REDISTRIBUTION OF CARRIERS BETWEEN VALLEYS IN AN ELECTRIC FIELD

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The passage of an electric current through plates, cut from a many-valley semiconductor such as n-type Ge, is considered. It is shown that at low temperatures, when the mean free path of the carriers associated with the intervalley scattering is sufficiently long, the conditions for the continuity of the electron current in each of the valleys lead to a strong departure from the equilibrium electron distribution between the valleys in the surface layer; consequently, some of the valleys are considerably enriched with electrons while others are depleted. When the free-transit time associated with the intervalley scattering is $\approx 10^{-9}$ sec, a considerable redistribution of carriers takes place, in fields of the order of several volts/cm, at depths up to $\approx 10\,\mu$. The intervalley redistribution leads to an electrical conductivity anisotropy, to its dependence on the surface band curvature (a kind of "field effect"), to the appearance of nonlinearity in weak fields, etc. It is also shown that weakly damped waves, associated with the intervalley redistribution of carriers, may appear in strong electric fields.

INTRODUCTION

MANY well-investigated n-type semiconductors (Ge, Si, several intermetallic compounds) have electron energy spectra with a many-valley structure. The contribution of each of the valleys to the electrical conductivity of a crystal is, as a rule, strongly anisotropic; however, the total electrical conductivity of cubic crystals of this type is isotropic because of the symmetrical distribution of the valley system.

Electrons in each of the valleys experience two types of collision: intravalley and intervalley. Collisions of the former type make the main contribution to the electrical resistance and are investigated by the usual methods employing transport processes. Collisions of the second type are associated with large momentum transfer (of the order of the reciprocal lattice periods) and, therefore, they are much less probable. In fact, during cooling, the probability of the intervalley lattice scattering decreases exponentially as the activation energy, equal to the energy of the intervalley phonons (i.e., energy of the order of the Debye energy) increases. The intervalley impurity scattering is also relatively weak compared with the intravalley scattering since it cannot be caused by long-range Coulomb interactions but is due to some special processes. Therefore, the influence of the intervalley scattering on the transport coefficients at low temperatures is weak; however, it increases considerably the absorption of ultrasound.[1,2] The free-transit times τ', associated with the intervalley scattering and found from the absorption of ultrasound in pure samples of Ge at 30° K, are longer than 10^{-9} sec,[2] which agrees with the mean free path lengths $l' = \bar{v}\tau' \approx 10^{-2}$ cm ($\bar{v}$ is the average thermal velocity).

The high value of τ' in perfect samples allows us to consider the electrons belonging to different valleys as, to a considerable extent, independent groups of carriers described by a system of interrelated diffusion equations. In the presence of a weak external electric field **E**, these equations may be satisfied if we assume that the densities in all the valleys are equal to their equilibrium values. A completely different situation obtains at the surface of the sample. Since the ellipsoidal constant-energy surfaces, corresponding to different valleys, are inclined at different angles to the surface, the electric field parallel to the surface plane accelerates some electrons to the surface but repels others away from it. If there is no very effective mechanism of intervalley scattering at the surface, which would re-establish equilibrium, then the density of electrons belonging to the former groups increases and the density of the latter groups decreases; carriers are "pumped" from some valleys to others. At higher values of l', the region of nonequilibrium distribution of electrons should have a macroscopic thickness considerably greater than the mean free path l associated with the intravalley scattering. In this region, the electrical conductivity should be strongly anisotropic.

We consider below the characteristics of the electrical conductivity of finite semiconductor samples, associated with the intervalley redistribution of carriers in the surface region, as well as the factors governing the magnitude of this effect. We show, moreover, that, for certain relationships between **E** and τ', weakly damped oscillations, accompanied by "leakage" of electrons between valleys, may be propagated in many-valley semiconductors.

2. INTERVALLEY REDISTRIBUTION

We shall assume that τ' is considerably greater than the characteristic time of the intravalley relaxation. Then we can write down the diffusion equation for electrons belonging to the α-th valley:

$$\frac{\partial n_\alpha}{\partial t} = \frac{1}{e}\operatorname{div}\mathbf{J}_\alpha + {\sum_\beta}' (R_{\beta\alpha} - R_{\alpha\beta}),$$

$$\mathbf{J}_\alpha = en_\alpha \hat{u}_\alpha \mathbf{E} + e\hat{D}_\alpha \nabla n_\alpha, \tag{1}$$

where n_α, $\mathbf{J}_\alpha$, $\hat{D}_\alpha$, $\hat{u}_\alpha$ are, respectively, the carrier density, current density, diffusion coefficient tensor, and the mobility tensor for electrons, and $R_{\alpha\beta}$ is the rate of transitions from valley α to valley β; the prime of the summation sign denotes that $\beta \neq \alpha$.

We shall consider only the case of weak fields **E**, when Eq. (1) can be linearized. For a plate bounded by the planes $y = \pm d$, we obtain, instead of Eq. (1),

$$\frac{\partial n_\alpha'}{\partial t} = D_{yy}{}^\alpha \frac{d^2 n_\alpha'}{dy^2} + n_\alpha{}^0 u_{yy}{}^\alpha \frac{dE_y}{dy} + {\sum_\beta}' \frac{n_\beta' - n_\alpha'}{\tau_{\alpha\beta}'}, \tag{2}$$

where n_α^0 and n_α' are, respectively, the equilibrium density of electrons in the α-th valley and the nonequilibrium increment of this density; obviously, n_α' and **E** can depend only on the coordinate y and, because curl E = 0, the components E_x and E_z are constant throughout the sample. If, moreover, the screening length l_D is considerably smaller than the dimensions of a region in which n_α' changes considerably, the number of equations in system (2) can be reduced by one, using the quasineutrality equation:

$$\sum_\beta n_\beta' = 0; \tag{3}$$

E_y is found from the condition that the total current along the direction y is equal to zero; it follows from Eq. (1) that for cubic (i.e., macroscopically isotropic) crystals with the electrical conductivity

$$\sigma_{ij} = e\sum_\alpha n_\alpha{}^0 u_{ij}{}^\alpha = \sigma\delta_{ij}$$

it has the form

$$E_y = -\frac{e}{\sigma}\sum_\beta D_{yy}{}^\beta \frac{dn_\beta'}{dy}. \tag{4}$$

Substituting Eq. (4) into Eq. (2) and using Eq. (3), we obtain a system of interrelated equations for n_β'. This system should be supplemented by boundary conditions, which can be easily formulated by introducing phenomenological rates of the intervalley scattering at the surface $S_{\alpha\beta}^{(\pm)}$:

$$\frac{1}{e}J_{\alpha y} = {\sum_\beta}' S_{\alpha\beta}{}^{(+)}(n_\beta' - n_\alpha') \quad \text{when} \quad y = +d,$$
$$\frac{1}{e}J_{\alpha y} = -{\sum_\beta}' S_{\alpha\beta}{}^{(-)}(n_\beta' - n_\alpha') \quad \text{when} \quad y = -d; \tag{5}$$

strictly speaking these conditions apply not to the surface itself but to the boundary of the quasineutral region near the surface.

The formula for the total current follows directly from Eq. (1):

$$I_i = \int_{-d}^{+d}\sum_\alpha J_{\alpha i}\,dy = 2d\sigma E_i + e\sum_\alpha D_{iy}{}^\alpha(n_\alpha'(d) - n_\alpha'(-d)). \tag{6}$$

In a Ge crystal, all four valleys are equivalent and, therefore, all n_α^0 and $\tau_{\alpha\beta}'$ are equal; if we use the notation $n_0 = n_\alpha^0$ and $\tau' = \tau_{\alpha\beta}'/4$, then the last term in Eq. (2) will be equal to $-n_\alpha'/\tau'$ as a consequence of Eq. (3). The coefficients $S_{\alpha\beta}^{(\pm)}$ are not independent either, but the nature of the relationships between them depends, in general, on how the plate is cut with respect to the crystallographic axes. We shall consider below two special cases, which allow us to explain all the most interesting features without a cumbersome treatment.

For simplicity, we shall restrict ourselves also to a constant electric field. For a field varying in accordance with the law $\exp(i\omega t)$, all the formulas may be obtained by the substitution $\tau' \to \tau'/(1 + i\omega\tau')$, which gives a frequency-dependent electrical conductivity beginning from $\omega \sim 1/\tau'$.

A. Plate bounded by (010) planes. In this case, the y axis is the fourfold axis of the whole system; therefore, the total electrical conductivity in the xz plane remains isotropic and all quantities

$D^{\alpha}_{yy} \equiv D$ are equal. However, it then follows directly from Eqs. (3) and (4) that $E_y = 0$, i.e., there is no transverse electric field and the equations in (2) can be separated. If the valleys lying, respectively, along the axes [111], [$\bar{1}$11], [1$\bar{1}$1], [11$\bar{1}$] are numbered 1, 2, 3 and 4, and E is directed along the x axis, it is evident from the considerations of the symmetry and electrical neutrality that

$$n_1' = n_4' = -n_2' = -n_3' \equiv n'. \qquad (7)$$

If we also allow for the fact that $S^{(\pm)}_{12} = S^{(\pm)}_{14}$ and if we use the notation $S^{(\pm)} = 2(S^{(\pm)}_{12} + S^{(\pm)}_{13})$, then instead of Eqs. (2) and (5) we obtain for n′

$$D\frac{d^2n'}{dy^2} - \frac{n'}{\tau'} = 0,$$

$$D\frac{dn'}{dy} + n_0 u_{yx}{}^1 E_x = \begin{cases} -S^{(+)}n' \text{ when } y = +d \\ S^{(-)}n' \text{ when } y = -d. \end{cases} \qquad (8)$$

The quantities D and $u_{yx}{}^1$ are expressed simply in terms of the principal values of the corresponding tensors for each of the valleys:

$$D = {}^1/_3(D_l + 2D_t), \qquad u_{xy}{}^1 = {}^1/_3(u_l - u_t). \qquad (9)$$

We shall write directly the formula for the effective electrical conductivity which is obtained by an elementary solution of Eq. (8) using Eq. (6):

$$\Sigma = \frac{I_x}{2dE_x} = \sigma\left\{1 - g\left(\frac{u_l - u_t}{u_l + 2u_t}\right)^2 \frac{\tanh(d/L)}{d/L}\right\} \qquad (10)$$

$$g = \frac{1 + 2(L/D)(S^{(+)} + S^{(-)})\coth(d/L)}{1 + (L/D)^2 S^{(+)}S^{(-)} + (L/D)(S^{(+)} + S^{(-)})\coth(2d/L)} \leqslant 1. \qquad (11)$$

The quantity $L = (D\tau')^{1/2}$ has the meaning of the diffusion length in the process of the establishment of equilibrium between electrons of different valleys; obviously, $L \sim (ll')^{1/2}$. When $l \sim 10^{-4}$ cm, $l' \sim 10^{-2}$ cm, we have $L \sim 10^{-3}$ cm. We note that the resultant situation is markedly similar to that which should be obtained near a boundary in macro scopically anisotropic bipolar semiconductors.[3]

Several conclusions follow from Eq. (10). Σ and σ differ even in the zeroth order with respect to the electric field. When $S^{(\pm)} \to 0$, $u_t \gg u_l$ and $d \approx 2.5L$, we obtain $(\sigma - \Sigma)/\sigma \approx 0.1$ and this fraction increases rapidly as d increases. The quantity Σ depends strongly on the surface state through the factor g; if we establish artificially, by an external transverse field, a blocking curvature of the bands, we can considerably reduce $S^{(\pm)}$ by making it difficult for electrons to reach the surface, and thus we can increase g and reduce Σ/σ. In this way, we obtain a kind of "field effect" associated not with a change in the total number of carriers but with their redistribution between valleys in a layer of thickness ~ L; when $L \gg l_D$, this effect may be stronger than the normal field effect.

The value of the nonequilibrium electron density at the boundary when $S^{(\pm)} = 0$ is given by the formula

$$\frac{n'(d)}{n_0} = \frac{u_l - u_t}{u_l + 2u_t}\frac{E_x}{E_L}\tanh\frac{d}{L}, \qquad E_L = \frac{D_l}{u_l L}; \qquad (12)$$

in the absence of degeneracy $D_l/u_l = k_B T/e$, and, for T = 30° K, L = 10 μ, we obtain $E_L \approx 2.5$ V/cm, i.e., the diffusion fields E_L, which determine the limit of the linear conditions, are weak; the fields $E_x \sim E_L$ permit considerable intervalley redistribution at the boundary. In accordance with the assumptions made above, τ′ is the longest of the relaxation times of the system and, therefore, the field E_L cannot heat carriers.

In spite of the fact that the total effective electrical conductivity Σ of a plate is isotropic, there is anisotropy in the surface layer, which follows directly from Eq. (12) and which may be detected from the reaction of the system to additional external fields (for example, microwave fields or infrared radiation, which do not cause a marked redistribution of carriers at $\omega\tau' > 1$). It follows from Eq. (12) that the principal axes of the conductivity ellipsoid at the surface are oriented along [110], [1$\bar{1}$0], and [001] and the corresponding principal values are

$$\sigma_{1,2} = \sigma\left[1 \pm \left(\frac{u_l - u_t}{u_l + 2u_t}\right)^2 \frac{E_x}{E_l}\tanh\frac{d}{L}\right], \qquad \sigma_3 = \sigma. \qquad (13)$$

It is evident that when $E \gtrsim E_L$ (i.e., in the nonlinear region), Σ itself becomes anisotropic.

B. Plate bounded by (1$\bar{1}$0) planes. This case differs from the preceding one in that the normal to the plate is a binary (twofold) axis and, therefore, we may expect anisotropy of Σ even in the linear region. If we select the x axis along the [110] direction, then, as can easily be shown, $u^{\alpha}_{xy} = 0$, for all ellipsoids and, therefore, an external field applied along the x-axis direction does not redistribute carriers and $\Sigma_x = \sigma$. If an external field is directed along the z axis, then $E_y = 0$, $n_1' = n_4' = 0$, $n_2' = -n_3' \neq 0$ and, by analogy with the preceding case, we can obtain

$$\Sigma = \sigma\left\{1 - g\frac{(u_l - u_t)^2}{(u_l + 2u_t)(2u_l + u_t)}\frac{\tanh(d/L)}{d/L}\right\}. \qquad (14)$$

The coefficients g and L which occur in the above equation are given by the same formulas as in the preceding case, but we now have

$$D = {}^1/_3(2D_l + D_t),$$
$$S^{(\pm)} = 4S_{12}^{(\pm)} = 4S_{13}^{(\pm)}. \quad (15)$$

Consequently, a plate cut in this way is anisotropic even in the linear approximation and the degree of anisotropy may be varied by varying $S^{(\pm)}$.

We shall note several other effects of the redistribution of carriers. In asymmetrically cut uniform plates with $S^{(+)} \neq S^{(-)}$, the passage of a current when $E \gtrsim E_L$ should be accompanied by rectification. A considerable departure from thermal equilibrium in layers of thickness $\sim L$ may cause various instabilities, in particular those associated with an intense emission of intervalley phonons.

3. INTERVALLEY WAVES

In conclusion, we shall consider briefly quasi-stationary long-wavelength oscillations ($\lambda\!\!\!^{-} \gg l_D$), accompanied by electron transitions between valleys, but we shall not consider the interesting region near the surface because it is too difficult to analyze. Taking the system of Eq. (1) in the presence of an external uniform electric field **E**, which is not assumed to be small, and linearizing it with respect to the amplitudes of the oscillations of the density $\tilde{n}_\alpha$ and field $\tilde{E}$, we can easily obtain an equation for the determination of the natural frequencies. If we neglect the dependence of $\hat{u}_\alpha$ on the densities and consider only waves of the $\exp[i(\mathbf{k}\cdot\mathbf{r} - \omega t)]$ type with $\mathbf{k} \parallel \mathbf{E}$ then

$$\omega_{[100]} = -\frac{u_l + 2u_t}{3} Ek - i\left[\frac{1}{\tau'} + \frac{D_l + 2D_t}{3} k^2\right],$$
$$\omega_{[110]} = -\frac{u_t(2u_l + u_t)}{u_l + 2u_t} Ek - i\left[\frac{1}{\tau'} + \frac{D_t(2D_l + D_t)}{D_l + 2D_t} k^2\right] \quad (16)$$

for the orientation of **E** along the directions [100] and [110], respectively; in the former case $\tilde{E} = 0$, while in the latter case $\tilde{E} \neq 0$.

The condition for weak damping of the intervalley waves, i.e., the smallness of the imaginary component of ω compared with the real one, is satisfied for waves with $\lambda\!\!\!^{-} = 1/k$ given by

$$L\frac{E_L}{E} \ll \lambda\!\!\!^{-} \ll L\frac{E}{E_L}. \quad (17)$$

The inequality (17) can be satisfied only if $(E/E_L)^2 \gg 1$. The velocity of propagation of the intervalley waves is governed by the average velocity of the electron drift; their characteristic damped wavelength is $\mathrm{Im}\,\lambda\!\!\!^{-} \sim LE/E_L$.

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