Relaxation of extrinsic excitation in silicon with group III and V dopants

Ya. E. Pokrovskiĭ and O. I. Smirnova
Institute of Radio Engineering and Electronics, Academy of Sciences of the USSR

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The kinetics of the extrinsic photoresponse of silicon doped with Ga, Bi, B, In, and As has been studied with static and microwave (37-GHz) bias voltages. In the case of a microwave bias, there is a slow relaxation (10^{-5} s) of the B, As, and In dopants as a result of the long lifetime of their deep excited states.

The cascade capture of charge carriers at an attractive center in a semiconductor[1] may be thought of as an energy diffusion along a quasicontinuum of excited levels of the center until the carrier reaches levels with an ionization energy substantially greater than the thermal energy kT (see the review by Abakumov *et al.*[2]). The magnitudes and temperature dependence of the cross sections for the capture of electrons and holes by group V donors and group III acceptors in silicon have been calculated on the basis of cascade theory, and the results agree with experimental data.[2] The relaxation of an excitation terminates, however, only after the carrier localizes in the ground state of the dopant as a result of transitions between deep and ground states accompanied by the release of an energy many times kT. Such transitions are generally possible as a result of multiphonon or radiative processes, whose probabilities are low. A lower limit on the lifetime of deep excited states can be estimated from the extrinsic absorption linewidths.[3] This lower limit turns out to be on the order of 10^{-10} s. We have observed that the excitation relaxation time for several dopants is many orders of magnitude greater.

We studied the photoresponse of silicon samples with dimensions of $10 \times 3.5 \times 1$ mm, doped at concentrations of 10^{16}–10^{17} cm^{-3}, with a microwave bias voltage (37 GHz) and a static bias voltage ($\leqslant 10$ V). The concentration of the compensating dopants in the original samples was 10^{12}–10^{13} cm^{-3}. In order to achieve a greater degree of compensation, we additionally doped several of the samples already doped with B and Ga with phosphorus, through neutron bombardment followed by annealing. Contacts on the samples for measurements at the static bias voltage were fabricated by ion implantation. The samples were excited by laser light (at 10.6 or 3.39 μm) modulated at a frequency of 10^2–10^7 Hz. The photoresponse was studied as a function of the temperature (5–50 K) and the modulation frequency f. From the f dependence of the photoresponse we can determine the relaxation times down to 10^{-8} s, and from the phase delay we can determine them down to 10^{-9} s. The experimental procedure is described in Ref. 4.

Figures 1 and 2 show the temperature dependence of the photoresponse of several silicon samples doped with Ga, Bi, B, In, and As. It can be seen from Fig. 1 that the temperature dependence of the photoresponse for the Ga and Bi dopants is the same for microwave bias and a static bias and is independent of f. These curves are typical of

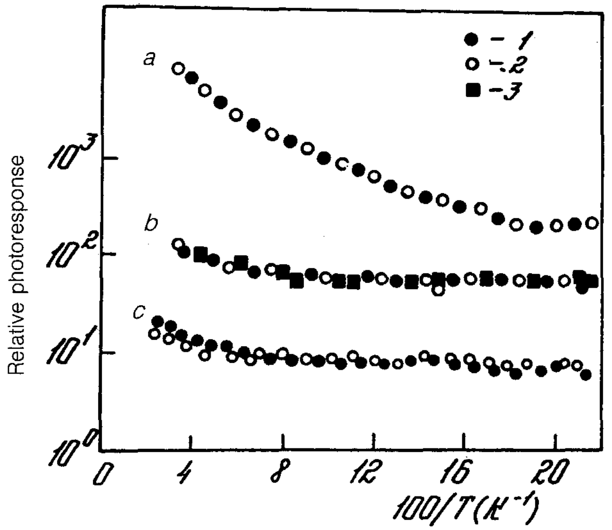

FIG. 1. Temperature dependence of the photoresponse of silicon with various dopants. *a*—Ga (3×10^{16} cm^{-3}, $N_d = 3\times10^{12}$ cm^{-3}); *b*—Ga (3×10^{16} cm^{-3}, $N_d = 2\times10^{14}$ cm^{-3}); *c*—Bi (1.2×10^{16} cm^{-3}). Microwave bias voltage: 1) $f = 800$ Hz; 2) $f = 0.5$–1.3 MHz. Static bias voltage: 3) $f = 800$ Hz.

silicon samples of this type.[2] For the silicon doped with B, In, and As, the situation is completely different (Fig. 2). With a static bias, the temperature dependence of the photoresponse does not depend on the modulation frequency up to $f \leqslant (2\pi\tau)^{-1}$, where τ is the lifetime of the photocarriers. The temperature dependence in this case is similar to that in Fig. 1. The same temperature dependence of the response with a microwave bias is observed only at $f > 10^5$ Hz. At lower values of f, the microwave response is the same as the dc response only at high temperatures. As the temperature is lowered, the response increases sharply. The difference between the microwave response at a low temperature and that at high and low frequencies becomes more pronounced as the concentration of the compensating dopant is increased. For example, at a donor concentration $N_d = 2\times10^{14}$ cm^{-3} in B-doped silicon this difference amounts to two orders of magnitude. The relaxation times of the photoresponse in the case of a microwave bias can be found from the frequency dependence of this response in Fig. 3. In the Ga-doped silicon, it is independent of f up to 10^6 Hz and then falls off because of the finite value $\tau = 1.5\times10^{-8}$ s. In the case of the B- and As-doped silicon, the decrease in the response is observed as early as $f > 10^3$ Hz, and the frequency dependence corresponds to a relaxation time on the order of 10^{-5} s. In the weakly compensated B-doped silicon, there is also a high-frequency region in which the response falls off and which corresponds to $\tau = 5\times10^{-8}$ s.

We believe that the slow relaxation of the microwave response is associated with the long lifetime $\tau_0 \approx 10^{-5}$ s of deep excited states of the B, In, and As dopant atoms. This interpretation is supported by the absence of a slow relaxation in the case of Ga and Bi, which is a consequence of the particular structures of their energy spectra. Specifically, we know[3] that the third excited state of Ga in silicon is resonant with an

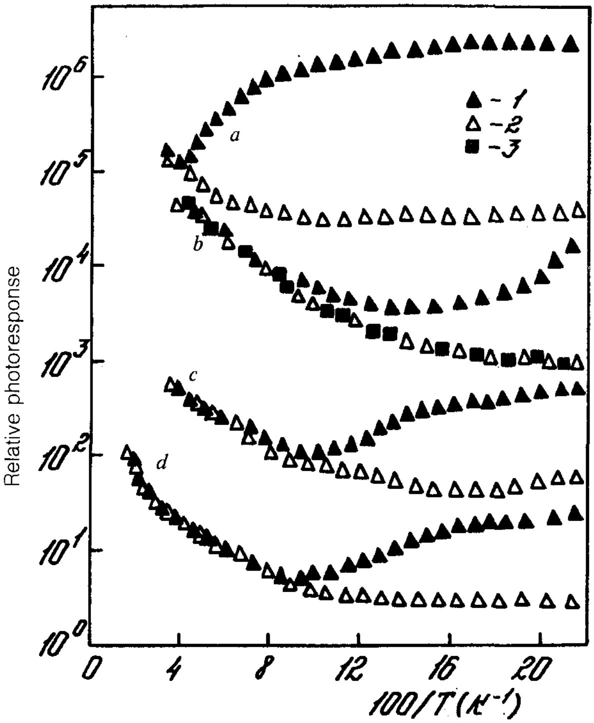

FIG. 2. Temperature dependence of the photoresponse of silicon with various dopants. *a*—B (3×10^{16} cm^{-3}, $N_d = 5\times10^{13}$ cm^{-3}); *b*—B (3×10^{16} cm^{-3}, $N_d = 8\times10^{12}$ cm^{-3}); *c*—As (2×10^{17} cm^{-3}); *d*—In (1.2×10^{17} cm^{-3}). Microwave bias voltage: 1) $f = 800$ Hz; 2) $f = 0.5$–1.3 MHz. Static bias voltage: 3) $f = 800$ Hz.

optical phonon and that its rapid relaxation leads to a catastrophic broadening of the corresponding line in the absorption spectrum. For the Bi dopant, whose $2P_0$ state is also at resonance with an optical phonon in the (110) direction, we find a similar situation. A resonant single-phonon relaxation of this type would not be possible either in the case of B and As (since their ionization potentials are lower than the energies of optical phonons) or in the case of In (the energy of its first excited state is much higher than the energy of optical phonons.

It follows from Figs. 1–3 that at $f > 10^5$ Hz the microwave response is determined by the lifetime of the photocarriers, τ. The concentration of excited dopant states at low temperatures does not depend on τ and must be determined by the lifetime of the excited states, $\tau_0 \approx 10^{-5}$ s, and the excitation rate G: $N^* = G\tau_0$. The increase in the difference between the microwave responses at low and high values of f with decreasing τ (with an increase in compensation) also agrees with the conclusion that the microwave response is determined by N^* at low temperatures. A temperature increase should empty the excited states because of their thermal ionization and an increase in the probability for multiphonon relaxation, in accordance with Fig. 2.

A change in N^* during photoexcitation should cause an increase in the dielectric

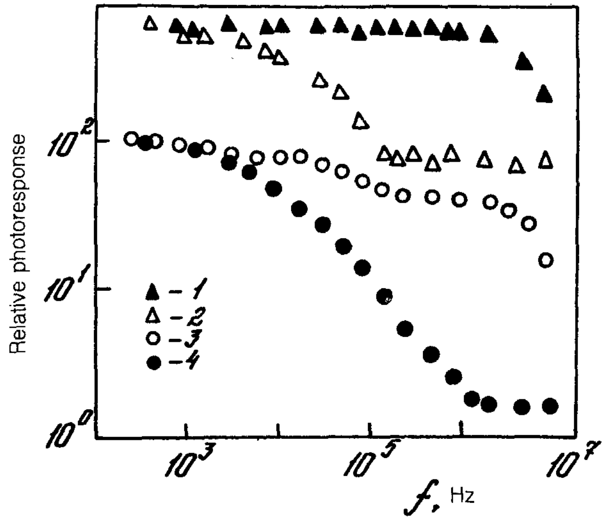

FIG. 3. Frequency dependence of the photoresponse of silicon with various dopants at 5 K, with a microwave bias voltage. 1—Ga (3×10^{16} cm^{-3}, $N_d=3\times10^{12}$ cm^{-3}); 2—As (2×10^{17} cm^{-3}); 3—B (3×10^{16} cm^{-3}, $N_d=8\times10^{12}$ cm^{-3}); 4—B (3×10^{16} cm^{-3}, $N_d=5\times10^{13}$ cm^{-3}).

constant of the sample, by virtue of the increase in the polarizability χ of the dopant atoms in the excited state. Consequently, a modulation of the microwave emission may result form a modulation of the dielectric constant, $\Delta\epsilon = 4\pi\chi N^*$. For a rough estimate we can set $\chi = r^3$, where $r \approx 10^{-6}$ cm is the radius of the excited state. With $G = 10^{18}$ cm$^{-3}\cdot$s^{-1} we find $N^* \approx 10^{13}$ cm^{-3} and $\chi \approx 10^{-4}$. Another possible mechanism for the onset of a microwave response would be a hopping conductivity involving a hopping among excited states of the dopants, as has been observed in diamond.[5] This photoconductivity, with a microwave bias, might be many orders of magnitude higher than the dc conductivity, by analogy with the hopping conductivity involving the ground states of silicon.[6]

We should stress that, regardless of the mechanism by which the excited dopant atoms interact with the microwave radiation, the lifetime of the excited states cannot be shorter than the relaxation time of the microwave response, ~10^{-5} s, which has been determined experimentally.

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