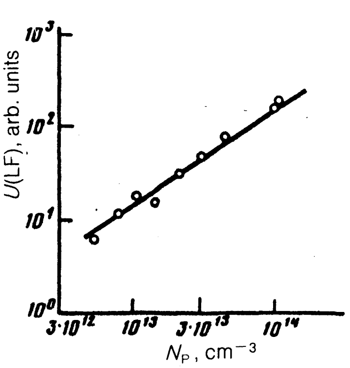

FIG. 9. The quasisteady photoconductivity signal U(LF) of samples with $N_B = 3.5\cdot10^{16}$ cm^{-3} versus the phosphorus concentration N_P at 5 K.

in the experiments the absolute values of the photoconductivity depended on the tuning of the waveguide section, the modulation depth of the exciting light, and other factors. This superposition of the curves made it possible to plot the ratio of the quasisteady response, U(LF), at 5 K to the response U(HF) at 30 K as a function of the boron concentration N_P (Fig. 8). We see that the ratio U(LF)/U(HF) increases as the square of the concentration N_P. At a given intensity of the excitation and a given tuning of the waveguide section, the photoconductivity increases in inverse proportion to N_P at 30 K. We accordingly replotted the experimental results in Fig. 6 for U(LF), shifting them along the ordinate in such a way that the photoconductivity at high temperatures corresponded to this behavior. At any temperature, U(LF) is then proportional to the microwave photoconductivity signal. This manipulation of the results allows us to determine how the steady-state microwave photoconductivity signal of the samples depends on the phosphorus concentration N_P even at low temperatures. This dependence is shown for 5 K in Fig. 9. We see that the photoconductivity increases in proportion to N_P.

4. DISCUSSION OF RESULTS

Let us examine these experimental results in light of the model of the polarization hopping conductivity in an alternating electric field.[6] This model is based on the following simple physical idea: In thermodynamic equilibrium, the state with the lowest energy is reached when the ionized atoms of the major dopant are nearest the ions of the compensating dopant. In an electric field, the potential changes near an ion, and a new equilibrium state is established as a result. This new state corresponds to different distances between the ions of the major and compensating dopants. In other words, the dipole moments of the ion pairs change. The time scale of this restructuring is equal in order of magnitude to the hopping time τ, and the resultant change in the polarization of the semiconductor in the alternating electric field is manifested as the flow of an alternating current. The ac conductivity may be many orders of magnitude greater than the dc conductivity. The conductivity of a semiconductor at a frequency ω, i.e., $\sigma(\omega)$, with a concentration N_B of the major (acceptor) dopant and with a compensating dopant concentration N_P, for a random distribution of the dopants, and for temperatures which are not too low, can be written[6]

$$\sigma(\omega) \approx \frac{e^2}{12kT} N_B N_P \int \tau^{-1} r^2 \left(\frac{w^2\tau^2 + iw\tau}{1+\omega^2\tau^2} \right) \cdot 4\pi r^2 \, dr, \tag{1}$$

$$\tau[\mathrm{s}] \approx 5\cdot10^{-13} (r/a)^{-3/2} \exp(2r/a) . \tag{2}$$

The integration here is over all distances r between the atoms of the major dopant, and a is the first Bohr radius of the ground state of the dopant.

It was shown in Ref. 6 that expression (1) agrees well with experimental results on the equilibrium conductivity of silicon doped with group-V donors at relatively low frequencies (10^2–10^5 Hz). In other words, this expression predicts that the real part of the conductivity depends linearly on the concentrations of the major and compensating dopants, slower than linearly on the frquency ($\omega^{0.8}$), and the absolute values of the conductivity are close to the experimental values.

In the case of hopping photoconductivity involving excited states, we would replace the concentration of the major dopant, N_B, in expressions (1) and (2) by the concentration of excited atoms, $N_B^* = g\tau^*$, where g is the excitation rate, and we would replace the Bohr radius of the ground state, a, by the Bohr radius of the excited state, a^*. In addition, the study was carried out at a very high frequency, $\omega = 2.3\cdot10^{11}$ s^{-1}, at which the condition $\omega\tau > 1$ held essentially up to $r \sim a^*$. The hopping between ionized and excited boron atoms separated by a small distance r therefore dominated the photoconductivity. The real part of the photoconductiv-

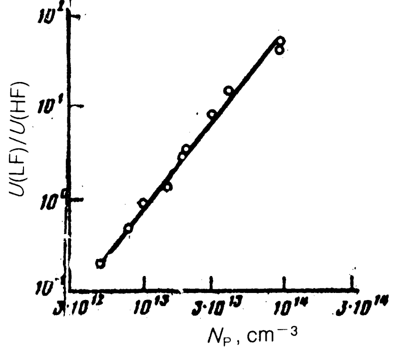

FIG. 8. Ratio of the quasisteady photoconductivity signal U(LF) at 5 K to the high-frequency photoconductivity signal U(HF) at 30 K as a function of the concentration N_P for samples with $N_B = 3.5\cdot10^{16}$ cm^{-3}.

ity was much greater than the imaginary part, and the frequency dependence of the real part was negligible. It should also be noted that the excited states have a finite lifetime τ^*. This time determines the relaxation kinetics of the photoconductivity, and it may also be important in the case of quasisteady excitation. Specifically, if transport of charge or excitation plays an important role in the photoconductivity, then τ^* may be too short for a quasiequilibrium distribution of ionized and excited atoms of the major dopant to be reached. We would expect that the rate at which equilibrium is reached would be extremely sensitive to the concentration of the major dopant. We take this point into account by incorporating a probability factor $W(N_B)$ in the expression for the photoconductivity. With these comments in mind, we write the photoconductivity as

$$U\,(\mathrm{LF}) \approx \frac{e^2}{12kT} N_P N_B^* \tau^* W\,(N_B) \int \tau^{-1} \cdot 4\pi r^4\, dr \qquad (3)$$

and we compare this expression with the experimental data.

It can be seen from Fig. 9 that the photoconductivity increases in proportion to the concentration of the compensating dopant over a broad range of N_P values, in accordance with (3). The photoconductivity is observed to depend linearly on the excitation intensity I, on the other hand, only up to a certain threshold, beyond which the photoconductivity increases more slowly than linearly (Fig. 4). To estimate absolute values of the excited-dopant concentration N^*, we determined the excitation rate g from the magnitude of the photoconductivity at a static bias voltage of a lightly compensated sample, with a boron concentration $N_B = 3.5 \times 10^{16}\ \mathrm{cm}^{-3}$ and a long lifetime, $\tau_P = 1.5 \cdot 10^{-8}$ s, at 30 K. The mobility of the photoholes in this material was determined from the scattering by neutral impurity centers and was taken to be $10^4\ \mathrm{cm}^2/(\mathrm{V \cdot s})$ (Ref. 8). The photoconductivity $U(\mathrm{LF})$ at a microwave bias voltage, for a sample with the same concentration N_B but with a compensating-dopant concentration $N_P = 10^{14}\ \mathrm{cm}^{-3}$, is shown in Fig. 10 as a function of the excitation rate g at two temperatures. The upper scale in this figure has values of $N_B^* = g\tau^*$, where $\tau^* = 4 \cdot 10^{-4}$ s. We see that the transition from a linear dependence to a sublinear dependence occurs at $N_B^* \approx N_P = 10^{14}\ \mathrm{cm}^{-3}$.

This agreement between the concentration of the ionized atoms of the major dopant and the threshold concentration of excited atoms indicates that the relaxation time τ^* is long enough that the ions and excited atoms manage to localize at a minimum distance from each other. As a result, there is a maximum hopping probability, and there is a maximum contribution to the photoconductivity. An increase in the concentration N_B^* above N_P does not make any important contribution to the photoconductivity, since all the neutral atoms closest to the boron ions are already in the excited state, and the subsequent change in the photoconductivity is slower than linear. Since the overwhelming majority of ions of the major dopant are localized at a minimum distance from the ions of the compensating dopant are low temperatures, the trapping of holes occurs primarily at these dipoles,[3] and it is unlikely that an ion of the major dopant will be near an excited atom immediately after it captures a hole. The formation of closely spaced pairs of an ion and an excited atom requires either diffusion of the ion to this closer position or diffusion of the excitation to the ion. This process is possible only if charges or excitations are transported by the set of neutral atoms of the major dopant. The transport probability should be very sensitive to the concentration of the major dopant.

To determine the role of the transport and the mechanism for it, we examine the results in Fig. 5, plotted as $U(\mathrm{LF})/U(\mathrm{HF})$ versus the average distance between the atoms of the major dopant, $r_{av} = (4/3N_B)^{-1/3}$ (Fig. 11). It can be seen from this figure that for $3 \cdot 10^{-6} > r_{av} > 2 \cdot 10^{-6}$ cm the ratio increases by more than two orders of magnitude, and it can be described by

$$U(\mathrm{LF})/U(\mathrm{HF}) \propto \exp(-r_{av}/r_0),$$

where $r_0 = 2 \cdot 10^{-7}$ cm. The fact that r_0 is close to the first Bohr radius of the major dopant indicates that the transport is possible because the wave functions overlap. It also indicates that the probability $W(N_B)$ that ionized and excited dopant atoms will move close to each other is determined by the probability for hopping transport over a distance close to the average distance. At relatively low concentrations N_B, for which the condition $\tau^* W(N_B) < 1$ holds, the photoconductivity should then increase exponentially with decreasing r_{av}. With increasing concentration, the transport probability becomes sufficient for the particles to move close to each

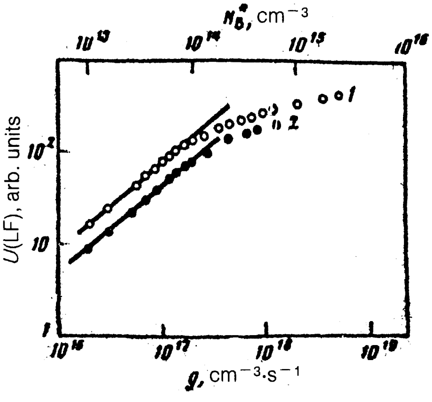

FIG. 10. The quasisteady photoconductivity signal $U(\mathrm{LF})$ versus the excitation rate g and the concentration of excited boron atoms, N_B^*, for a sample with $N_P = 10^{14}\ \mathrm{cm}^{-3}$ and $N_B = 3.5 \cdot 10^{16}\ \mathrm{cm}^{-3}$ T: *1*—5 K and *2*—12 K.

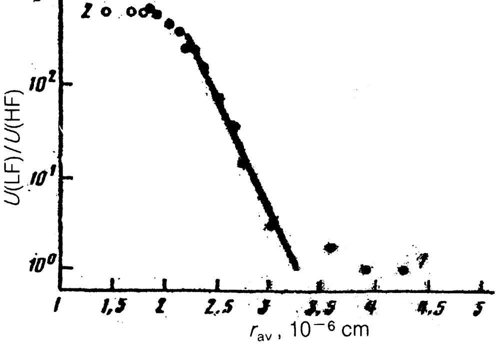

FIG. 11. Ratio of the photoconductivity signal at a low modulation frequency, $U(\mathrm{LF})$, to that at a high frequency, $U(\mathrm{HF})$, at 5 K for samples with $N_P = 10^{14}\ \mathrm{cm}^{-3}$ as a function of the average distance between boron atoms, $r_{av} = (4/3 \cdot \mathrm{cm}\, N_B)^{-1/3}$. *1* ●—$f = 70$ Hz; *2* ○—$f = 800$ Hz. The straight line is a plot of $\exp(-r_{av}/r_0)$, where $r_0 = 2 \cdot 10^{-7}$ cm.

other over a time τ^*. When N_B, increases further the dependence on the concentration should weaken, and at high concentrations the entire hopping-photoconductivity process can be regarded as a quasiequilibrium process.

Under quasiequilibrium conditions we can estimate the ionization potential of the excited state of the dopant boron from the temperature dependence of the photoconductivity (Fig. 5). It can be seen from this figure that the photoconductivity varies only slightly in the interval 5–15 K at a high concentration N_B. As the temperature is raised further, the photoconductivity falls off exponentially, with an activation energy close to 20 meV. This value of the ionization potential also agrees with the following simple estimate. The exponential decrease of the photoconductivity due to the thermal empyting of the boron ground state, with an ionization potential of 46 meV, begins at 30 K. The emptying of the excited state begins at a temperature lower by a factor of about 2 (Fig. 5); correspondingly, the ionization energy is lower by a factor of 2. The existence of an excited state with an ionization potential of 23 meV in the spectrum of the dopant boron in silicon seems quite likely.[4] According to the calculations of Ref. 9, this state $1S(P_{1/2})$, is formed from the wave functions of a branch of the valence band which is split off by the spin-orbit interaction and which is the lowest in the $P_{1/2}$ series. Optical transitions between this state and the $1S(P_{3/2})$ ground state is forbidden, and they should not be seen in the *ir* absorption spectrum of a boron dopant in silicon. In the Raman spectrum, in contrast, this state should be seen quite reliably.[4] We would expect this metastable state to be responsible for hopping conductivity. We then find a natural explanation for the long lifetime of the excited state, $\tau^* = 4\cdot 10^{-4}$ s, which is considerably longer than the radiative lifetime of excited states of the $P_{3/2}$ series which exhibited in the absorption spectra.

In summary, it has been shown here, for the particular case of boron in silicon, that the behavior of the extrinsic photoconductivity in an rf electric field as a function of the temperature, the concentrations of the major and compensating dopants, and the modulation frequency and intensity of the photoexcitation can be explained, at least qualitatively, by the polarization model of hopping photoconductivity involving excited states of the major dopant.

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