

The experiments described have been carried out in argon, nitrogen, and helium gases, with no significant difference in the results obtained. Additional work in isopentane to 30 000 kg per cm² at room temperature seems to suggest a small increase in the electron mobility with pressure, but the trapping effects make this less certain. However, no violent change in the electron mobility such as has been found for germanium⁸ was observed. It must be emphasized that the trap effects which mask the mobility changes are not important at the highest temperatures, so that the decrease in resistivity with pressure there is genuine, and the deduction of an energy gap decrease with pressure could be invalidated only by improbably large increases in one or both of the carrier mobilities. The results reported

here have been checked by examining the change in the optical absorption edge with pressure, up to 8000 kg/cm². The shift in the edge is towards longer wavelengths, or smaller energies, and is of about the same magnitude as in the above experiments.⁷ It is intended to further check the results by examining the change in Hall mobility of electrons and holes with pressure.

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⁷ Warschauer, Paul, and Brooks, *Bull. Am. Phys. Soc.* **30**, No. 1, 54 (1955).

Optical and Impact Recombination in Impurity Photoconductivity in Germanium and Silicon

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The impact (three-body) recombination and optical recombination coefficients are calculated for hydrogen-like impurity centers in extrinsic germanium and silicon in thermal equilibrium. These have been compared with the phonon recombination coefficient calculated by Gummel and Lax for a similar model. It is found that the optical coefficient is always less than the phonon coefficient in the temperature range of interest. The impact ionization coefficient which is proportional to the free carrier concentration may be comparable with or greater than the phonon recombination coefficient at 4.2°K in the presence of background radiation and definitely exceeds it at higher temperatures. Comparison with experimental data indicates that none of the mechanisms considered can yet explain the observed time constants.

IN phenomena involving deviations from the free charge carrier equilibrium concentration in semiconductors, there are generally several different mechanisms that tend to bring the system back to equilibrium. The time constant for the phenomenon will depend on which mechanism is dominant in effecting the return to equilibrium. The purpose of this note is to analyze the mechanisms contributing to the time constant for impurity photoconductivity in extrinsic semiconductors. This is accomplished by comparing the various recombination coefficients calculated on the basis of a simplified model. The recombination coefficients considered to be of importance are B_p , B_0 and B_{In} . B_p is the phonon (nonradiative) recombination coefficient which consists of recombination with the emission of phonons; B_0 is the optical (radiative) recombination coefficient which consists of recombination with the emission of photons, and B_{In} is the impact (three-body) recombination coefficient which consists of recombination with the excitation of a second free carrier, i.e., the inverse of impact ionization. The simplified model used consists in representing the impurity centers as hydrogen-like. The

bound charge carrier of effective mass m^* is considered to exist in a stationary state about the impurity ion under the influence of a net unit charge reduced by the dielectric constant of the medium. By using this model, the optical (radiative) and impact (three-body) recombination coefficients are calculated and compared with the phonon (nonradiative) coefficient calculated by Gummel and Lax for a similar model. Unfortunately, none of the mechanisms considered can yet explain the short time constants found experimentally.

Impurity photoconductivity due to the photoionization of bound charge carriers at neutral impurity centers is observed at low temperatures in germanium and silicon doped with elements from the III and V columns of the periodic table.^{1,2} Under conditions of small signals, where deviations from the equilibrium concentration of charge carriers are small and where thermal equilibrium between the charge carriers and the lattice

¹ Burstein, Oberly, and Davisson, *Phys. Rev.* **89**, 331 (1953).

² V. B. Rollin and E. L. Simmons, *Proc. Phys. Soc. (London)* **B65**, 995 (1952); Burstein, Davisson, Bell, Turner, and Lipson, *Phys. Rev.* **93**, 65 (1954).

may be considered to be preserved, the equation governing the photoresponse is

$$\Delta\sigma/\sigma = \Delta n/n = S\tau/n, \quad (1)$$

where $\Delta\sigma/\sigma$ is the fractional change in conductivity produced by the incident radiation and $\Delta n/n$ is the corresponding fractional change in free charge carrier concentration. S is the rate of optical generation of carriers per unit volume by the incident radiation and τ is the time constant for photoconductivity which may be written as

$$\tau = 1/(B_T N_c) \text{ sec.} \quad (2)$$

Here N_c is the concentration of compensated centers (equal to concentration of acceptors in n -type material and concentration of donors in p -type material) and B_T is the total recombination coefficient.

$$B_T = B_p + B_0 + B_I n \text{ cm}^3 \text{ sec}^{-1}. \quad (3)$$

From Eq. (3) we see that when one of the recombination coefficients becomes dominant, it controls the time constant for photoconductivity.

The rate equation, neglecting diffusion and surface effects, which describes the transient behavior of the free charge carriers is

$$\frac{dn}{dt} = (A_p + A_0 + A_I n)(N - N_c - n) + S - (B_p + B_0 + B_I n)n(N_c + n). \quad (4)$$

N is the concentration of photoconductive centers, A_p is the probability of "thermal" ionization of the centers by the absorption of phonons associated with the lattice vibrations; A_0 is the probability of "thermal" ionization by the absorption of photons associated with the black body radiation within the specimen; and $A_I n$ is the probability of "thermal impact ionization" of the centers by free carriers. The word "thermal" here denotes that the processes described occur at thermal equilibrium. The B_p , B_0 , and $B_I n$ are the corresponding "thermal" recombination coefficients already defined.

The A 's and B 's are related by the principle of detailed balance:

$$A_p/B_p = A_0/B_0 = A_I n/B_I n = K, \quad (5)$$

where K , the equilibrium constant, is

$$K = (2\pi m^* kT/h^2)^{3/2} \exp(-E_i/kT), \quad (6)$$

where m^* is the effective mass of the charge carrier, E_i is the ionization energy of the center, and T is the absolute temperature. The other symbols have their customary meanings.

The impurity levels of the group III and group V impurity centers in germanium and silicon can be interpreted in terms of a hydrogen model.^{3,4} The applicability of the hydrogen model allows ready calculation of the pertinent recombination coefficients by

³ G. L. Pearson and J. Bardeen, *Phys. Rev.* **75**, 865 (1949).

⁴ Burstein, Bell, Davison, and Lax, *J. Phys. Chem.* **57**, 849 (1953).

suitable modification of the theoretical results already available for the hydrogen atom. Each of the coefficients involve recombinations to excited states as well as to the ground state. For the purpose of comparing the relative order of magnitude of the coefficients, however, recombinations involving transitions only to the ground state are considered.

We now calculate B_0 , the optical recombination coefficient. The cross section, R_0 ,⁵ for the optical recombination of a hydrogen-like center in the medium of the semiconductor for the range of velocities of interest here is

$$R_0 = \frac{(n')^3 2^8 \pi^2 e^2 \hbar E_i}{D 3m^{*2} c^3 W} (\exp-4) \text{ cm}^2. \quad (7)$$

(n') is the refractive index, D is the dielectric constant of the medium, c is the velocity of light, W is the kinetic energy of the free carrier, and the other symbols have their customary meanings. The optical coefficient B_0 is obtained by multiplying R_0 by the speed of the charge carrier, v , weighting with the Boltzmann distribution and integrating over the speeds of the carriers.

$$B_0 = \int_0^\infty R_0(v) v f(v) dv \text{ cm}^3 \text{ sec}^{-1}, \quad (8)$$

where

$$f(v) = \frac{4\pi B^3}{\pi^{3/2}} v^2 \exp(-B^2 v^2),$$

with $B^2 = m^*/2kT$. Upon carrying through the indicated integration we obtain

$$B_0 = \frac{(n')^3 (m_0)^{5/2}}{D (m^*)} \times 1.21 \times 10^{-12} \frac{E_i \text{ (ev)}}{T^{3/2}} \text{ cm}^3 \text{ sec}^{-1}, \quad (9)$$

where m^*/m_0 is the ratio of effective mass to free-electron mass.

To calculate $B_I n$, the impact recombination coefficient, we calculate the rate of ionization and then use the principle of detailed balance to obtain the desired result. The cross section, Q_0 , for ionization of a hydrogen-like center calculated by the Born approximation⁶ is

$$Q_0 = 0.285 \frac{4\pi e^4}{DE_i W} \ln \left(\frac{4WD}{0.048E_i} \right) \text{ cm}^2. \quad (10)$$

The use of the Born approximation tends to overestimate the cross section but it is known to give the correct order of magnitude. The probability of ionization, A_I , due to this mechanism is

$$A_I = \int_{v_i}^\infty Q_0 v f(v) dv \text{ cm}^3 \text{ sec}^{-1}, \quad (11)$$

⁵ H. Bethe, *Handbuch Der Physik* (Verlag Julius Springer, Berlin, 1933), second edition, Vol. 24.1, pp. 477, 488.

⁶ N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1952), second edition, p. 247.

TABLE I. Summary of recombination coefficients at 4.2°K for hydrogen-like impurities in silicon and germanium.

Quantity ^a	Germanium		Silicon	
	<i>n</i> -type	<i>p</i> -type	<i>n</i> -type	<i>p</i> -type
E_i ionization energy (ev)	0.01	0.01	0.04	0.046
m^*/m effective mass ratio ^b	0.2	0.2	0.4	0.5
B_0 optical coefficient $\text{cm}^3 \text{sec}^{-1}$	1.3×10^{-12}	1.3×10^{-12}	7.9×10^{-13}	5.2×10^{-13}
B_p phonon coefficient $\text{cm}^3 \text{sec}^{-1}$	3.5×10^{-9}	7.3×10^{-9}	1.0×10^{-8}	1.9×10^{-8}
B_p/B_0	2.7×10^3	5.6×10^3	1.3×10^4	3.7×10^4
$B_I n$ impact coefficient $\text{cm}^3 \text{sec}^{-1}$	$3.5 \times 10^{-18} n$	$3.5 \times 10^{-18} n$	$2.9 \times 10^{-19} n$	$1.2 \times 10^{-19} n$
$B_p/B_I = n^* \text{cm}^{-3}$	1.0×10^9	2.1×10^9	3.5×10^{10}	1.6×10^{11}
T^* (°K)	7.0	7.5	27	38

^a n^* is the calculated free carrier concentration when the coefficients for impact and phonon recombination are equal. T^* is the minimum temperature at which n^* is given by Eq. (15) with $(N - N_c)/N_c$ chosen equal to 10.

^b m^*/m is adjusted to fit the hydrogen model and is used for free as well as bound carriers.

where the lower limit of the integral is v_i , the velocity of the charge carriers corresponding to the ionization energy. This gives

$$A_I = \frac{5.88 \times 10^{-4}}{E_i \text{ (ev)} T^{3/2}} \left(\frac{m_0}{m^*} \right)^{3/2} \times \frac{(1 + 0.522 \log_{10} D)}{D} \exp(-E_i/kT). \quad (12)$$

The principle of detailed balance yields

$$B_I = A_I/K. \quad (13)$$

Combining Eqs. (12), (13), and (6), we get the result

$$B_I = \frac{2.44 \times 10^{-19}}{T^2 E_i \text{ (ev)}} \left(\frac{m_0}{m^*} \right)^2 \frac{(1 + 0.522 \log_{10} D)}{D} \text{cm}^6 \text{sec}^{-1},$$

and the impact recombination coefficient

$$B_I n = \frac{2.44 \times 10^{-19}}{T^2 E_i \text{ (ev)}} n \left(\frac{m_0}{m^*} \right)^2 \times \frac{(1 + 0.522 \log_{10} D)}{D} \text{cm}^3 \text{sec}^{-1}. \quad (14)$$

For the range of temperatures where impurity photoconductivity is measured, the thermal equilibrium concentration of free carriers may be expressed as

$$n = [(N - N_c)/N_c] K. \quad (15)$$

The impact ionization recombination constant then becomes

$$B_I n = \frac{5.88 \times 10^{-4}}{E_i \text{ (ev)}} \frac{N - N_c}{N_c} \left(\frac{m_0}{m^*} \right)^{3/2} \frac{1}{T^{3/2}} \times \frac{(1 + 0.522 \log_{10} D)}{D} \times \exp(-E_i/kT). \quad (16)$$

In practice, photoconductivity is usually measured in the presence of background radiation, in which case n

will be orders of magnitude higher than that given by Eq. (15).

The phonon coefficient for recombination has been calculated by Gummel and Lax.⁷ Their result is

$$B_p = \frac{256\pi^3 \Omega \epsilon_1^2}{M E_i a b} \frac{1}{(\tau_0 a)^4} \left(\frac{\hbar^2}{2m^* a^2 k T} \right)^{3/2} \text{cm}^3 \text{sec}^{-1}, \quad (17)$$

where Ω is the volume of unit cell, ϵ_1 is the Bardeen-Shockley deformation potential constant, M is the mass of one atom, b is the velocity of sound, a is the Bohr radius in the crystal, and τ_0 is the propagation constant of a phonon whose energy is equal to the ionization energy E_i . The constant ϵ_1 may be evaluated⁸ in terms of the lattice mobility, the elastic constants of the material, and the effective masses of the charge carriers. Depending on the values of effective mass used, this coefficient may vary by a factor of two or three. If we take the mass of the free carrier equal to mass of the bound carrier, the effective masses cancel and we obtain

$$B_p = \frac{6.2 \times 10^{-38} b^5}{T^{3/2} [E_i \text{ (ev)}]^2 \mu_L(300^\circ\text{K})}. \quad (18)$$

E_i , the ionization energy, is expressed in electron volts, and $\mu_L(300^\circ\text{K})$ is the lattice mobility at 300°K. The above discussion is based on the applicability of the hydrogen model to impurities in silicon and germanium. For those impurities such as gold and copper which cannot be described in this way, the discussion does not apply although qualitatively similar discussions may be possible. Deviations from the simple hydrogen model also occur even for doping elements from the III and V columns of the periodic table, which may be attributed to the fact that the model does not take into account the structure of the conduction and valence band and the nature of the central atom of the impurity center.⁹ Further, it should be emphasized that the recombination coefficients that have been calculated apply only when the temperature of the charge carrier and that of the lattice are the same. When this is not true, as for

⁷ H. Gummel and M. Lax, Phys. Rev. **97**, 1469 (1955).

⁸ W. Shockley and J. Bardeen, Phys. Rev. **77**, 407 (1950).

⁹ Burstein, Picus, Hennis, Schulman, and Lax (to be published).

TABLE II. Comparison of theoretical and experimental time constants.

Specimen No.	Concentration of photoconductive centers $N - N_e$ (cm^{-3})	Concentration of compensated centers N_e (cm^{-3})	Conc. of free charge carriers in the presence of background radiation ^a n (cm^{-3})	τ (theoretical) (sec)	τ (experimental) (sec)
Ge 132	4×10^{15} (<i>p</i>)	$10^{13} - 10^{15}$	2×10^{10}	$10^{-6} - 10^{-8}$	5×10^{-11}
Si I-123 ^b	2×10^{17} (<i>p</i>)	$10^{15} - 10^{17}$	6×10^7	$10^{-7} - 10^{-9}$	2×10^{-12}
Si I-103 ^b	4×10^{15} (<i>n</i>)	$10^{14} - 10^{15}$	1×10^8	$10^{-6} - 10^{-7}$	5×10^{-9}
Si (R and S) ^c	2×10^{16} (<i>p</i>)	10^{16}	5×10^8	4×10^{-8}	5×10^{-11}

^a Estimated by assuming mobility of 10^4 $\text{cm}^2/\text{volt sec}$ for the germanium at 4.2°K and 10^3 $\text{cm}^2/\text{volt sec}$ for the silicon.

^b Burstein, Oberly, and Davisson, Naval Research Laboratory Report No. 3880, 1952 (unpublished).

^c Data of Rollin and Simmons (reference 2) carried out at 20°K .

impact ionization induced by an electric field,¹⁰ a somewhat different treatment must be used.¹¹

We compare the recombination coefficients for the different processes at a given temperature, 4.2°K . This comparison is summarized in Table I for typical *n*- and *p*-type germanium and silicon specimens. The values given for the competing recombination coefficients have been calculated by assigning the effective masses indicated in the table. These were determined by requiring the hydrogen model to give the correct ionization energy. No allowance has been made for the structure of the valence and conduction band and for the differences in the effective masses for free and bound electrons, in view of the approximate nature of the calculation. From the table, we see that B_0 is always smaller than B_p , the ratio of these constants being about 10^3 and 10^4 in germanium and silicon, respectively. Further, from the identical temperature dependence of these coefficients, this will be the same for all temperatures in the range of interest. Thus, the optical process may always be neglected in favor of the phonon process in determining the time constant. It may be noted, however, that the impact recombination coefficient $B_{I'n}$ is not necessarily small compared to B_p . Included in Table I is the concentration of free charge carriers n_f^* needed to make $B_{I'n}$ equal to B_p . Such concentrations may actually occur in the presence of background radiation, so that, in the absence of explicit information about the free carrier concentration, it is not clear which mechanism is dominant at 4.2°K . Even in the absence of background radiation, however, the exponential temperature dependence of n_f^* causes the impact recombination to become dominant at higher temperatures. The minimum temperature T^* for which this occurs is seen to be about 7°K for germanium and about 30°K for silicon.

It is of interest to compare the time constants obtained by using Eq. (2) with experimentally measured values. To calculate the theoretical value, it is necessary to know the concentration of compensated centers and in the case of impact recombination, the concentration

of free charge carriers. The concentration of compensated centers depends on the purification of the specimens and in this respect, earlier materials are likely to have higher concentrations of compensated carriers. Depending on the concentration of the dominant impurity, the concentration may vary from 10^{13} – 10^{17} cm^{-3} . The concentration of free charge carriers can be obtained from an actual measurement of the Hall constant or from a measurement of the conductivity, and an estimate of the mobility. Using the latter method, we find that concentrations of free carriers in the presence of background radiation may attain the order of 10^{10} cm^{-3} in germanium and somewhat less than this in silicon. Of the three processes considered, this would make "impact" recombination dominant in germanium and phonon recombination dominant in silicon. In Table II¹² are listed the calculated time constants for *p*- and *n*-type silicon and for a *p*-type germanium sample together with experimental values of the time constant. Experimentally it is difficult to measure directly time constants shorter than about 10^{-4} second because of the combination of high specimen resistances, small signals and unavoidable capacitance associated with the mounting of the specimens in low-temperature dewars. From Eq. (1), however, it is possible to obtain an estimate of the time constant by determining experimentally $\Delta\sigma/\sigma$, S , and n and this is how the experimental time constants in Table II were obtained.

The theoretical results appear to give time constants that are larger than the experimental results by a factor of about a thousand. Recombination to higher bound states as well as to the ground state considered, may be expected to yield contributions to the recombination coefficients which will be of the same order of magnitude. This will not greatly affect the theoretical estimate of the time constant and does not resolve the discrepancy. It is felt that the use of the hydrogen model to describe impurities in germanium and silicon is not the cause of the large discrepancy but rather that it is due to another unknown mechanism for recombination which is dominant and which has not yet been considered.

¹⁰ Sclar, Burstein, Turner, and Davisson, Phys. Rev. **91**, 215 (1953). Sclar, Burstein, and Davisson, Phys. Rev. **92**, 858 (1953).

¹¹ N. Sclar and E. Burstein (to be published).

¹² Lerman, Sclar, and Burstein (unpublished).