Effect of electron-electron collisions on the trapping of free carriers by shallow impurity centers in germanium

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Cascade Auger recombination of free carriers on shallow impurities in Ge is investigated under quasi-equilibrium conditions ($T = 2$–12 K) and in impurity breakdown. The Auger capture cross sections are found to be $\sigma_{in} = 5\cdot 10^{-19} T^{-5} n$ cm^2 for donors and $\sigma_{ip} = 7\cdot 10^{-21} T^{-5} p$ cm^2 for acceptors. It is shown that in an isotropic semiconductor (p-Ge) σ_i is well described by the cascade-capture theory that takes into account only electron-electron collisions. In an anisotropic semiconductor σ_i is considerably larger (n-Ge, strongly uniaxially compressed p-Ge). Under impurity breakdown conditions the electron-electron collisions determine the lifetimes of the free carriers only in samples with appreciable density of the compensating impurity ($N \gtrsim 10^{13}$ cm^{-3}).

1. INTRODUCTION

Recombination of free carriers with shallow charged centers in semiconductors is usually regarded as cascaded capture with emission of acoustic phonons.[1,2] With increasing current density, however, Auger processes may become more significant, in which the energy loss due to electron-electron collisions becomes more effective than in electron-phonon interaction.

Many recent papers report investigations of Auger recombination in semiconductors. All, however, deal only with processes in which an electron, recombining with a hole or captured by a deep center, transfers all of its excess energy in one collision to another electron whose energy is thereby greatly increased. When carriers are captured by shallow charged centers, single-event processes are as a rule immaterial, since there is a much higher probability of cascade capture consisting of a large number of collisions with low energy loss in each act (transitions between the excited states). Hardly any attention was paid to Auguer recombination processes of this type in semiconductors. From among the theoretical studies, only the already mentioned classical paper[1] is known, but it is assumed in it that the electron-electron collisions play a significant role only during the first stage of carrier capture by a center, viz., an energy $\varepsilon \approx kT$ is transferred from one center to the other, and the subsequent descent through the excited states is due to the electron-phonon interaction. The following expression is cited in Ref. 1, without a detailed discussion, for the cross section of this process:

$$\sigma_i = \frac{2\pi^2}{3}\left(\frac{e^2}{\varkappa kT_e}\right)^3\left(\frac{e^2}{kT}\right)^2 n, \qquad (1)$$

where T_e and T are respectively the temperatures of the electron gas and of the crystal lattice, $\varkappa$ is the dielectric constant, and n is the free-electron density.

The cross sections for cascade capture with emission of acoustic phonons, likewise calculated in Ref. 1, were thoroughly reviewed in Sec. 2, where an error in Ref. 1 was found; in addition, a more convenient method for calculating the cross section was used in Ref. 2, where the capture was treated as continuous carrier diffusion, in total-energy space, from the region of positive energies to negative ones. A carrier is captured when it drops through the excited states to an energy $|\varepsilon| \approx kT$. Such a viewpoint was developed earlier in papers on electron recombination in a low-temperature dense weakly ionized plasma,[3] where energy is lost to electron-electron collisions during the electron capture. The results of Ref. 3 describe well electron capture in a hydrogen plasma under the conditions of Ref. 4. However, notwithstanding the ease with which the expression obtained in Ref. 3 for the cascade Auger-capture cross section can be written in the simplest case for a single charged center in a semiconductor with dielectric constant $\varkappa$:

$$\sigma_i = \frac{\pi^2}{9}\left(\frac{e^2}{\varkappa kT_e}\right)^5 n \ln 2, \qquad (2)$$

we can apparently not expect to describe in detail the experimental data with the aid of this expression. In contrast to a plasma in a vacuum, the rates at which energy is low in electron-electron collisions and by phonon emission can be comparable in a wide range of experimental conditions. Furthermore, the real band structure of a semiconductor—anisotropy of a free band or its degeneracy—can greatly modify the capture process both quantitatively and qualitatively. Nonetheless, it can be seen from a comparison of (1) and (2) that they yield similar temperature dependences for σ_i only at $T_e = T$, but substantially different ones when $T_e > T$. The values of σ_i at a given temperature, on the other hand, differ greatly already at $T_e = T$.

Despite the importance of the mechanism of free-carrier Auger capture by shallow impurities, no reliable experimental data were available until recently even for so well studied semiconductors as Ge and Si. The only experimental papers known to us are Refs. 5 and 6 for Ge and Ref. 7 for Si. To produce a sufficient free-carrier density all the measurements were made under advanced breakdown conditions,

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when $T_e \gg T$, and the results are unsatisfactory. Thus, the Auger-recombination coefficient was found in Ref. 5 to be $B_i = \sigma_i v/n$ (v is the average carrier velocity corresponding to T_e) and the value of B_i under the experimental conditions (electric field intensity $E = E_{br} = \text{const}$) was found to depend strongly on n, although the average free-carrier energy remained constant in the entire range of n so long as E was constant. It is noted in Ref. 7 that the measurement procedure used yields values of B_i that have low accuracy; the same holds equally well for Ref. 6. The results of these studies are difficult to extrapolate to equilibrium conditions, since the measurements of Refs. 5–7 do not give the field dependence of B_i. At the same time, our initial experiments demonstrate the possibility of studying Auger recombination of carriers with shallow impurities in Ge under equilibrium conditions (Refs. 8, 9).

The present paper is devoted to a detailed investigation of cascade Auger recombination of carriers with shallow impurity centers in Ge both under equilibrium conditions and in the presence of substantial auxiliary illumination, as well as in a breakdown-producing electric field, when $T_e \gg T$. This work was greatly helped by the progress achieved in the last few years in the understanding of cascade recombination with emission of acoustic phonons. It follows from experimental data[10,11] that the calculation in Ref. 2 yields reliable capture cross sections for this process. It is shown furthermore in Ref. 10 that a study of the kinetics of cascade capture must take into account the difference between the lifetimes τ_c of the free carriers and the relaxation times τ_p of the impurity photoconductivity relaxation that results from carrier sticking in high excited states of the impurity centers and in some of the low-mobility free states in a region where the impurity potential fluctuates. This last circumstance is important also for the study of Auger recombination. In particular, it accounts for the data of Ref. 5, where no Auger recombination was apparently observed at all, and for the incorrect conclusion that B_i is considerably altered in breakdown stems from measurements of τ_p, which was identified with τ_c. The study of the kinetics of the impurity photoconductivity is supplemented by registration of linewidths of bound-electron transitions between different excited states, which reveals the role played by electron-electron collisions in energy loss of a bound carrier as it goes to the ground state. A useful role in the understanding of the cause of the observed appreciable difference between the rates of carrier Auger recombination with donors and acceptors in Ge is played by an experiment in which the energy structure of the valence band of a p-Ge crystal is greatly altered by strong uniaxial compression.

2. EXPERIMENTAL PROCEDURE

We studied Auger recombination of carriers with shallow impurity centers mainly by the method used for cascade capture with emission of acoustic phonons, viz., by measuring the carrier lifetime τ_c and the impurity-photoconductivity relaxation time τ_p in submillimeter spectra due to photometric ionization of excited impurity states.[10] The most important differences were in the experimental conditions and in the choice of the sample parameters, viz., the free-carrier density was sufficient to make the contribution of the electron-electron collisions to the energy loss in the recombination with impurity centers comparable with (or larger than) that of the electron-phonon interaction. The cross section for Auger capture of free carriers by shallow impurity centers was calculated from the measured values of τ_c and τ_p. The photoconductivity kinetics and the photothermal-ionization linewidths were investigated with a submillimeter spectrometer with backward-wave oscillators at wavelengths 0.4–1.5 mm at $T = 1.6$–12 K.[10,12] The values of τ_p were determined from the dependence of the photoconductivity signal on the modulation frequency of the submillimeter radiation. To obtain the dependence of τ_c on the temperature and on the electric field, the sample was connected in a dc circuit and the ac component $\Delta\sigma$ of the conductivity was measured at low modulation of the background radiation I ($\Delta I \approx 0.01 I$). The density change ΔN was calculated from $\Delta\sigma$ and σ with allowance for the values of n obtained from measurements of the Hall constant. At a constant photoexcitation level, such that $\Delta n \ll n$ and $n \ll N_d - N_a$ (N_d and N_a are, respectively, the donor and acceptor densities), the value of $\Delta N(T,E)$ determines τ_c (T,E) uniquely. The absolute values of τ_c in weak fields, for a small number of recombination centers ($< 10^{11}$ cm^{-3}) and for n so small that Auger recombination can certainly be neglected, were obtained by the same tie-in with τ_p as used in Ref. 10. This yielded the values of τ_c in different samples in the entire range of temperatures, background illumination, and electric fields.

We recorded $\tau_c(E)$ with the sample shunted by a resistance $R_{sh} \ll R_{diff}$ (R_{diff} is the differential resistance of the sample), to prevent the nonlinearity of the current-voltage characteristics (R_{diff} is substantially lower than the ohmic resistance R under breakdown conditions) from influencing the photoconductivity signal.[13] In addition, the Hall constant R_H was measured under these conditions in weak magnetic fields ($H < 200$ Oe), when the current-voltage characteristic of the sample is independent of H.

To investigate hole recombination with shallow acceptors in uniaxially compressed Ge, a sample measuring $10 \times 2.5 \times 2.5$ mm, oriented along the [111] axis of the crystal, was placed between anvils lined with lead–tin alloy 2.5 mm thick and uniformly deformed at pressures up to 400 MPa.[14] The submillimeter radiation and the background were applied to the sample through the optical window of the cryostat, through a gap between the superconducting Helmholtz coils, with horizontal axes, used for the Hall measurements. Current contacts were coated on the perimeter of each sample face, as well as Hall point contacts. The intensity of the background radiation was adjusted with a movable cold shutter covering the optical window of the cryostat. The shutter position was varied with a rod extending through the cryostat cover. This system permitted uniform background illumination of the sample, and variation of its intensity by a factor of 200. The intensity was calibrated (in relative units) against the resistance of a small pure p-Ge sample ($N_d + N_a$

TABLE I.

No.; п/п	Type of conductivity	N_d, cm^{-3}	N_a, cm^{-3}	K, %
1	n	$8.5\cdot10^{12}$	$4.5\cdot10^{11}$	53
2	n	$4.7\cdot10^{12}$	$1.1\cdot10^{12}$	23.4
3	n	$1.1\cdot10^{13}$	$2.5\cdot10^{12}$	22.7
4	n	$1.7\cdot10^{14}$	$3.1\cdot10^{12}$	1.82
5	n	$9.3\cdot10^{12}$	$4.8\cdot10^{12}$	51.6
6	n	$4.2\cdot10^{13}$	$5\cdot10^{12}$	11.9
7	n	$1.8\cdot10^{14}$	$2\cdot10^{13}$	11.1
8	p	$2.5\cdot10^{11}$	$2.8\cdot10^{12}$	8.9
9	p	$6.2\cdot10^{11}$	$5.7\cdot10^{12}$	10.8
10	p	$7.2\cdot10^{12}$	$1.1\cdot10^{13}$	65.4
11	p	$1.7\cdot10^{13}$	$1.4\cdot10^{14}$	12.1
12	p	$2\cdot10^{13}$	$5.9\cdot10^{14}$	3.4

$< 10^{14}$ cm^{-3}) placed in front of the deformed sample of the side facing the optical window of the cryostat. For measurements in the range $T = 4.2$–12 K the compression unit was placed in an evacuated vessel equipped with an optical window. The necessary temperature was set by varying the current through a wire-wound heater. The temperature was monitored with a germanium thermometer.

A set of n- and p-Ge samples were investigated (Table I). Since the Auger-capture probability, in contrast to recombination with phonon emission, is proportional to the free-carrier density, the degree K of impurity compensation becomes one of the most important sample parameters and governs the values of n and p, given T and E. Choosing samples with close values of the compensating-impurity density and varying K by more than a decade, we can change from one recombination mechanism to the other without changing the experimental conditions.

3. RESULTS OF EXPERIMENT

Figure 1 shows plots of $\tau_c(T)$ and $n(T)$ measured in a weak electric field ($E \lesssim 0.3$ V/cm) for two n-Ge samples with different degrees of impurity compensation (Nos. 4 and 5, Table I). The absolute values of τ_c are tied in with τ_p at $T = 4.2$ K. It can be seen that the plots of $\tau_c(T)$ have maxima at temperature T_{max} that increases with K. The values of n at $T \approx T_{max}$ are $n_4 \approx 10^{10}$ cm^{-3}, $n_5 \approx 3\cdot10^{10}$ cm^{-3} and $n_{4,5} \ll N_a$ (here and henceforth the number subscripts represent the samples listed in Table I). The measurement results show that with increase of the background intensity I the values of τ_c at $T = 4.2$ K remains constant up to a definite value $I = I_k$. At larger values of I, the value of decreases with I in the region $T < T_{max}$, and at $T > T_{max}$ it is independent of I as before (the dark experimental points (●) in Fig. 2a were obtained for $I > I_k$. The same figure shows a plot of $\tau_p(T)$ for sample No. 4. It can be seen that the decrease of τ_p also sets in at $T = T_{max}$, but $\tau_p > \tau_c$ in the entire temperature range.

Figure 2 shows plots of $\tau_c(n)$ under conditions of impurity breakdown at $T = 4.2$ K for several n-Ge samples with different impurity centers, and a plot of $\tau_p(n)$ for one of the samples. The absolute values of τ_c and τ_p are tied-in in a weak electric field ($E \approx 0.1$ V/cm); the arrows note the values of n corresponding to the start of the vertical sections of the current-voltage characteristics of the samples at breakdown. It can be seen that τ_c and τ_p have maxima. We have $\tau_c \propto n$ at $n \ll n_{max}$ and $\tau_c \propto n^{-1}$ at $n \gg n_{max}$. The τ_p is practically equal to τ_c at $n > n_{max}$ and substantially larger than τ_c at

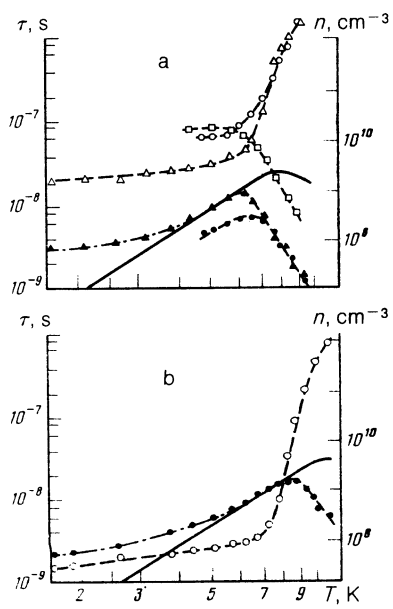

FIG. 1. Plots of $\tau_c(T)$, $\tau_p(T)$ and $n(T)$ for n-Ge. a) Sample No. 4: ▲—τ_c, □—τ_p, △—n and $I < I_k$, ●—τ_c, ○—n and $I > I_k$. b) Sample No. 5: ●—τ_c, ○—n and $I < I_k$.

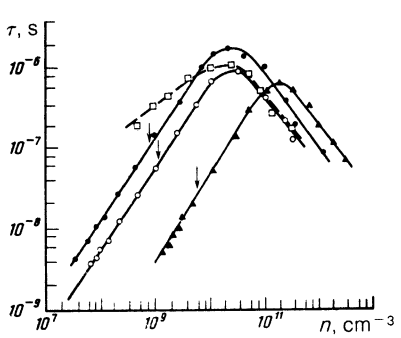

FIG. 2. Plots of $\tau_c(n)$ for samples No. 5—●, No. 6—▲, No. 7—○ and of $\tau_p(n)$ for sample No. 7—□ at n-Ge and $T = 4.2$ K, $I < I_k$. The arrows mark the changes of n corresponding to the start of the vertical sections of the current-voltage characteristics of the samples at breakdown.

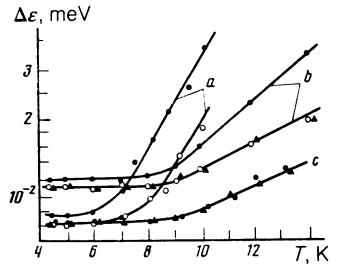

FIG. 3. Plots of $\Delta\varepsilon(T)$ for n-Ge samples: ●—No. 4, ○—No. 2, ▲—No. 1; a-transition $2p_{\pm1}\rightarrow 3d_{\pm2}$, b-transition $3p_0\rightarrow 3d_{\pm1}$, c-transition $2s\rightarrow 2p_{\pm1}$.

$n < n_{\max}$. As a result, the $\tau_c(n)$ plot has a steeper peak than that of $\tau_p(n)$.

Figure 3 shows the temperature dependences of the width ($\Delta\varepsilon$) of several impurity photothermal ionization lines corresponding to transitions of bound carriers between different excited states: 1) $2p_{\pm1}\rightarrow 3d_{\pm2}$ (1.73 meV→0.69 meV), 2) $3p_0\rightarrow 3d_{\pm1}$ (2.56 meV→1.25 meV) and 3) $2s\rightarrow 2p_{\pm1}$ (3.60 meV→1.73 meV) (the numbers in the parentheses are the level energies.) The samples measured were Nos. 1, 2, and 4 and differed greatly in compensation, i.e., in the free-carrier density at the given temperature ($n_4{:}n_2{:}n_1 = 60{:}4{:}1$). The aggregate of the experimental results for a set of samples with different N_d and N_a shows that the values of $\Delta\varepsilon$ in pure n-Ge ($n_d \lesssim 10^{14}$ cm^{-3}, $N_a \lesssim 10^{13}$ cm^{-3}) do not depend on the impurity density at low temperature. It can be seen from Fig. 3 that the values of $\Delta\varepsilon$ depend little on T for the line c corresponding to a transition between deep excited states, and are the same for all three samples in the temperature interval employed. For transition b to a higher state, a similar result is obtained already for

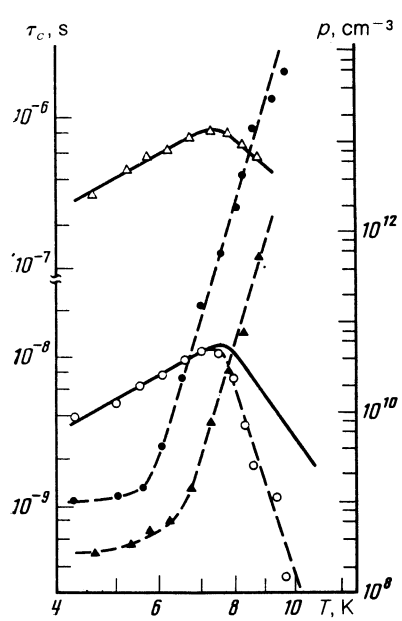

FIG. 4. Plots of $\tau_c(T)$ and $p(T)$ for p-Ge. Sample No. 8: Δ—τ_c, ▲—p; sample No. 12 ○—τ_c, ●—p.

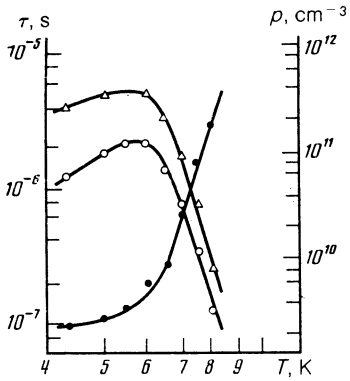

FIG. 5. Plots of $\tau_c(T)$ (○), $\tau_p(T)$ (Δ), $p(T)$ (●) for sample No. 8 (p-Ge) under strong uniaxial compression.

only two samples, while for the third, which has the highest free-carrier density, the values of $\Delta\varepsilon$ increase with temperature more rapidly. An even stronger $\Delta\varepsilon(T)$ dependence is exhibited by line a for samples 2 and 4; furthermore, the plots of $\Delta\varepsilon_2(T)$ and $\Delta\varepsilon_4(T)$ are parallel at high temperatures. Note that the change of the slope of the $\Delta\varepsilon(T)$ plots of these lines is observed in both samples at values of T corresponding to $T_{\max}$ in the $\tau_c(T)$ plots (Fig. 2). Measurement of the widths of these same lines under impurity breakdown conditions shows that they remain not broadened all the way to $n \approx 10^{12}$ cm^{-3}.

For p-Ge the plots of $\tau_c(T)$ (Fig. 4) are similar to the corresponding plots for n-Ge. However, maxima are observed in them at higher T, when $p \approx N_d$ for all but the most doped low-compensation samples (Nos. 11 and 12). Strong uniaxial compression leads to a noticeable shift of the maximum towards lower T and p (Fig. 5), and now $p \ll N_d$ at the maximum. (The method of tying-in the values of τ_c and τ_p is discussed later.)

The maximum values of the background intensity I_k differ greatly in deformed and nondeformed p-Ge: in the absence of compression does not depend on I at all at the employed background-intensity values (Fig. 6), while under strong uniaxial compression I_k is substantially less than in n-Ge. Note that the smallest employed value of I is found to be

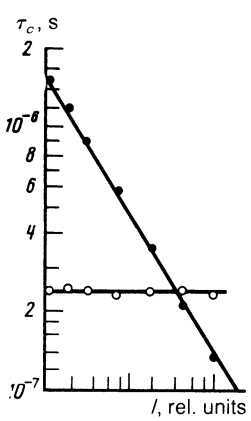

FIG. 6. Plots of $\tau_c(I)$ for sample 8 under strong uniaxial compression (●) and without compression (○), $T = 4.2$ K.

larger than I_k for deformed p-Ge, so that τ_c depends on I in the entire range of I ($\tau_c \propto I^{-1/2}$, Fig. 6).

Unixaxial compression to n-Ge does not affect in any way the experimental results.

4. DISCUSSION

1. Kinetics of impurity photoconductivity under quasiequilibrium condition ($T_e = T$)

It is convenient to begin the analysis of the temperature dependences of the carrier lifetimes in n- and p-Ge, shown in Figs. 1 and 4, by comparing the results with the theory of capture cascade by charged centers in interactions between free carriers and acoustic phonons.[2] The theoretical $\tau_c(T)$ dependences are represented in these figures by solid curves. The lower calculated values at sufficiently high T are due to the increase of the number of captured centers upon thermal ionization of the impurities; it is taken into account (with n-Ge as the example) in the following manner[15]:

$$\tau_c = 1/\sigma_{ph} v (N_a + 2n + n_i), \tag{3}$$

where $n_i = N_c T^{3/2} \exp(-\varepsilon_d/kT)$, N_c is the carrier density, ε_d is the impurity ionization energy, σ_{ph} the cross section for capture in cascade recombination, and v is the thermal velocity of the carriers.

It can be seen that this calculation describes well the experimental data for n-Ge in a restricted temperature range at $T < T_{max}$ and $I < I_k$. For non-deformed p-Ge, the agreement is good in the entire range of experimental conditions, except at the very highest T, for samples 11 and 12. In the range $T = 4.2$–1.6 K (Fig. 1) the $\tau_c(T)$ plots are much less steep than those predicted by the theory for capture by isolated centers.[2] It is noted in the very same reference, however, that the presence of compensated impurities leads under equilibrium conditions to "freezing" of the Coulomb capture centers when the temperature is lowered, i.e., to formation of dipoles and of more complicated complexes, and the probability of capture by these is much lower than by a single charged center. The calculated $\tau_c(T)$ with allowance for formation of complexes is shown in Fig. 1 by the dash-dot line. Good agreement with the experimental results is observed also in this temperature region, although one might think that at the background intensities employed all complexes should break up. This was noted in Ref. 2. Thus, the mechanism of cascade capture with carrier-energy loss through interaction with phonons describes only a part of the experimental results. The remaining data, which are more important for our purposes, can be explained only by resorting to a supplementary recombination mechanism. Corresponding to them for n-Ge in Figs. 1 and 4 are the conditions $T > T_{max}$ at $I < I_k$ and the entire temperature range at $I > I_k$. For deformed weakly compensated and sufficiently doped p-Ge ($p > 10^{12}$ cm^{-3}) we have $T > T_{max}$ at all the employed values of I. The abrupt decrease of τ_c with increase of T at a constant number of capture centers, when the expression for $\tau_c(T)$ is close to $\tau_c \propto \exp(\varepsilon_d/kT)$, is evidence that the capture cross section under these conditions should be proportional to n. Such a mechanism is Auger recombination. The data of Figs. 1 and 4 can then be used to calculate the cross sections σ_i for Auger recombination. To this end it is necessary to take into account the increase of the number of capture centers at $n \gtrsim N_d$. Following Ref. 15, we find that at $\sigma_i \gg \sigma_b$ we have

$$\tau_c = 1/2\sigma_i v (N_a + 1.5n + 0.5n_i). \tag{4}$$

The coefficient (2) in the denominator of (4) is due to the fact that the Auger-recombination probability is proportional to n^2 ($\sigma_i \propto n$), while $\tau_c = \Delta n/G$. If the temperature and the carrier density are such that the cascade processes with energy loss to electron-phonon and electron-electron interaction have close cross sections ($\sigma_i \approx \sigma_{ph}$), it is necessary to take both recombination mechanisms into account.

Figure 7 shows the values of σ_i/n and σ_i/p in the temperature interval 4.2–12 K, calculated from (4) from the data of Figs. 1 and 4. The calulated ratios are useful from two viewpoints. First, they allow us to separate in the experimental results the explicit $\sigma_i(T)$ dependence and exclude the much stronger $n(T)$ dependence. Second, they permit a direct comparison of n-Ge with p-Ge (the frequently employed quantity $B_i = \sigma_i v/n$ is less convenient, since it depends on the carrier effective mass). It can be seen that for n-Ge the values of σ_i/n of all samples, for a given T, are practically equal in the range $T = 4.2$–12 K, viz., $\sigma_i/n \propto T^{-\alpha}$, where $\alpha = 5 \pm 0.2$, in agreement with the theory of cascade Auger capture. When the temperature is lowered (to $T < 4.2$ K for sample No. 4 at $I > I_k$), just as in the case of capture with participation of acoustic phonons, τ_c depends less on temperature; just as previously, this can be attributed

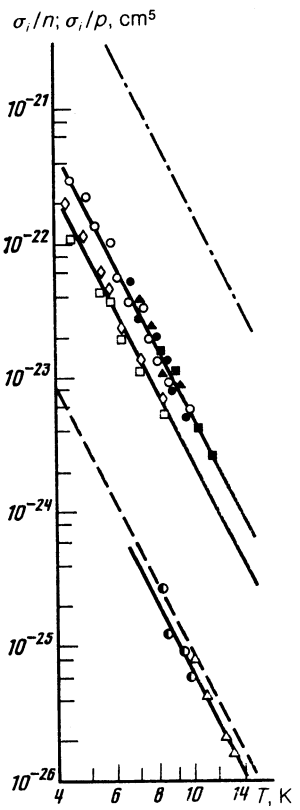

FIG. 7. Temperature dependences of σ_i/n, σ_i/p. The results correspond to n-Ge samples: ▲—No. 3, ○—No. 4, ■—No. 5; p-Ge without compression: △—No. 11, ◐—No. 12; p-Ge under strong compression; ◇—No. 8, □—No. 9. The plots calculated from (1) and (2) are dash-dot and dashed, respectively.

to freezing of the Coulomb capture centers and to the appearance of dipoles. The values of σ_i/p for p-Ge are substantially lower than σ_i/n (it is this which determines the narrower temperature interval of the obtained values of σ_i/p).

The noted large difference between the rates of Auger recombination of electrons with donors and of holes with acceptors is to some extent unexpected: the theory does not contain explicitly a difference between the parameters that describe the corresponding carrier groups. The most likely of the various suggestions is that this fact is due to the influence of the strong anisotropy of the conduction band. A natural check would be provided by experiments on uniaxially compressed p-Ge, which would lead to a considerable anisotropy of the valence band: strong uniaxial compression lifts the degeneracy of the valence band at $K=0$, while the upper split-off band becomes anisotropic with $m_\perp = 0.13m_0$ and $m_\parallel = 0.04m_0$. These experimental data (Figs. 5 and 6) were found to be wholly governed by a single recombination mechanism—cascade Auger capture. Upon compression, the maxima of the temperature dependences of τ_c and τ_p shift towards lower temperatures, where $p \ll N_d$ and τ_c^{-1} has a square-root dependence on I in the entire range of background intensities, down to the lowest hole densities $p \approx 10^8$ cm^{-3} at $T=4.2$ K. The data of Figs. 5 and 6 were used to calculate the values of σ_i/p (Fig. 7); just as in the absence of compression, $\sigma_i/p \propto T^{-5}$, but the values of σ_i/p at the corresponding temperatures are larger by an approximate factor of 40 and almost reach the values of σ_i/n in n-Ge. Note that the absolute values of τ_c shown in Figs. 5 and 6 were obtained from τ_p data, as before, although the validity of this tie-in was verified in Ref. 10 only for nondeformed n- and p-Ge. Experiment shows that the relations between τ_c and τ_p (Ref. 10) are valid also for compression. This is not surprising: they do not contain the band-structure parameters.

A similar influence of the band anistropy on the energy loss by carriers bound to shallow impurities is realized for the first excited states of donors and acceptors in Ge.[16,17] It is shown in Ref. 18 that the short lifetime of this state of a donor, compared with that of an acceptor, is due to the abruptly increased probability of emitting a phonon having the rather high energy needed for the transition when the free-band effective-mass anistropy is increased. Such calculations would be very useful also for cascade capture with energy loss on account of electron-electron collisions.

Note that the appearance of Auger recombination at very low free-hole densities in deformed p-Ge is evidence of a decrease, by more than an order of magnitude, of the cross section σ_{ph} for cascade capture accompanied by acoustic-phonon emission. This behavior of σ_{ph} was predicted in Ref. 19 and attributed to a change of the free-hole band parameters.

We proceed now to compare the theoretical and experimental cross sections for Auger recombination. The values calculated from (1) and (2) are shown in Fig. 7. Whereas their temperature dependences are the same, they differ greatly in magnitude. As noted in the Introduction, this is due to the different approach to the details of Auger capture: according to (1), only the first recombination act (transition to a level with a binding energy $\varepsilon \approx kT$) is due to electron-electron collisions. The succeeding energy loss is due to phonon emission, and according to Eq. (2) the entire process of cascade capture is due to electron-electron collisions. In the theory, however, no account was taken of the free-band anisotropy; it appears therefore that only a small fraction of the experimental data can be quantitatively compared with calculation, viz., the values of σ_i/p for nondeformed p-Ge. The fact that the experimental σ_i/p are close to those calculated from (2) indicates that it is correct to take only electron-electron collisions into account in Auger recombination.

Nonetheless, the data on the temperature dependences of the photothermal-ionization linewidths of excited states of donors (Fig. 3) show that in some cases it is necessary to allow for the influence of electron-phonon collisions on Auger capture. In contrast to the experiments with free carriers, which were discussed above and which yield only integral information on the recombination process, determination of the lifetime of bound carriers in various excited states from the linewidths of impurity transitions can identify the interactions that determine the energy lost when the carrier descend to the ground state.

There are several known mechanisms that determine the linewidths of transitions between excited impurity levels in semiconductors. As shown in Ref. 20, in weakly doped n-Ge with $N_d \lesssim 2\ 10^{14}$ cm^{-3} and $N_a \lesssim 10^{13}$ cm^{-3}, and at low temperatures, the principal broadening mechanisms of not too highly excited states are electron-phonon and electron-electron interactions; the contribution of the latter increases abruptly when the temperature is raised under conditions of thermal equilibrium, when $n \propto \exp(-\varepsilon_d/kT)$. The main contribution to the linewidth is usually made by the final state of the given transition, since both electron-phonon and electron-electron interactions are as a rule more effective when the carrier binding energy is lowered. As already noted, the contribution of each broadening mechanism can be separated by comparing the width of one and the same line, under identical experimental conditions, of several sufficiently pure samples with different values of K, and hence also n. So long as the linewidth $\Delta\varepsilon$ is independent of K, it is determined by the interaction of bound electrons with phonons,[20] an interaction characterized by a weak temperature dependence of $\Delta\varepsilon$. The increase of $\Delta\varepsilon$ with increasing K points to the onset of a contribution from electron-electron collisions. The form of the curves of Fig. 3 shows that the phonon broadening mechanism determines completely the linewidth of the transition between deep excited states (line c) in all samples, the width of line b in samples 1 and 2 which have higher compensation, and the widths of all lines for all samples at low temperatures. The abrupt change of the temperature dependence of line a in samples 2 and 4 and of line b in sample 1 at a certain value T_1 unique to the given sample and to each line, are evidence of the onset of a new broadening mechanism, viz., interaction of bound electrons with free ones. It can be seen from the data of Fig. 3 that for a transition with lower final-state binding energy (line a) the electron-electron collisions become decisive at lower tempera-

tures, and accordingly at lower free-carrier densities. For line a this mechanism is therefore substantial also in sample b, but at higher T. Electronic line broadening can be due, generally speaking, both to shortening of the bound-state lifetime (Born approximation) and to phase loss of the atomic oscillator as a result of the interaction between a bound carrier and a free one (adiabatic approximation).[20] Estimates show that the adiabatic approximation does not hold for high excited states of impurity atoms, in view of the small energy gaps between neighboring excited states. The Born approximation is therefore apparently better suited for estimates of the widths of lines a and b, which have rather high final states.

Thus, analysis of the experimental $\Delta\varepsilon(T)$ and $\tau_c(T)$ dependences shows that in n-Ge the Auger processes determine the lifetimes of bound carriers in high excited states in the same temperature region in which free-carrier Auger recombination predominates. The cascaded descent of a bound carrier from a lower excited state to the ground state is determined by interaction with acoustic phonons. The energy limit (ε_{lim}) at which the energy-loss mechanism changes depends on the free-carrier temperature and density. At a constant temperature, ε_{lim} decreases with increase of n. When $|\varepsilon_{\text{lim}}| \gtrsim kT$, allowance must be made for the inelastic electron-electron collisions when the free-carrier lifetime is calculated.

2. Photoconductivity kinetics under impurity breakdown conditions

Additional data on the Auger-recombination cross section σ_i and its dependence on the electron-gas temperature T_e can be obtained by measuring $\tau_c(n)$ and $\tau_p(n)$ dependences under impurity breakdown conditions (Fig. 2). As already explained in the Introduction, however, it is much more difficult to obtain quantitative estimates of the contributions of various mechanisms to the capture from these experiments than under equilibrium conditions. The primary reason is that the information on the numerical values of the kinetic coefficients and on their dependence on the electric field is incomplete. Reliable data on σ_i can therefore be obtained only by comparing the results for a number of samples with different parameters, since this adds to the corresponding kinetic equations a set of values of the compensation and density of the capture centers.

Under impurity-breakdown conditions, when the generation carrier flux into the band, due to impact ionization of the neutral impurities, becomes larger than the background flux, the lifetime $\tau_c = \Delta n/\Delta G$ is a function of the electric current flowing through the sample, and hence also of the density of the free carriers ($E_{\text{br}} = \text{const}$). As expression for $\tau_c(n)$ can be obtained from the kinetic equations that determine the density of the free carriers and its change Δn due to modulation of the impurity illumination ΔG (Ref. 5):

$$\begin{aligned} a-bn-cn^2&=0,\\ d\Delta n/dt&=\Delta G-(b+2cn+3dn^2)\Delta n. \end{aligned} \tag{5}$$

Here, as in Ref. 5,

$$\begin{aligned} a&=(A_{\text{T}}+A_{\text{ph}})(N_{\text{d}}-N_{\text{a}}),\\ b&=B_{\text{T}}N_{\text{a}}+A_{\text{T}}+A_{\text{ph}}-A_i(N_{\text{d}}-N_{\text{a}}),\\ c&=B_{\text{T}}+A_i+B_iN_{\text{a}}, \quad d=B_i, \end{aligned}$$

A_{T}, A_{ph}, and A_i are coefficients that determine the respective rates of the thermal, phonon, and impact generation of the free carriers; we neglect terms nonlinear in Δn in view of the smallness of ΔG.

It follows from (5) the Δn relaxes with a time constant τ_c, where

$$\tau_c^{-1}=a/n+cn+2dn^2, \tag{6}$$

and is determined not only by recombination processes but also by impact ionization of neutral centers; τ_c depends on n and goes through a maximum at $n_{\max}\approx(a/c)^{1/2}$ (in this case usually $c\gg 2dn_{\max}$).

In the samples employed, having a density $N_{\text{d}}-N_{\text{a}} \leqslant 10^{14}$ cm^{-3} and $K\lesssim 50\%$, the impurity breakdown is observed at $E_{\text{br}} = 3$–3.5 V/cm. In this range of E, the coefficients A_{T} and A_{b} can be assumed constant. In addition, at $N_{\text{d}}-N_{\text{a}} \lesssim 5\cdot 10^{14}$ cm^{-3}, the energy lost by the free carriers by impact ionization of the impurity neutral atoms is found to be much less than in the case of spontaneous emission of acoustic phonons. The free-carrier distribution function, and hence also the coefficients B_{T}, B_{ph}, and A_i which depend only on the carrier energy, are also determined only by E. They should therefore remain constant at $E = E_{\text{br}}$ in the entire range of variation of the density n. Since the values of E_{br} of all the samples used are close, one should expect the average carrier energy in the course of breakdown and the coefficients B_{T} and B_i of the samples to differ little.

Indeed, the data of Fig. 2 show that at $E\approx E_{\text{br}}$, under conditions when we still have $\tau_c = 1/B_{\text{T}}N_{\text{a}}$, the values of B_{T} for all samples are $\approx 5\cdot 10^{-6}$ cm$^{-3}\cdot$s^{-1} (Auger recombination can be neglected in this case, since $I<I_k$ and the n are small). At $n>n_{\max}$, when the first term of (6) can be neglected, we have

$$\tau_c^{-1}=cn+2dn^2=[A_i+B_{\text{T}}+B_i(N_{\text{a}}+2n)]n=An. \tag{7}$$

The values of the coefficient A calculated from the data of Fig. 2 at $n>n_{\max}$ were different for the various samples but, as expected, were independent of n. For sample 6 we have $A_6 = 5\cdot 10^{-6}$ (and close values are obtained for samples 3 and 4), $A_5 = 10^{-5}$ cm$^{-3}\cdot$s^{-1} for sample 5, and $A_7 = 2\cdot 10^{-5}$ cm$^{-3}\cdot$s^{-1} for sample 7. Note that samples 4–6 have close values of N_{a}, but different impurity compensations: $K_{4,6} \lesssim 10\%$, $K_5\approx 50\%$. In addition, $N_{\text{a4}}<N_{\text{a5,6}}<N_{\text{a7}}$.

The differences in the values of A can be easily explained by assuming that in breakdown Auger recombination influences τ_c only in sample 7 with the largest A. Indeed, if we neglect in (7) the term $B_i(N_{\text{a}}+2n)$ for samples 4–6, we obtain

$$\tau_c^{-1}=B_{\text{T}}n+A_in;$$

for weakly compensation samples 4 and 5 it follows from the breakdown condition

$$A_i(N_{\text{d}}-N_{\text{a}})=B_{\text{T}}N_{\text{a}},$$

that

$$A_i = B_T N_a/(N_d - N_a) \ll B_1$$

and $A_{4,6} \approx B_T$. Confirming this conclusion is also the fact that $A_{4,6}$ is equal to the value B_7 obtained above for E close to but less than E_{br}. For sample 5, the term $A_i n$ in (7) cannot be neglected since $A_i \approx B_7$ and A_5 must be twice as large as in samples 4 and 6; this agrees with the experimental value A cited above. Since $A_7 \gg B_T$ and $A_i \ll B_T$ ($K_7 \approx 10\%$) for sample 7, the value of τ_c is entirely determined by Auger processes, $\tau_c^{-1} \approx B_i N_a n$ ($n \ll N_a$ for this sample under the experimental conditions), and $B_i \approx 10^{-16}$ cm$^6 \cdot$s^{-1}.

Let us compare now the value of B_i obtained under breakdown conditions with the values calculated from Eqs. (1) and (2). To this end we estimate first, from the measurements of $\tau_c(E)$ in the prebreakdown region, the electron temperature T_e at $E = E_{br}$ for sample 7. Since $B_T \propto (T_e/T)^{1.5}$ (Ref. 21) and changes by approximately a decade when E increases to E_{br} (Fig. 2), we get $T_e \approx 20$ K. In this case, we should have $B_i \approx 3 \cdot 10^{-17}$ cm$^6 \cdot$s^{-1} according to Eq. (1) and $B_i \approx 5 \cdot 10^{-19}$ cm$^6 \cdot$s^{-1} according to Eq. (2) ($B_i \approx 1.1 \cdot 10^{-15}$ cm$^6 \cdot$s^{-1} at $T = 4.2$ K). The latter value is much closer to the experimental one. It follows hence that under nonequilibrium conditions the capture process is governed solely by electron-electron collisions.

Note that even though in sample 7 the Auger processes do control the lifetimes of the photoexcited carriers at breakdown, they do not determine at $n \lesssim 10^{12}$ cm^{-3} the recombination flux $B_T N_a n + B_i N_a n^2$, since $B_T \gg B_i n$. This is confirmed also by measurements of the widths $\Delta\varepsilon(n)$ of the impurity lines—the values of $\Delta\varepsilon$ are constant right down to $n \approx 10^{12}$ cm^{-3} for all lines.

The foregoing analysis of the experimental results makes it clear that the treatment of the data in Ref. 5 is incorrect, since the investigated n-Ge samples had $N_a \approx 10^{12}$ cm^{-3}, i.e., close to our samples 1–4. As already noted, the plot of $\tau_p(n)$ near the maximum spans a larger range of n than the corresponding $\tau_c(n)$ plot, in view of the difference between τ_p and τ_c at $n \lesssim n_{max}$ (see Fig. 2). Only τ_p was measured in Ref. 5 and was identified without justification with τ_c. Therefore the values of A in the region of the maximum, calculated using Eq. (7) from the experimental $\tau_p(n)$ dependences turned out to be too high and dependent on n, while past the maximum ($n > n_{max}$) they tended to a constant value A_0. If the experimental data of Ref. 5 are recalculated using the equations of Ref. 10 and with allowance for the difference between τ_p and τ_c, then A_0 turns out to be close to B_T in the pre-breakdown region. The authors of Ref. 5, having obtained the $A(n)$ dependence, conclude incorrectly that $B_T(n)$ has the same dependence that B_T in A can be neglected. In our opinion, the Auger-recombination conditions were not realized at all in Ref. 5.

Thus, while study of cascade Auger recombination on shallow impurities in pure Ge by increasing the free-carrier density via impact ionization of impurity centers at fixed temperature does lead to noncontradictory results, it calls for a more thorough analysis. In addition, in the case of breakdown the electron temperature turns out to be quite high, and since the B_i depends on T_e more strongly than B_T, the conditions that permit Auger recombination to predominate become more stringent.

5. CONCLUSION

Our experiments have shown that cascade Auger recombination of carriers on impurity centers are qualitatively correctly described by the calculation of Ref. 3. At the same time, for a quantitative comparison it is necessary to take into account in the theory a number of additional factors, primarily the real band structure of the semiconductor and the electron-phonon collisions. The former, as shown by the experiments, can alter significantly the cross section, and the latter is needed to estimate the lifetimes of the impurity centers in excited states.

The results are important also for some practical purposes. One is the development of impurity photoresistors for the long-wave region of the IR spectrum. The aim here is to increase the lifetimes of the photocarriers and to decrease the impurity compensation. It is clear by now that it is useful to lower the compensation only to a certain limit that depends on the background level. It is particularly important that in isotropic semiconductors τ_c can be more significantly increased by lower K.

Another approach in which it is important to take into account the change of the recombination mechanism when the phonon background illumination is increased is a new method for the analysis of extremely pure semiconductors, viz., determination of the density of the residual shallow impurities by measuring the impurity-photoconductivity relaxation time.[22] In this case, increasing the carrier density with increase of the background lowers the sample resistance and by the same token simplifies the measurements considerably, but can lead to errors if $\sigma_i \gtrsim \sigma_{ph}$.

Our experiments, naturally, do not solve the problem completely. It is of interest to extend the methods developed here to research into silicon. In addition, it is apparently necessary to study in greater detail uniaxially compressed p-type semiconductors. Compressing crystals in different directions will permit a detailed measurement of the dependence of σ_i on the anisotropy, cast light on the conditions for realizing cascade recombination with emission of acoustic phonons under strong uniaxial compression, and determine the cross section of this process. We are now at work on this subject.

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