Slow relaxation of excited acceptor states in silicon

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Recombination radiation has been observed to arise in indium- and boron-doped silicon in the region 30–100 μm at low temperatures during extrinsic photoexcitation. A long-term relaxation of this emission has been observed. A slow relaxation of the absorption of light in the region 6–10 μm has also been observed in indium-doped silicon. These optical experiments confirm the existence of long-lived excited states of acceptors in silicon.

A slow relaxation ($\sim 10^{-5}$ s) of the extrinsic photoresponse of silicon doped with several group-III and -V dopants in concentrations above 10^{16} cm^{-3} during application of a microwave field (8 mm) was observed in Refs. 1 and 2. This effect was attributed to the existence of long-lived excited impurity states, which lead to a pre-

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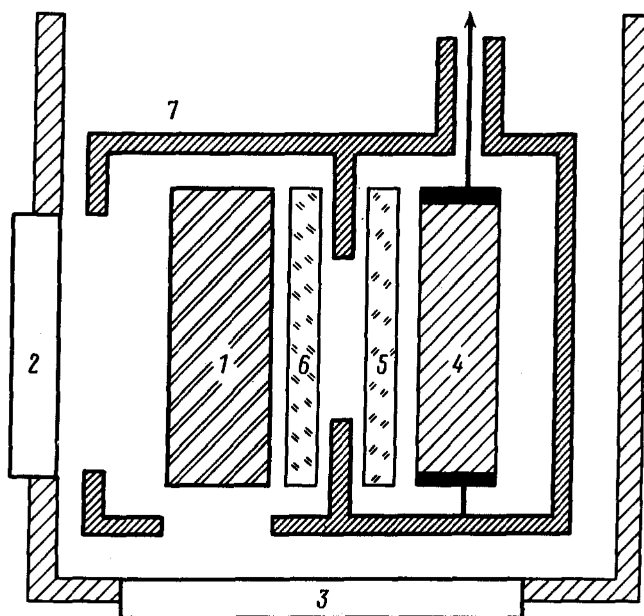

FIG. 1. Experimental layout.

dominance of a hopping photoconductivity in an rf electric field.[2] In this letter we are reporting optical experiments which confirm the existence of long-lived excited states of indium and boron dopants in silicon.

Figure 1 shows the experimental layout. Silicon test sample *1* is excited by a laser beam modulated at a frequency f in the range 40–10^5 Hz. For effective excitation of the indium, we use light with a wavelength of 3.39 μm; light with a wavelength of 10.6 μm is used in the case of boron. The light is coupled into the cryostat through window *2* or *3*, made of crystalline quartz or germanium. The emission which results, or the modulation of the absorption of the room-temperature background radiation transmitted through the sample, is detected by a photoresistor *4*, made of antimony- or mercury-doped germanium.[3] An optical filter *5*, made of a polyethylene film, is placed in front of the photoresistor to protect it from the 3.39-μm exciting light; silicon carbide is used to protect it from the light at 10.6 μm. Optical filters *6*, made of various materials with various transparency regions,[4] are used to distinguish various spectral regions of the light reaching the photoresistor. The test sample, the photoresistor, and these filters are housed in a metal shield *7*, with windows for the exciting light, the recombination emission, and the background radiation. The shield is immersed in liquid helium. We study the alternating component of the response of the photoresistor as a function of the intensity and frequency of the modulation of the exciting light and the spectrum of the detected and background light singled out by filter *6*.

During extrinsic excitation of the silicon samples doped with either indium or boron at an intensity of 5–50 mW, the antimony-doped germanium photoresistor exhibits a response three or four times the noise level. The magnitude of this response is

essentially independent of whether background light strikes the photoresistor after passing through the test sample. It can thus be concluded that the response is determined by the recombination emission, rather than by a modulation of the absorption of the background radiation. The antimony-doped germanium has a high photosensitivity in the region 50–100 μm. The crystalline-quartz filter, which does not transmit in the region 6–35 μm, reduces the magnitude of the response by only 10%. The fused-quartz filter, with an absorption band of 6–80 μm, reduces the response by a factor of 10. The KRS filter reduces the response by a factor of 6. This filter is transparent to 30 μm. It transmits essentially no recombination radiation. It follows that the recombination radiation is in the long-wavelength part of the spectrum; at any rate, its wavelength is greater than 30 μm. In other words, the photon energy is less than 40 meV. This energy is clearly lower than the energy required to excite a hole from the ground state of an indium center to any of the excited states of the "$P_{3/2}$ series," including the lowest-lying of them (at 142 meV; Ref. 5). At least in the case of indium, the long-wavelength emission thus arises as a result of transitions of holes between excited states.

The photoresistor made of the mercury-doped germanium has a high sensitivity in the spectral region to 12 μm. A photoresponse at this detector arises only when room-temperature background radiation passes through the indium-doped silicon sample *1*, through germanium window *2*, and to the detector. In this case, the extrinsic excitation is usually carried out through quartz windows *3*. If crystalline quartz, which does not transmit in the region 6–12 μm, is used as window *2*, a photoresponse is not detected. It follows that the alternating signal detected by the mercury-doped germanium photoresistor arises from a modulation of the intensity of the background radiation transmitted to the detector through the indium-doped silicon sample during extrinsic excitation of the sample. The spectral region in which the photoresponse is observed in this case corresponds to the energies of hole transitions from the ground state of the indium dopant to excited states of the $P_{3/2}$ series.[5] A modulation of the background intensity can arise from a partial emptying of the ground state; this emptying turns out to be substantial because of the localization of nonequilibrium holes during the cascade capture at a long-lived excited state of the indium impurity.[1,2]

This conclusion is supported by the dependence of the magnitude of the photoresponse and the absorption of the indium-doped silicon on the frequency at which the exciting light is modulated (Fig. 2). We see from this figure that both (a) the kinetics of the photoresponse of the samples with the various indium contents during the application of a microwave signal and (b) the kinetics of the decay of the recombination radiation and the relaxation of the modulation of the absorption are determined by long-term processes. The relaxation time $\sim 10^{-5}$ s of the fastest process—the microwave response—is longer by at least three orders of magnitude than the lifetime of the free photoholes in these samples, $\sim 10^{-8}$ s. The longest relaxation time, $\sim 10^{-3}$ s, is seen in the modulation of the absorption of the background radiation. As we have already mentioned, this absorption occurs in the spectral region 100–200 meV. This region corresponds to the excitation of holes from the ground state of the indium dopant. The time scale for the equilibrium filling of this state should be determined by the longest lifetime of the holes in the excited states. On the other hand, the differences in the kinetics of the rf hopping conductivity, the recombination radiation, and the

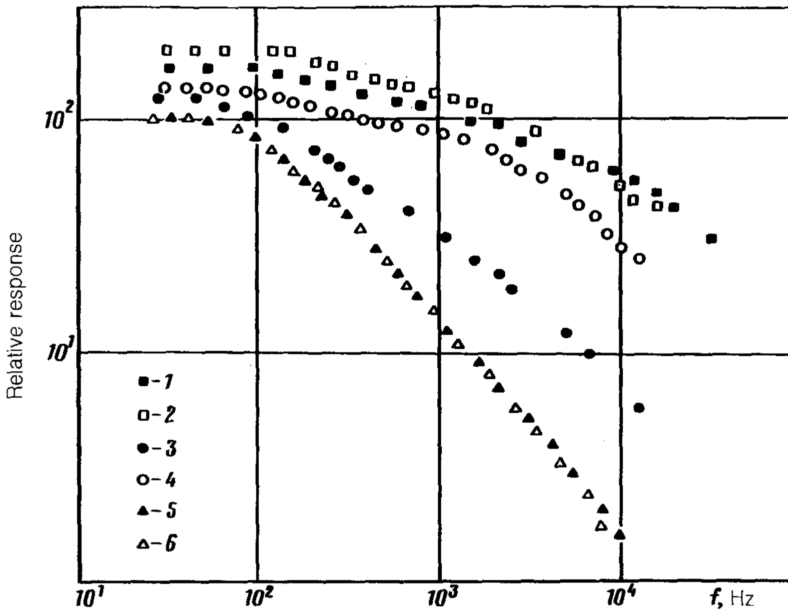

FIG. 2. Various properties as functions of the frequency (f) at which the exciting radiation is modulated. *1,2*—Photoresponse during the application of a microwave field; *3,4*—intensity of the recombination radiation; *5,6*—absorption modulation depth for silicon doped with indium to various concentrations. *1,3,5*) 7×10^{16} cm^{-3}; *2,4,6*) 1.2×10^{16} cm^{-3}.

absorption may occur because different excited states, with different hole lifetimes, play leading roles in these processes.

Figure 3 shows the frequency dependence of the photoresponse of boron-doped silicon during the application of a microwave field, along with the response of the antimony-doped germanium photoresistance, to long-wavelength recombination radiation. We see that these curves essentially coincide for the case of excitation by a laser beam at 10.6 μm. We also see that the relaxation time of approximately 10^{-5} s is independent of the concentration of the compensating donors in the test samples. The long-wavelength recombination radiation with the complex kinetics is also observed in silicon samples doped with boron to concentrations less than 10^{16} cm^{-3}. This recombination radiation disappears only at concentrations of about 10^{14} cm^{-3}, because the absorption of the exciting light is insignificant. It follows that the recombination radiation results from in-center transitions of holes and is unrelated to the collective properties of the dopant in the silicon. The slow relaxation of the photoconductivity during the application of a microwave field, on the other hand, is seen only at boron concentrations above 10^{16} cm^{-3}. This result is one piece of evidence confirming that this conductivity is of a hopping nature.

To determine the energy positions and physical nature of the long-lived excited states of the acceptors in silicon, it is necessary to carry out a spectral analysis of the long-wavelength recombination radiation. Such a study is rather complicated because

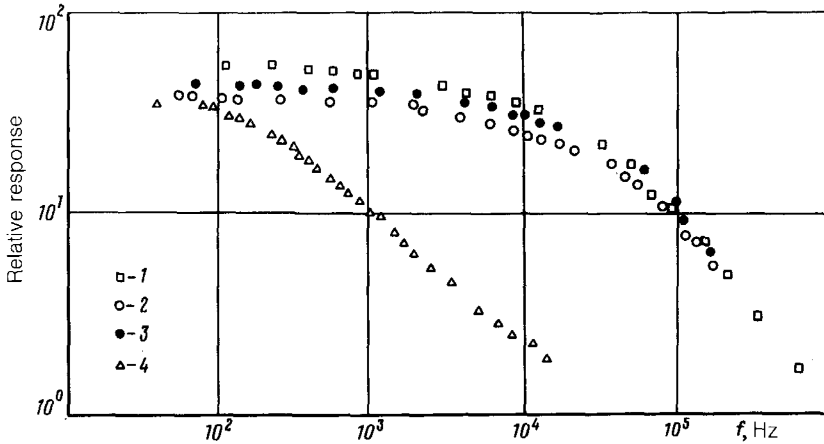

FIG. 3. Various properties versus the frequency (f) of the modulation of the exciting light. *1–3*—The wavelength of the exciting light is 10.6 μm; *4*—3.39 μm. *1*) Photoresponse during the application of a microwave field; *2–4*) intensity of the recombination radiation for silicon doped with boron to a concentration of 3.6×10^{16} cm^{-3}. *1,3,4*—The donor concentration is 5×10^{13} cm^{-3}; *2*—5×10^{12} cm^{-3}.

of the low intensity of this radiation. Here we may see manifestations of states of the $P_{1/2}$ series, associated with the branch of the silicon valence band split off 43 meV by the spin-orbit coupling.[5] Indirect confirmation for this suggestion, in our opinion, comes from the effect of the energy of the exciting photons on the kinetics of the recombination radiation. Specifically, we see from Fig. 3 that during excitation of boron-doped silicon by light at 3.39 μm (366 meV) the relaxation time increases to 10^{-3} s. In other words, it reaches a value two orders of magnitude longer than the relaxation time during excitation by light at 10.6 μm (117 meV). These energies are much higher than the ionization potential of the boron dopant (45.7 meV; Ref. 5), and the holes are excited deep in the valence band in both cases. Their energy relaxation and their subsequent trapping in a process involving optical phonons, however, may lead to a localization of holes in various excited states of the boron dopant, with various lifetimes.

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