Impurity–impurity recombination in a random potential of charged impurities

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(Submitted 5 August 1993)
Pis'ma Zh. Eksp. Teor. Fiz. **58**, No. 7, 529–533 (10 October 1993)

The random Coulomb potential of charged impurities affects the impurity–impurity recombination of a neutral donor and a repulsive acceptor in Ge. The coefficient of impurity–impurity recombination depends on the temperature and the illumination intensity, because impurity levels are spread out by the random potential.

The spectra of the emission which arises in the case of neutral-donor–neutral-acceptor impurity–impurity transitions have been studied thoroughly (see, for example, Ref. 1). In such experiments, the photoneutralization of the donors and acceptors is followed first by a recombination of close donor–acceptor (DA) pairs and then by a recombination of progressively more distant pairs. In the steady state, on the other hand, the impurity–impurity recombination should be dominated by the DA pairs with a certain optimum separation. In addition, the random Coulomb potential of charged impurities may become important at low temperatures. In this letter we are reporting a study of the steady-state impurity–impurity recombination in compensated Ge in the presence of a random Coulomb potential.

The n-Ge test samples were doped with multiply charged acceptors (Cu) and partially compensated with shallow donors (Sb) (Fig. 1). At equilibrium the crystal contains only doubly and triply charged negative copper ions; the donors are completely ionized. The conductivity σ results from an optical excitation of electrons from deep copper levels (E_c—0.26 eV). At low temperatures T, at which shallow donors (E_c—0.01 eV) begin to freeze out, the optical excitation sends electrons from acceptors to donors. On the plot of σ versus $1/T$ (the lower curves in Fig. 1) we see an exponential region with an activation energy ($\simeq 8$ meV) which depends weakly on the illumination intensity I. The observed decrease in conductivity cannot be caused by a freezing out of free electrons as the random potential falls below the mobility threshold, since the activation energy is much larger than the amplitude of the random potential, which is found from the magnitude of the negative magnetoresistance,[2] and since it is virtually independent of the impurity concentration in the interval 10^{14}–5×10^{16} cm^{-3}.

The density of electrons bound at donors (the density of neutral donors, N_D^0) can be determined by ionizing neutral donors by electric-field pulses which are short enough (1 μs) to avoid a trapping of electrons by deep acceptors. Figure 1 shows the maximum conductivity σ_m in a strong electric field versus $1/T$. The density N_D^0 found from σ_m is much lower than the densities of doubly and triply charged copper ions (respectively N_2 and N_3) and antimony (N_D) over a wide range of I. It can thus be

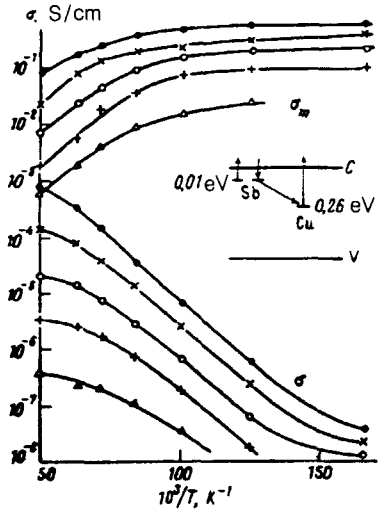

FIG. 1. Temperature dependence of the dc conductivity σ and of the maximum conductivity σ_m in a pulsed field. The inset shows the scheme of recombination transitions.

assumed that N_2 and N_3 are essentially constant over the T and I ranges studied. This case can occur only if there is an intense recombination flux from neutral donors to doubly charged acceptors. If direct DA recombination is unimportant, both impurity levels are at equilibrium with the conduction band. In particular, for the acceptors the optical-generation coefficient is $gN_3=\alpha nN_2$ ($g\propto I$), where α is the coefficient of the light-induced generation and consequently the capture of electrons for acceptors, and n is the density of free electrons. Since the coefficient α for trapping by repulsive impurities falls off with decreasing T, the value of n should rise, not fall (Fig. 1). The DA recombination flux should thus be much larger than the band–acceptor flux, and the corresponding equation should be

$$gN_3=\beta N_2N_D^0, \tag{1}$$

where β is an impurity–impurity recombination coefficient. We thus conclude that the density N_D^0 should increase with the illumination; this is what is seen experimentally (Fig. 1).

The coefficient β found from the experimental data turns out to depend on T and I; it also depends weakly on the impurity density. On the other hand, the probability for donor–acceptor tunneling can depend on only the distance between the donor and the acceptor. The reason for the dependence of β on T and I may be a random potential of charged impurities which broadens the spectrum of impurity states and significantly lowers the donor Fermi level ϵ_{FD} (Ref. 3). At low values of T, the donor levels below ϵ_{FD} are filled by electrons. The energy dependence of the density of donor states, $\rho_D(\epsilon)$, can be found from the plot of N_D^0 versus ϵ_{FD}. We determined the Fermi energy from the free-electron density n from the data in Fig. 1. Figure 2 shows $\log N_D^0$ versus the shift of the Fermi energy for two values of the impurity density. This plot turns out to be linear; i.e., we have $\rho_D(\epsilon)\propto\exp(-|\epsilon/\gamma|)$, where the energy is reckoned from the donor energy in the absence of a random potential. The Fermi energy of the donors is thus given by

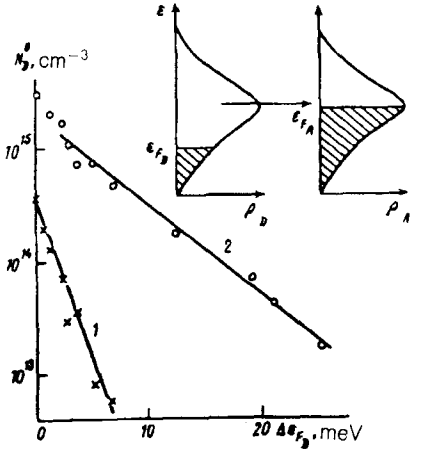

FIG. 2. Donor filling versus the shift of the Fermi quasilevel. 1) $N_D=1.5\times10^{15}$; 2) 1.2×10^{16} cm^{-3}.

$$\epsilon_{FD}=\gamma\ln(2N_D^0/N_D). \tag{2}$$

The value of γ increases with increasing impurity density and is the same as the amplitude of the random potential found from the magnitude of the negative magnetoresistance.[2] The $\rho_D(\epsilon)$ dependence found experimentally is much weaker than that predicted by the theory[3] [$\propto\exp(-\epsilon^2/\gamma^2)$].

Because of the blurring of impurity levels, Eq. (1) must be of the form

$$gN_3=\beta^*N_DN_A\int_{-\infty}^{+\infty}d\epsilon f_D(1-f_A)\rho(\epsilon). \tag{3}$$

Here β^* is the impurity–impurity recombination coefficient, averaged over all radii of the recombining DA pairs, and N_A is the acceptor density. We now assume that the occupation numbers of the donors, f_D, and the acceptors, f_A, are of a Fermi nature with corresponding Fermi energies ϵ_{FD} and ϵ_{FA}. In other words, we assume $f_D=[1+\exp(\epsilon-\epsilon_{FD})/kT]^{-1}$ and $1-f_A=[1+\exp(\epsilon_{FA}-\epsilon)/kT]^{-1}$. As $\rho(\epsilon)$ we use the density of states found experimentally, in the form $\rho(\epsilon)=(1/2\gamma)\exp(-|\epsilon/\gamma|)$. Correspondingly, the energy ϵ in f_D and f_A is reckoned from the unperturbed ionization potentials of the donors or acceptors. In the limit $kT\to0$, the integral on the right side of (3) is given approximately by

$$\frac{1}{2\gamma}\int_{-\infty}^{+\infty}d\epsilon\exp\left(\frac{\epsilon_{FD}-\epsilon}{kT}\right)\exp\left(\frac{\epsilon-\epsilon_{FA}}{kT}\right)\exp(-|\epsilon/\gamma|)=\exp[(\epsilon_{FD}-\epsilon_{FA})/kT].$$

We finally find

$$gN_3=\beta^*\exp\left(\frac{\epsilon_{FD}-\epsilon_{FA}}{kT}\right)N_AN_D. \tag{4}$$

Substituting ϵ_{FD} from (1) and the corresponding expression $\epsilon_{FA}=\gamma\ln(2N_3/N_A)$ into (4), we find

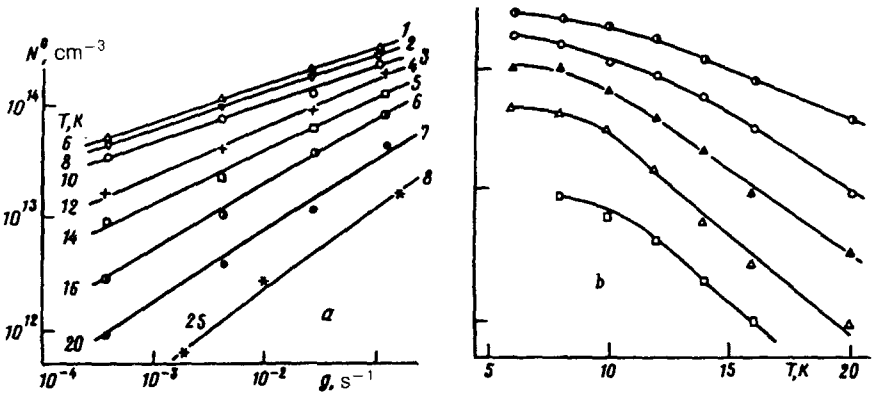

FIG. 3. Donor filling versus (a) the rate of optical generation at various temperatures and (b) the temperature for various illumination intensities.

$$gN_3=\beta^* N_A N_D\left(\frac{N_D^0}{N_D}\frac{N_A}{N_3}\right)\frac{\gamma}{kT}. \tag{5}$$

The physical meaning of this result is as follows. The large-scale random Coulomb potential smears the donor and acceptor states identically (see the inset in Fig. 2). The recombining DA pairs are in the same cell of the random potential. If we assume that the pair separation, which is important for recombination, is much larger than the first Bohr radius, then we can ignore the Coulomb interaction in the pair. The impurity–impurity transition thus occurs between a donor and an acceptor which have identical energy shifts with respect to the unperturbed ionization potential. The rate of impurity–impurity recombination is proportional to the probability that the donor of the pair is occupied by an electron, while the acceptor is empty. Under our experimental conditions the condition $N_D^0 \ll N_3$ held; i.e., the Fermi energy of the donors was much lower than that of the acceptors (Fig. 2). At an energy below ϵ_{FD} the acceptors in the pairs are essentially completely occupied; at $\epsilon > \epsilon_{FA}$, few of the donors are occupied. At low T the impurity–impurity transitions thus occur because of a thermal activation of electrons from the donor Fermi energy to the acceptor Fermi energy.

Figure 3a shows experimental results on $\log N_D^0$ as a function of $\log g$. According to expression (5), the plots are linear, with a slope proportional to the temperature. The values found for γ from the slopes of these curves are 2.6 and 5.7 meV for the two impurity densities; these values agree with those found from the curves in Fig. 2. Figure 3b shows $\log N_D^0$ versus T for various values of g. The fact that these curves are linear in a certain temperature interval shows that the value of β^* is essentially independent of T. The value of β^* is also independent of g. The physical meaning here is that there exists an optimum radius of the recombining pairs, whose value depends only weakly on the temperature and the illumination intensity.

It would appear at first glance that small-radius DA pairs should dominate the impurity–impurity recombination. In the steady state, however, the occupation of

donors in tight pairs should be small, for two reasons: the high probability for impurity–impurity transitions and the binary Coulomb interaction, which lowers the ionization potential of the donor. It was shown in Ref. 4 that the first of these circumstances gives rise to an effective recombination radius, much larger than the Bohr radius, which depends weakly on T and g, and that at low temperatures this effective radius tends toward the average distance between impurities. The second circumstance would apparently not cause any important change in this result.

In summary, the spreading of impurity levels by the random potential of the charged impurities has the consequence that impurity–impurity recombination, which plays a governing role at low temperatures, turns out to be an activation process with an activation energy equal to the difference between the relative Fermi quasilevels of the donors and acceptors (with the latter energies being reckoned from their values in the absence of the random potential). The rate of impurity–impurity recombination is a function of the illumination intensity and the temperature because of a change in the Fermi energy of the impurities (the donors in this case), which depends on the amplitude of the random potential γ. Impurity–impurity recombination in a random potential turns out to be nonquadratic in the impurity density, since the position of the Fermi quasilevels depends on γ.

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Translated by D. Parsons