Effect of Hydrostatic Pressure on Excess Carrier Lifetimes in Germanium*

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The effect of hydrostatic pressure up to $10\ 000\ \text{kg/cm}^2$ on excess carrier lifetime in single-crystal samples of *n*- and *p*-type germanium has been studied over a temperature range of $200^\circ-350^\circ\text{K}$. 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 shown⁵ that for small flaw densities and low injection levels, the lifetime obtained through transient measurements is identical to that obtained by Shockley and Read¹ under steadystate conditions, i.e.,

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

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, $\sigma_n =$ capture cross section
- c_p hole capture coefficient.

Equation (2.1) follows from the rate equations

$$d\delta n/dt = -c_n [N_r^0 \delta n - (n_0 + n_1) \delta n_r]$$

$$d\delta p/dt = -c_n [N_r^- \delta p + (p_0 + p_1) \delta n_r], \qquad (2.2)$$

and the equation of charge neutrality

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

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

$$r = (c_p N_r)^{-1} \left(1 + \exp \frac{E_r - E_f}{kT} \right) + (c_n N_r)^{-1} \frac{N_v}{N_c} \frac{\exp(E_v - E_r)/kT}{\exp(E_f - E_c)/kT}, \quad (2.4)$$

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

or



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

$$d\delta n/dt = -c_{n_1} [N_1^0 \delta n - (n_0 + n_{11}) \delta n_{r_1}] -c_{n_2} [N_2^0 \delta n - (n_0 + n_{12}) \delta n_{r_2}], d\delta p/dt = -c_{p_1} [N_1^- \delta p + (p_0 + p_{11}) \delta n_{r_1}] -c_{p_2} [N_2^- \delta p + (p_0 + p_{12}) \delta n_{r_2}]$$
(2.5)

and the equation of charge neutrality is

$$\delta n_{r_1} + \delta n_{r_2} + \delta n = \delta p. \tag{2.6}$$



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

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

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

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 im-



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

possible 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.

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

$$\begin{aligned} \pi &= (c_p N_r)^{-1} (n_1/n_0) = (c_p N_r n_0)^{-1} N_c \exp[(E_r - E_c)/kT] \\ &= [2(2\pi m_n *k)^{3/2}/c_p N_r n_0 h^3] T^{3/2} \\ &\times \exp[(E_r - E_c)/kT]. \quad (3.1) \end{aligned}$$

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

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