Slow relaxation of an excited state of an arsenic donor impurity in germanium

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There are long-lived excited impurity states in germanium, as in diamond and silicon. In the case of an arsenic donor impurity, a long-lived excited state is manifested in a slow (3×10^{-5} s) relaxation of the impurity photoconductivity when a microwave bias voltage is applied. © *1995 American Institute of Physics.*

It has been shown in several studies (e.g., Refs. 1–3) that the relaxation time of excitations of several impurities in diamond (boron) and silicon (group-V donors and group-III acceptors) is many orders of magnitude longer than the lifetime of free charge carriers. During impurity photoexcitation of these semiconductors, carriers accumulate in long-lived excited states of the impurities. At low temperatures and at a sufficiently high impurity concentration, this accumulation leads to, in particular, a predominant hopping photoconductivity involving excited states when a static bias voltage is applied (in the case of diamond[1]) or when a microwave bias voltage is applied (silicon[2,3]). The existence of these long-lived excited states of impurities has been linked with the complex energy-band structure of diamond-like semiconductors. For example, the spin–orbit splitting of the valence band gives rise to a spectrum of excited acceptor states associated with the split valence band Γ_7. If the spin–orbit splitting is small, as it is in diamond (6 meV) and silicon (44 meV) (Ref. 4), then the $1S(\Gamma_7)$ state of this spectrum lies in the band gap and is the lowest excited state of the acceptor. Optical and one-phonon transitions between these excited and ground states of the acceptor are forbidden.[5] Since the spin–orbit splitting is large in germanium (290 meV; Ref. 4), the impurity states associated with the Γ_7 band fall in the valence band[5] and cannot be long-lived. In the case of a donor, the situation in silicon and germanium is analogous: The $1S$ donor state is split by the valley–orbit interaction. In germanium, these states are the $1S(\Gamma_1)$ ground state and the $1S(\Gamma_5)$ lowest-lying excited state, optical transitions between which are forbidden.[5] One would thus expect the $1S(\Gamma_5)$ state to be a long-lived state. In the present study we have investigated the kinetics of the impurity photoconductivity at static and microwave voltages. The results confirm this conclusion experimentally.

In selecting experimental conditions we noted that the ionization energy of the donors in germanium is much lower than that in silicon, and the hopping conductivity is manifested at lower impurity concentrations. The experiments were accordingly carried out at lower temperatures and at lower impurity concentrations than in the case of silicon. The best impurity here is arsenic, since this donor in germanium has the largest ionization energy (14.18 meV) and the largest valley–orbit splitting (4.24 meV) (Ref. 5). Since the polarization hopping photoconductivity in an rf electric field depends strongly on the difference between the probabilities for the hop of an electron between the ground state

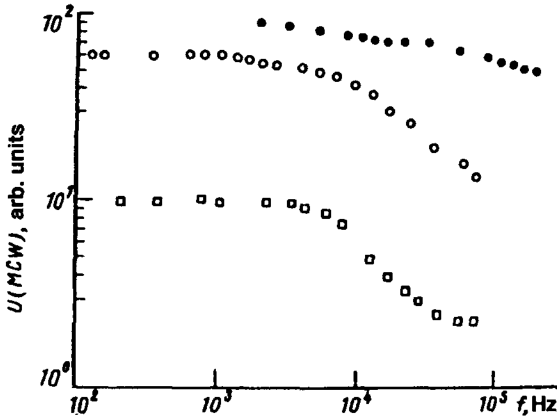

FIG. 1. The microwave photoresponse $U(MCW)$ of a germanium sample doped with arsenic to a concentration of 10^{16} cm^{-3}. □—At a temperature of 4.2 K; ○,●—2.2 K. □,○) Excitation by radiation at 3.39 μm, 1 mW; ●)—10.6 μm, 20 mW.

and the excited states,[6] this difference should be at a maximum for an arsenic impurity, and the temperature interval over which the hopping photoconductivity is predominant should be fairly broad.

We studied the impurity photoresponse of germanium samples doped with arsenic to concentrations of 1.6×10^{14} and 10^{16} cm^{-3}, and containing compensating acceptors in concentrations on the order of 10^{13} cm^{-3}. The samples were excited with laser light at a wavelength of 3.39 or 10.6 μm at a power of 1–50 mW, mechanically chopped at a frequency f in the range 0.2–200 kHz. At temperatures above 4.2 K, the exciting radiation was delivered by an 8-mm waveguide, which served as a microwave line.[7] At lower temperatures we used an optical cryostat. The waveguide with the test sample was immersed in the helium bath in the cryostat, and photoexcitation was carried out through a window of the cryostat. The results were combined at 4.2 K.

Figure 1 shows the microwave photoresponse $U(MCW)$ versus the modulation frequency f of the radiation for a sample with an arsenic concentration $N=10^{16}$ cm^{-3} at various temperatures and excitation intensities. We see from this figure that at both 4.2 and 2.2 K, at a low excitation level, the frequency dependence of $U(MCW)$ corresponds to a relaxation time $\tau^* \approx 3\times 10^{-5}$ s. As the excitation level is raised, the frequency dependence weakens. For the sample with $N=1.6\times 10^{14}$ cm^{-3} the frequency dependence of $U(MCW)$ exists at any excitation level. With a static bias voltage, the photoresponse $U(DC)$ is independent of f for both samples, over the entire frequency range studied.

Figure 2 shows the quasisteady ($f=800$ Hz) response $U(MCW)$ plotted as a function of the photoexcitation intensity I for the sample with $N=10^{16}$ cm^{-3}. We see that at both 4.2 K and 2.2 K the dependence is linear at low intensities and becomes sublinear when the intensity rises above a certain level. The response $U(DC)$ is a linear function of I over the entire range studied.

Figure 3 shows the temperature dependence of the quasisteady photoresponse for a static bias voltage, $U(DC)$, and for a microwave bias voltage, $U(MCW)$, at a low

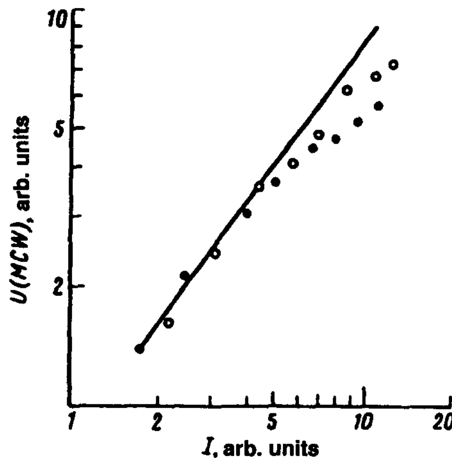

FIG. 2. Quasisteady photoresponse $U(MCW)$ versus the excitation intensity I for a sample with $N=10^{16}$ cm^{-3}. ○—At a temperature of 4.2 K; ●—2.2 K.

excitation level for both samples. We see from this figure that the $U(MCW)$ and $U(DC)$ curves for the sample with $N=1.6\times10^{14}$ cm^{-3} coincide. A weak temperature dependence of the photoresponse up to the beginning of thermal ionization of the arsenic impurity is typical of a photoconductivity due to free charge carriers. A corresponding temperature dependence for the sample with $N=10^{16}$ cm^{-3} was observed only at a static bias voltage. In the case of a microwave bias voltage, $U(MCW)$ increased by nearly two orders of magnitude as the temperature T was lowered from 10 to 2.2 K.

The plots of $U(MCW)$ and $U(DC)$ versus the modulation frequency, the intensity of the exciting radiation, and the temperature in Figs. 1–3 for the germanium samples doped lightly and heavily are similar to the plots found for silicon. They agree at a qualitative level with the model of an rf hopping photoconductivity.[6] According to that

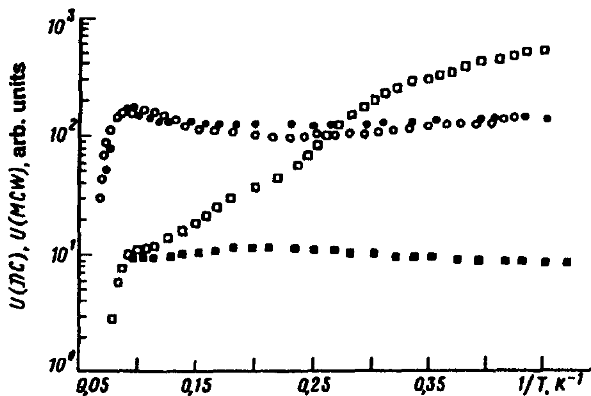

FIG. 3. Temperature dependence of the quasisteady photoresponse for a static bias voltage, $U(DC)$, and for a microwave bias voltage, $U(MCW)$, for samples with various arsenic concentrations (cm^{-3}): ○, ●—1.6 $\times10^{14}$ cm^{-3}; □, ■—10^{16} cm^{-3}; ●, ■—$U(DC)$; ○, □—$U(MCW)$.

model, the polarization photoconductivity is proportional to the concentration of trios of atoms consisting of an ion of the compensating impurity and two atoms of the major impurity localized nearby, one excited and one ionized. The microwave electric field induces hopping transitions between these atoms. These trios arise when free charge carriers are trapped at dipoles consisting of ions of the major and compensating impurities, and ions of the major impurity then undergo a hopping drift toward the charged pairs which form as a result of the trapping. Effective formation of these trios is possible only if the lifetime of the excited states, τ^*, is sufficiently long, if the concentrations of the major and compensating impurities are sufficiently high, and if the temperature is sufficiently low, such that impurity ions are bound in dipoles.

It follows from Fig. 1 that the lifetime of the excited state of the arsenic impurity in germanium, 3×10^{-5} s, is much longer than the lifetime of the free photoelectrons, but it is substantially shorter than the typical lifetime of excited atoms of group-III and -V impurities in silicon (10^{-3} s; Refs. 2 and 3). Consequently, in germanium, in contrast with silicon,[3] the background radiation at room temperature has only a minor effect on the population of the excited level of the arsenic impurity: There is no change in τ^* when the background is screened out by a cold filter of fused quartz. As the intensity of the photoexcitation is raised, however, the relaxation time τ^* decreases (Fig. 1), and the behavior of the quasisteady photoresponse, $U(MCW)$, becomes sublinear in germanium also (Fig. 2). It is natural to attribute this effect to the formation of trios at essentially all dipoles at a sufficiently high excitation intensity, beyond which the increase in $U(MCW)$ with increasing I slows down. A thermal destruction of the dipoles may be involved in the decrease in $U(MCW)$ in the heavily doped sample as the temperature is raised (Fig. 3). The binding energy of the dipoles at $N=10^{16}$ cm^{-3} is close to 3 meV. This figure is comparable to both the valley–orbit splitting and the ionization energy of arsenic atoms in germanium. Consequently, the contribution of the dipoles can be important all the way to temperatures ~ 10 K, at which an intense thermal ionization of the impurity ground state begins.

In conclusion, we should emphasize that a hopping photoconductivity is manifested in diamond, silicon, and germanium, because of the existence of long-lived excited states of impurities. The ranges of the concentrations and the temperature in which the hopping photoconductivity becomes predominant are very different for these three diamond-like semiconductors. The differences stem from both the degree of localization of charge carriers at impurity atoms and the lifetime of the excited states. One might expect that long-lived excited states of impurities would be characteristic of semiconductors of other types with a complex energy-band structure.

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