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Effect of Hydrostatic Pressure on Excess Carrier Lifetimes in Germanium*

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The effect of hydrostatic pressure up to 10 000 kg/cm² on excess carrier lifetime in single-crystal samples of *n*- and *p*-type germanium has been studied over a temperature range of 200°–350°K. The results of the experiments are interpreted in terms of existing theories of charge carrier recombination via recombination centers, and expressions for the variation of recombination level energies within the forbidden energy gap as a function of pressure are inferred. These variations are understandable on the basis of a simple Bohr model of defect levels in a dielectric medium whose dielectric constant varies with pressure. Tentative suggestions relating the recombination centers in the experimentally investigated samples to the presence of interstitial and substitutional impurity atoms are advanced.

I. INTRODUCTION

Excess carrier lifetime is a highly structure-sensitive parameter of a semiconducting crystal. When the equilibrium carrier concentration is disturbed, processes are initiated which act to return the system to equilibrium. In semiconductors such as germanium and silicon, the primary mechanism responsible for the establishment of equilibrium appears to be recombination of these carriers via certain types of impurity centers, defects or flaws in the bulk of the crystal. Energy levels in the bandgap are associated with distortions of the periodicity of the lattice caused by these defects. The application of hydrostatic pressure may be expected to produce a change in the energy of these levels relative to the band edges and the Fermi level, altering their occupation statistics and consequently the excess carrier lifetime. Experimentally determined changes in excess carrier lifetime can be related to changes in the characteristics of the defect levels, and can be used to obtain useful data involving the fundamental nature of these levels.

II. INTERACTION OF EXCESS CARRIERS WITH RECOMBINATION CENTERS

The kinetics of the recombination process have been treated by various authors,[1–4] and a comprehensive discussion is given by Blakemore.[5] In the experiments to be described, the lifetimes are measured under transient conditions. It can be shown[5] that for small flaw densities and low injection levels, the lifetime obtained through transient measurements is identical to that obtained by Shockley and Read[1] under steady-state conditions, i.e.,

$$\tau=(c_pN_r)^{-1}(n_0+n_1)/(n_0+p_0)+(c_nN_r)^{-1}(p_0+p_1)/(n_0+p_0), \quad (2.1)$$

where

n_0 equilibrium density of electrons in the conduction band
p_0 equilibrium density of holes in the valence band
n_1 density of electrons in the conduction band when the flaw level coincides with the Fermi level
p_1 density of holes in the valence band when the flaw level coincides with the Fermi level
N_r flaw density
c_n electron capture coefficient, defined by $c_n=\sigma_n\langle v_n\rangle$, where $\langle v_n\rangle$ = average thermal velocity, σ_n = capture cross section
c_p hole capture coefficient.

Equation (2.1) follows from the rate equations

$$d\delta n/dt=-c_n[N_r^0\delta n-(n_0+n_1)\delta n_r]$$
$$d\delta p/dt=-c_p[N_r^-\delta p+(p_0+p_1)\delta n_r], \quad (2.2)$$

and the equation of charge neutrality

$$\delta n_r+\delta n=\delta p, \quad (2.3)$$

where δn is the density of excess electrons in the conduction band, δp is the density of excess holes in the valence band, δn_r is the density of excess electrons in the flaws, N_r^- is the equilibrium density of occupied flaws (filled with electrons) and N_r^0 is the equilibrium density of empty flaws (filled with holes). In this treatment, it is assumed that electrons and holes recombine via a single discrete recombination level. For *n*-type material, Eq. (1.1) becomes

$$\tau=(c_pN_r)^{-1}\left(1+\exp\frac{E_r-E_f}{kT}\right)+(c_nN_r)^{-1}\frac{N_v\exp(E_v-E_r)/kT}{N_c\exp(E_f-E_c)/kT}, \quad (2.4)$$

where the following definitions have been used:

$$n_1=N_c\exp(E_r-E_c)/kT$$
$$p_1=N_v\exp(E_v-E_r)/kT$$
$$n_0=N_c\exp(E_f-E_c)/kT$$
$$p_0=N_v\exp(E_v-E_f)/kT.$$

In these expressions N_c and N_v are the effective density of conduction and valence band levels, and E_c, E_v, E_r, and E_f are the energies associated with the conduction band edge, the valence band edge, the recombination level, and the Fermi level, respectively. The variation

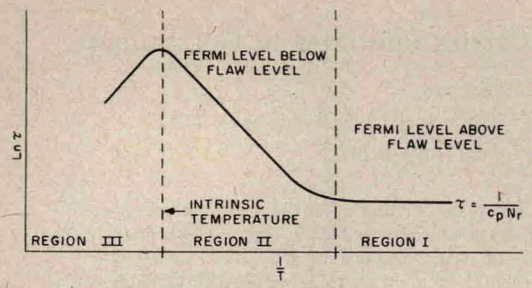

FIG. 1. Variation of excess carrier lifetime with temperature of n-type material when the recombination level is in upper half of the bandgap. The temperature dependence of excess carrier lifetime for n-type crystals when the recombination level is in the lower half of the bandgap is essentially similar, although the functional relationships differ.

of lifetime with temperature for an n-type sample is shown in Fig. 1.

Measurement of the lifetime in Region II reveals the separation of the defect (recombination) level from the nearest band edge. It is possible to determine which band edge is involved provided information concerning the capture coefficients is known. This information may be obtained by comparing the low-temperature lifetime $1/c_pN_r$ with the intercept of the line in Region II.[6]

The n-type sample used in these experiments exhibited the characteristics of recombination at a single flaw level. Another important case involves two defect levels, one functioning as a recombination center and the other as a trap.[7] The rate equations are easily extended to the case of two flaw levels (again assuming low injection conditions). They become

$$d\delta n/dt = -c_{n_1}[N_1^0\delta n - (n_0+n_{11})\,\delta n_{r_1}] - c_{n_2}[N_2^0\delta n - (n_0+n_{12})\,\delta n_{r_2}],$$

$$d\delta p/dt = -c_{p_1}[N_1^-\delta p + (p_0+p_{11})\,\delta n_{r_1}] - c_{p_2}[N_2^-\delta p + (p_0+p_{12})\,\delta n_{r_2}] \quad (2.5)$$

and the equation of charge neutrality is

$$\delta n_{r_1}+\delta n_{r_2}+\delta n = \delta p. \quad (2.6)$$

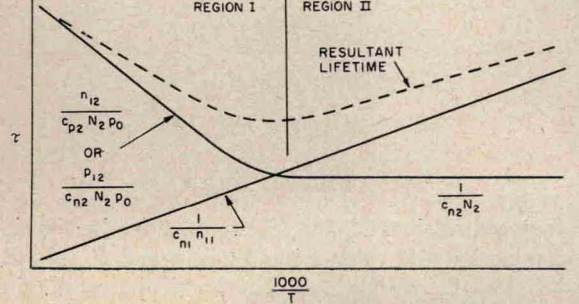

FIG. 2. Resultant excess carrier lifetime in p-type material containing a recombination center and an electron trap.

The subscripts refer to the two flaws, 1 and 2. The direct transfer of a carrier from one flaw to the other is neglected, since the flaws are spatially separated in the crystal. For p-type material containing an electron trap ($c_{p_1}=0$), again assuming small flaw densities, the resultant lifetime is

$$\tau = (1/c_{n_1}n_{11})+(1/c_{n_2}N_2)+(n_{12}/c_{p_2}N_2p_0), \quad (2.7a)$$

or

$$\tau = (1/c_{n_1}n_{11})+(1/c_{n_2}N_2)+(p_{12}/c_{p_2}N_2p_0), \quad (2.7b)$$

depending upon whether the recombination center is in the upper or lower half of the bandgap. Note that the first term describes the effect of the trap, and the last two terms describe the effect of the recombination center. Similar equations evolve for p-type material containing a hole trap and a recombination center, and the results of both these cases are shown in Figs. 2 and 3. It is noted that when trapping is present it is impossible to determine in which half of the bandgap the recombination center lies, since the low-temperature lifetime limit $1/c_{n_2}N_2$ is masked by the presence of the trap. The lifetime in the high-temperature region (Region I) is governed by the recombination center, and in the low-temperature region (Region II) by the trap.

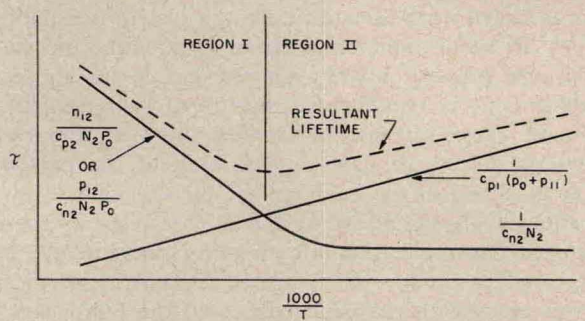

FIG. 3. Resultant excess carrier lifetime in p-type material containing a recombination center and a hole trap.

III. PRESSURE EFFECTS

One may now proceed to derive expressions for the excess carrier lifetime as a function of pressure in a variety of circumstances. It is assumed that the effective masses and capture coefficients are independent of pressure; the validity of these assumptions will be examined later. The first case to be considered is that of n-type containing a single recombination center whose energy lies in the upper half of the bandgap. The lifetime in Region II of Fig. 1 is

$$\tau = (c_pN_r)^{-1}(n_1/n_0) = (c_pN_rn_0)^{-1}N_c\exp[(E_r-E_c)/kT] = [2(2\pi m_n{}^*k)^{3/2}/c_pN_rn_0h^3]T^{3/2} \times \exp[(E_r-E_c)/kT]. \quad (3.1)$$

The conduction band-edge energy E_c can be written in the form

$$E_c \equiv E_{\text{gap}}(P,T) = E_{\text{gap}}(0,0)+\alpha P-\beta T, \quad (3.2)$$

where α and β are the pressure and temperature coefficients of the bandgap. It is assumed in writing this expression that E_v, the valence band-edge energy, is zero. It is now assumed that the change in the recombination center energy may be described by

$$E_r(P)=E_r(0)+\gamma P, \tag{3.3}$$

where γ is the pressure coefficient of the recombination center. Equation (3.1) becomes

$$\tau=\frac{2(2\pi m_n{}^*k)^{3/2}}{c_pN_rn_0h^3}T^{3/2}\exp\frac{[E_r(0)-E_{\rm gap}(0,0)]}{kT}\times\exp\frac{(\gamma P-\alpha P+\beta T)}{kT}. \tag{3.4}$$

In this equation $E_r(0)-E_{\rm gap}(0,0)$ may be inferred from the variation of lifetime with temperature (the slope of the curve in Region II of Fig. 1). The measurement of lifetime as a function of pressure then yields the pressure coefficient of the recombination-center energy.

When the recombination-center energy lies in the lower half of the bandgap, the excess carrier lifetime, in Region II, is

$$\tau=[2(2\pi m_p{}^*k)^{3/2}/c_nn_0N_rh^3]T^{3/2}\exp[(E_v-E_r)/kT], \tag{3.5a}$$

resulting in a pressure-dependent lifetime given by

$$\tau=[2(2\pi m_p{}^*k)^{3/2}/c_nn_0N_rh^3]T^{3/2}\times\exp[-E_r(0)/kT]\exp(-\gamma P/kT). \tag{3.5b}$$

In deducing this expression from (3.5a) it should be recalled that one assumes that $E_v=0$ to fix the origin of the energy scale.

The low-temperature lifetime in Region I of Figs. 1 and 2 is given by

$$\tau=1/c_pN_r,$$

regardless of the position of the recombination center. In this region, pressure experiments may reveal an effect upon the hole capture coefficient, testing the validity of the assumption of constant capture coefficients. It is assumed that the uniform hydrostatic compression does not change the density of defects.

Turning now to the situation where a recombination center is present in conjunction with a trap, it was shown in Figs. 2 and 3 that in the low-temperature region, the excess carrier lifetime is governed by the trap, and in the high-temperature region by the recombination center. The energies of these levels are obtained from the slope of the curve in the two regions. The pressure coefficients of the defect levels, which may be of different types, can be determined by performing the pressure experiments in each region, thus isolating the dominant effect.

The lifetime in the high-temperature region is (for

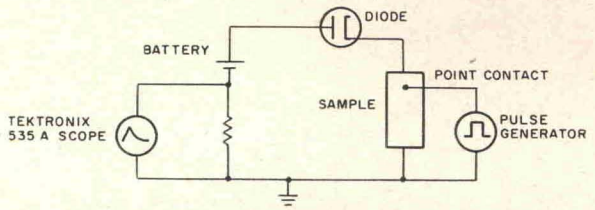

FIG. 4. Circuit used to inject excess carriers and to measure the change in conductivity.

p-type material)

$$\tau=n_{12}/c_{p_2}N_2p_0=[2(2\pi m_n{}^*k)^{3/2}/c_{p2}N_2p_0h^3]T^{3/2}\times\exp[(E_r-E_c)/kT], \tag{3.6a}$$

or

$$\tau=p_{12}/c_{n_2}N_2p_0=[2(2\pi m_p{}^*k)^{3/2}/c_{n_2}N_2p_0h^3]T^{3/2}\times\exp(-E_r/kT), \tag{3.6b}$$

depending upon whether the recombination center is in the upper or lower half of the bandgap. The pressure-dependent expressions are obtained in the same manner as were Eqs. (3.4) and (3.5). For the case of electron trapping, the lifetime in the low-temperature region (Fig. 2) is

$$\tau=1/c_{n_1}n_{11}=[h^3T^{-3/2}/c_{n_1}2(2\pi m_n{}^*k)^{3/2}]\times\exp[(E_c-E_t)/kT],$$

which results in a pressure-dependent lifetime

$$\tau=[h^3T^{-3/2}/c_{n_1}2(2\pi m_n{}^*k)^{3/2}]\times\exp\{[E_{\rm gap}(0,0)-E_t(0)]/kT\}\times\exp[(\alpha P-\gamma P-\beta T)/kT]. \tag{3.7}$$

The hole-trapping situation may be treated similarly.

IV. EXPERIMENTAL

Two samples were used; the first was a 14-Ω cm n-type antimony-doped germanium sample, and the other a 5-Ω cm p-type gallium-doped germanium sample. The quoted resistivities are room-temperature (300°K) values. The sample dimensions were approximately $0.80\times2.90\times0.65$ cm. They were lapped and polished (the final polishing stage using 1-μ diamond polish) and finally etched with a standard CP4 etchant.

Excess carriers were electrically injected through a point contact, and the lifetime deduced from the time decay of the excess conductivity. The circuit used to inject the carriers and measure the change in conductivity is shown in Fig. 4.

The temperature range covered in these experiments was from −70° to 80°C. The lower-temperature measurements (from −70°C to room temperature) were performed by placing the sample in an evacuated brass can and immersing the assembly in a Dewar containing a mixture of dry ice and acetone. Measurements were made while the mixture warmed up to room tempera-

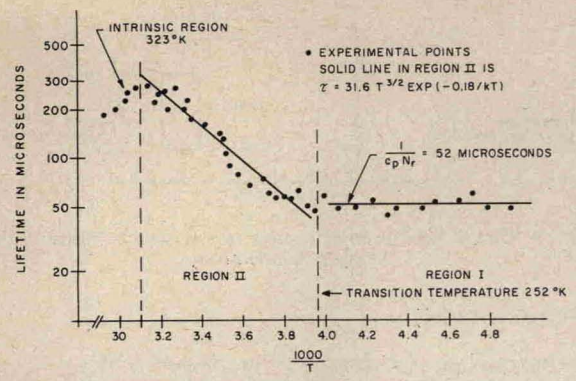

FIG. 5. Variation of excess carrier lifetime with temperature for 14-Ω cm n-type germainum.

ture. To go above room temperature, the dry-ice–acetone mixture was replaced by glycerin, into which was inserted a heater. Temperatures were measured with a Chromel–Alumel thermocouple attached to a piece of germanium of the same dimensions as the sample, and located in close proximity to it.

The pressure experiments are performed in an apparatus capable of generating a hydrostatic pressure to 10 000 kg/cm². The pressure is measured with a manganin resistance coil, which has been calibrated using a dead-weight gauge. The pressure bomb containing the sample was immersed in an oil bath provided with a heater and a temperature-regulating circuit.

V. RESULTS

The results of the measurements of lifetime versus temperature for the 14-Ω cm n-type sample are shown in Fig. 5. Comparison with Fig. 1 suggests that this sample contains a single recombination center. The position of the recombination center in the bandgap is calculated from the slope in Region II. A least-squares fit of the data leads to an equation of the form

$$\tau = 31.6T^{3/2}\exp(-0.18/kT). \qquad (5.1)$$

In this equation cgs units are used, the activation energy being expressed in electron volts. Comparison with Eqs. (3.1) and (3.5a) shows that

$$(1/c_p N_r n_0)[2(2\pi m_n{}^* k)^{3/2}/h^3] = 31.6 \text{ deg } \mu\text{sec}$$

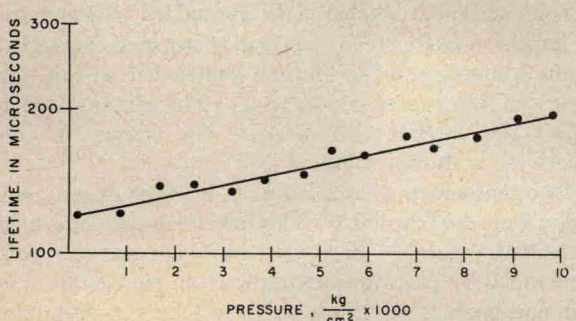

FIG. 6. Variation of excess carrier lifetime with pressure for 14-Ω cm n-type germanium at $T = 298°K$.

or

$$(1/c_n N_r n_0)[2(2\pi m_p{}^* k)^{3/2}/h^3] = 31.6 \text{ deg } \mu\text{sec},$$

depending upon the position of the recombination center. Upon substitution of the known constants,[8] these equations give

$$1/c_p N_r = 7 \ \mu\text{sec} \quad \text{or} \quad 1/c_n N_r = 4 \ \mu\text{sec}.$$

However, from the low-temperature lifetime in Region I, it is known that $1/c_p N_r = 52$ μsec. Since there is about an order-of-magnitude difference between $1/c_p N_r$ as given by the lifetime in Region I and the quantity $1/c_p N_r$ as calculated from the slope in Region II, it may be inferred that the quantity calculated from the slope is in fact $1/c_n N_r$. Consequently, the recombination process takes place via a level 0.18 eV above the valence band, and since $c_n > c_p$, the defect is donor like.

In view of the above result, the variation of lifetime

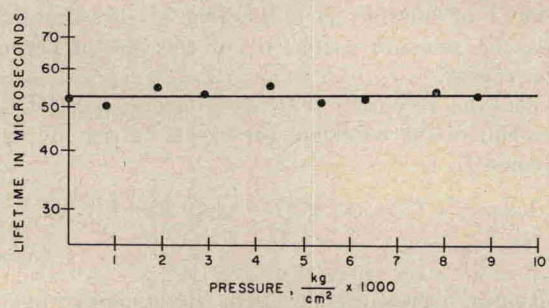

FIG. 7. Excess carrier lifetime versus pressure for n-type sample at $T = 244°K$.

with pressure for the n-type sample is described by Eq. (3.5b). Figure 6 shows the results of pressure measurements at 24.8°C, or $1000/T = 3.36$. A least-squares fit of the data to Eq. (3.5b) in the form

$$\tau = A\exp(-\gamma P/kT),$$

results in a pressure coefficient having the value

$$\gamma = -1.2\times10^{-6} \text{ eV cm}^2 \text{ kg}^{-1}. \qquad (5.2)$$

Thus the recombination center approaches the valence band at the above rate.

A measurement of the lifetime as a function of pressure in the low-temperature region of Fig. 5 should reveal information concerning the capture coefficient c_p. Figure 7 shows the effect of pressure on the lifetime at $1000/T = 4.1$ ($T = 244°K$). As one may easily see, the lifetime is approximately constant over the pressure range, indicating that the capture coefficient c_p is practically independent of pressure.

The variation of lifetime with temperature from the gallium-doped 5-Ω cm p-type germanium is shown in Fig. 8. A comparison with Figs. 2 and 3 suggests that both a recombination center and a trap are present. At temperatures in excess of $1000/T = 4.06$ (246°K) the lifetime limiting process is dominated by the recombination center. The lifetime in this region is given through

Eqs. (1.7a) and (1.7b) by

$$\tau = n_{12}/c_{p_2}N_2P_0 = [2(2\pi m_n{}^*k)^{3/2}/c_{p_2}N_2p_0h^3]T^{3/2} \times \exp[(E_2-E_c)/kT], \quad (5.3a)$$

or

$$\tau = p_{12}/c_{p_2}N_2p_0 = [2(2\pi m_p{}^*k)^{3/2}/c_{p_2}N_2p_0h^3]T^{3/2} \times \exp[(E_v-E_2)/kT]. \quad (5.3b)$$

A least-squares fit of the data gives

$$\tau = 4.1T^{3/2}\exp(-0.13/kT). \quad (5.4)$$

The recombination center lies 0.13 eV from one of the band edges. For this case, it is not possible to differentiate between Eqs. (5.3a) and (5.3b) since the constant low-temperature lifetime $1/c_{n_2}N_2$ is masked by the presence of the trap.

At temperatures below $1000/T=4.06$, the excess carrier lifetime increases, which is characteristic of a trapping process. The slope in the trapping region indicates that the trap lies 0.05 eV from one of the band edges.

The measurement of lifetime as a function of pressure was performed at $1000/T=3.10$, which is well into the region dominated by the recombination center. The results are shown in Fig. 9. A fit of the data to Eqs. (5.3a) and (5.3b) (substituting the pressure-dependent terms) results in a pressure coefficient of

$$\gamma = -1.5\times10^{-6}\ \text{eV cm}^2\ \text{kg}^{-1},$$

and the recombination level approaches the nearest band edge at the above rate. No pressure measurements were made in the trapping region, since the temperatures well into the trapping region where the measurements should be made are too low to permit the high-pressure system to function properly.

VI. DISCUSSION

In order to interpret the experimental results, it is necessary to examine the various types of flaws and dislocations which may function as recombination and trapping centers.

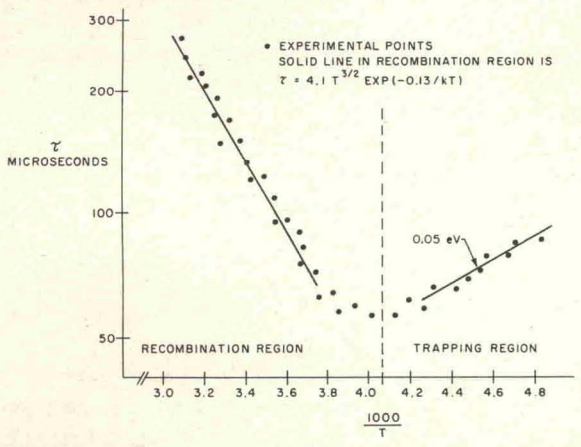

FIG. 8. Excess carrier lifetime for 5-Ω cm p-type sample as a function of temperature, showing both a recombination center and a trap.

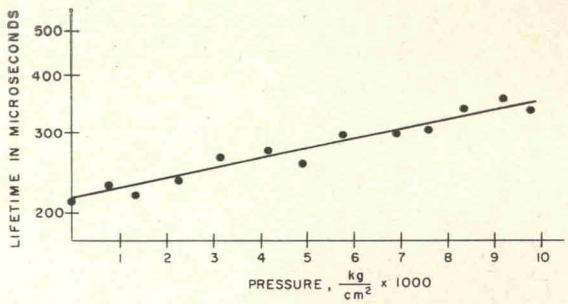

FIG. 9. Excess carrier lifetime versus pressure for 5-Ω cm p-type sample at $T=322$°K.

Consider first the introduction of chemical impurities in the germanium lattice. Depending upon their size and nature, these impurity atoms may be incorporated in the lattice either substitutionally or interstitially. Atoms which are easily ionized, and known to be partially present interstitially in germanium such as copper, nickel, and lithium are expected to act as donors, since none of the electrons of these atoms are required for bonding purposes. Unfortunately, a general theory of the electrical effects of interstitial atoms in semiconductors is nonexistent, and it is difficulty to infer anything about the depth of these donor levels. However, when metal ions such as these are substitutionally placed, they act as acceptors, since there is then a deficiency of electrons. Table I shows the position and character of the energy levels associated with the more common chemical impurities in germanium.[9]

The effect of hydrostatic pressure on these impurity levels may be deduced in a simple manner by assuming that a hydrogenic atom model is applicable. The ionization energy is then given by

$$E_i = me^4/2K^2\hbar^2, \quad (6.1)$$

where K is the dielectric constant. The applicability of this picture, particularly in a quantitative sense, is circumscribed by the fact that the Bohr radii for levels as deep lying as these are so small that the region of the crystal enclosed by them is not very well represented as a uniform linear dielectric. Nevertheless in the absence of any more sophisticated theory (and there appears to be none applicable to deep-lying states) we shall use this simple picture as a basis for discussion of our experimental results. The dielectric constant for germanium is known to decrease with pressure.[10] Therefore, on the basis of this admittedly naïve and oversimplified model, a donor level would be expected to shift toward the valence band, and an acceptor level toward the conduction band. Dislocation defects, due to the unpaired or "dangling" bond which inevitably results, are expected to act as acceptor centers.

The use of radiation as a method of introducing rec-

TABLE I. Activation energies of chemical impurities in germanium. E_c: Energy of conduction band edge. E_v: Energy of valence band edge. E_i: Energy of impurity level. A: Acceptor. D: Donor.

Element	Type	E_c-E_i (eV)	E_i-E_v (eV)
Cu(1)	A	...	0.32
Cu(2)	A	...	0.04
Cu(3)	A	0.26	...
Au(1)	D	...	0.05
Au(2)	A	...	0.15
Au(3)	A	0.20	...
Au(4)	A	0.04	...
Ag(1)	A	...	0.14
Ag(2)	A	0.28	...
Ag(3)	A	0.09	...
Ni(1)	A	...	0.22
Ni(2)	A	...	0.30
Fe(1)	A	...	0.34
Fe(2)	A	0.27	...
Co(1)	A	...	0.25
Co(2)	A	0.31	...
Mn(1)	A	...	0.16
Mn(2)	A	0.35	...

tain types of defects has resulted in a wealth of information on the nature of defect structures. The subject has been extensively reviewed.[11,12] The energy levels which have been observed in germanium irradiated by deuterons, electrons, neutrons, and gamma rays have been discussed by Fan and Lark-Horovitz.[13] A donor level appearing at 0.18 eV above the edge of the valence band has been attributed to an interstitial atom.[14]

The recombination center in the n-type sample was found to be a donor-type level 0.18 eV from the valence band. If the donor level is associated with a chemical impurity, then Eq. (6.1) can be used to calculate the change in ionization energy with pressure. The fractional change in dielectric constant with pressure $(1/K)(dK/dP)$, is -1.2×10^{-6} cm^2/kg, and the fractional change in the effective mass is $(1/m)(dm/dP)=5\times10^{-6}$ cm^2/kg. Equation (6.1) may be differentiated and written in the form

$$dE_i/dP=(me^4/2K^2\hbar^2)\times[(1/m)(dm/dP)-(2/K)(dK/dP)]. \quad (6.2)$$

If the factor multiplying the right-hand side of Eq. (6.2) is assumed to be 0.18 eV, then

$$dE_i/dP=0.18(5\times10^{-6}+2\times1.2\times10^{-6})$$
$$=1.3\times10^{-6}\text{ eV cm}^2\text{ kg}^{-1}$$

which is a value remarkably close to that found from the measurements.

The agreement between the above results and the measurements must be regarded as somewhat fortuitous, since it is not at all clear that Eq. (6.1) is applicable to deep-lying levels. For example, if one calculates the radius of the first Bohr orbit corresponding to an energy of 0.18 eV and a dielectric constant of 16, the result is a radius of about 3 Å, or just slightly more than the interatomic distance in germanium (2.44 Å). The concept of a dielectric constant loses its meaning under these circumstances. Reference to Table I shows that none of the common chemical impurities behave as a donor level 0.18 eV from the valence band. It is therefore regarded as unlikely that the recombination process proceeds via a substitutional chemical impurity.

The donor nature of the recombination center mitigates against an edge (or any other) dislocation acting as a recombination center since, due to the "dangling" bonds which are present in such dislocations, they are expected to act as acceptors.

It is known from the effects of neutron radiation that heavy particle radiation can result in an atom moving to an interstitial site, and it is also quite possible that such an interstitial results during the growth of the crystal.[15] The interstitial atom may act as a donor, and may result in a donor level 0.18 eV from the valence band. The application of pressure, resulting in a compression of the lattice and an increase in the interaction between neighboring atoms, is expected to increase the activation energy of the recombination level, and the measurements show this to be the case. Therefore, it is suggested that for the n-type sample the recombination process occurs via a center which is associated with an interstitial atom.

The other terms in the expression for the lifetime [Eq. (3.5a)] which may contribute to a change in the excess carrier lifetime, are the electron capture coefficient c_n and the hole effective mass m_p^*. The change in effective mass is approximately 2% in 10 000 kg/cm^{-2}. This increase is not nearly enough to account for the increase in lifetime by approximately 60%. In addition, Fig. 7 shows that the hole capture coefficient is independent of pressure. It is considered unlikely, then, that the electron capture coefficient is strongly pressure dependent. It is possible to explain the results of Fig. 7 using a simple model of carrier capture.[4] An estimate of the capture coefficient can be made by assuming that the carrier will be captured if the Coulomb binding energy is comparable to kT. Then there will be some capture "radius" r such that

$$e^2/Kr=kT.$$

The capture cross section is then

$$\sigma=\pi r^2=\pi[e^4/K^2(kT)^2].$$

The capture cross section and the capture coefficient are related by the thermal velocity of the carrier, i.e., $c=\sigma\langle v\rangle$, where $\langle v\rangle=(8kT/\pi m)^{1/2}$. The above equation

may be differentiated and written in the form

$$dc/dP=-[(8\pi)^{1/2}e^4/(kT)^{3/2}m^{1/2}K^2]$$
$$\times\{2[K^{-1}(dK/dP)]+\tfrac{1}{2}[m^{-1}(dm/dP)]\}.$$

The terms in the bracket are of comparable magnitude and opposite sign, and the capture coefficient is therefore approximately independent of pressure. For this reason the change in excess carrier lifetime with pressure may be attributed almost entirely to a change in the energy of the recombination level.

The analysis of the data for the p-type sample is complicated by the fact that a trapping center exists in conjunction with a recombination center. This situation results in a loss of information in the low-temperature region about the capture coefficient, and hence a determination of the type of centers (donor or acceptor) is impossible. The recombination level lies 0.13 eV from one of the band edges, and approaches that band edge as the pressure increases. If the recombination level results from a chemical impurity, Table I shows that there are three impurities having ionization energies close to 0.13 eV: Au, 0.15 eV; Ag, 0.14 eV; and Mn, 0.16 eV. Lacking any more definitive information about the parameters of this recombination center, it is not constructive to speculate further about its specific character.

The slope of the lifetime–temperature curve in the low-temperature region indicates that the trapping center is close to one of the band edges, thus confirming its behavior as a trap. However, no other information is available concerning the nature of the trap.

VII. SUMMARY

Measurements of the excess carrier lifetime as a function of temperature and pressure have been made on n- and p-type germanium.

The 14-Ω cm n-type sample contains a donor-type recombination level 0.18 eV from the valence band, as determined from the temperature variation of the lifetime utilizing the Shockley–Read theory. Measurement of the pressure dependence of the lifetime up to 10 000 kg/cm^{-2} indicates that this recombination level approaches the valence band at the rate of 1.2×10^{-6} eV cm^2 kg^{-1}. From the behavior of the lifetime under hydrostatic pressure, it was inferred that the level is associated with an interstitial impurity. Low-temperature ($\sim$240°K) data indicate that the electron and hole capture coefficients are independent of pressure.

The 5-Ω cm p-type sample contains a recombination level 0.13 eV from one of the band edges, and a trap level 0.05 eV from one of the band edges. Pressure measurements on the recombination level showed that it approaches the nearest band edge at a rate of 1.5×10^{-6} eV cm^2 kg^{-1}.

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[7] The distinction between the recombination center and the trap is governed by the relative probability of capture of the opposite type carrier and the thermal emission of a carrier back to its respective band. If, for example, a flaw captures an electron and the next most probable event is the subsequent capture of a hole, the flow is acting as a recombination center. On the other hand, if the next most probable event is the emission of that electron back to the conduction band, the flaw is acting as a trap.

[8] Using $m_n^*=0.25m_0$, $m_p^*=0.40m_0$, where m_0 is the free electron mass, and using an average value of the majority carrier density n_0 over the temperature range covered in Region II of 1.4×10^{-14} cm^{-3}.

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[15] In view of the possibility of thermal migration of impurity atoms during the growth process, and the possibility of their interaction with vacancies and dislocations, it is not entirely clear that significant concentrations of interstitial atoms may result from normal crystal growth. Under the circumstances, this suggestion should be regarded as tentative and qualified, but it is not inconsistent with the evidence now available. It should also be noted that concentrations of recombination centers much smaller than those normally associated with substitutional doping impurities may be quite significant in affecting excess carrier lifetime in germanium crystals.

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