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Carrier statistics and thermal relaxations in inhomogeneous semiconductors

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The statistics of electrons in an inhomogeneous semiconductor in which the energy bands are modulated by a Gaussian random potential are considered. It is assumed that only one type of partially compensated donor level is present in the semiconductor. The position of the chemical-potential level, the degeneracy criterion, the features of the temperature dependences of the free carrier density, and conductivity are investigated, as is also the kinetics of the establishment of the stationary conductivity following an abrupt variation of the sample temperature. It is shown that in an inhomogeneous and weakly compensated semiconductor the process is characterized by anomalously high relaxation times that have an activation dependence on the temperature.

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1. INTRODUCTION

It is well known that statistical fluctuations or technological inhomogeneities of the impurity ion concentration can produce in semiconductors an inhomogeneous electrostatic potential that modulates the energy bands. In some cases (for example in strongly compensated or irradiated semiconductors) the amplitude of this potential can become appreciable. This leads to a number of singularities in the kinetic properties of the semiconductors, such as a residual photoconductivity, an anomalous temperature dependence of the Hall mobility, etc.^[1] These phenomena are observed in experiment quite frequently, as is evidenced by the significant inhomogeneity of many real semiconductors. A consistent theoretical study of the properties of inhomogeneous semiconductors is therefore useful.

This paper deals with the statistics of the carriers and, in particular, with the question of the temperature dependences of the equilibrium concentration and conductivity in inhomogeneous semiconductors. The kinetics of the establishment of the indicated equilibrium values following an abrupt change of temperature is also investigated.

2. CHEMICAL-POTENTIAL LEVEL AND DEGENERACY CRITERION

We consider a semiconductor with a modulating random potential $V(\mathbf{r})$ described by a distribution function $F(V)$. Assume that the sample contains uniformly distributed donor levels with concentration N_D and binding energy ε_i . The random potential is due to the inhomogeneous distribution of the acceptors having an average concentration N_A .¹⁾ If the correlation length of $V(\mathbf{r})$ exceeds the radius of the donor states, then the energy of the latter can be described by the same distribution function F .

We assume that the electron density n in the band is quite small, $n \ll N_A$. We can then neglect the dependence of the random potential on n , and determine the chemical-potential level ζ from the expression

$$\int_{-\infty}^{\infty} dV F(V) f(V - \varepsilon_i) = (N_D - N_A) / N_D \quad (1)$$

where $f(\varepsilon)$ is the Fermi function. There being no alternate assumptions, we take the random potential to be Gaussian

$$F(V) = (1/\pi^{1/2} \Delta) \exp(-V^2/\Delta^2)$$

(the energy is reckoned from the mean value of the bottom of the conduction band). All the conclusions obtained below remain in force qualitatively also if the random potential has a different character. From (1) and (2) we obtain the answer for ζ in the form

$$\zeta = -\epsilon_i + \lambda \Delta. \quad (2)$$

The dependence of the factor λ on the parameters of the problem is shown in Fig. 1. It is seen that at temperatures several times smaller than the average amplitude Δ of the inhomogeneities, the value of λ tends to a constant λ_0 , i. e., ζ ceases to depend on the temperature.

The average free-carrier density

$$n = 2^{1/2} m^{3/2} \pi^{-2} \hbar^{-3} \int_{-\infty}^{\infty} d\epsilon f(\epsilon) \int_{-\infty}^{\infty} dV (e-V)^{1/2} F(V) \quad (3)$$

is described in the nondegenerate case by the expression

$$n = N_c \exp[(\zeta/T) + (\Delta/2T)^2], \quad (4)$$

$$N_c = 2(mT/2\pi\hbar^2)^{3/2}.$$

and in the case of the completely degenerate case at $\zeta < 0$ we have (the inhomogeneities play an insignificant role at $\zeta > 0$):

$$n \sim (m\Delta/\hbar^2)^{3/2} \exp(-\zeta^2/\Delta^2). \quad (5)$$

Comparing (4) with (5) we obtain the nondegeneracy criterion $\zeta < -\Delta^2/2T$, or

$$n \ll N_c \exp(-\Delta^2/4T^2). \quad (6)$$

It is seen that in an inhomogeneous semiconductor the degeneracy sets in at a lower carrier density than in a homogeneous one. We are referring here, of course, to degeneracy "in the mean," since an inhomogeneous sample, at any carrier density, can contain both degenerate and nondegenerate sections.

3. TEMPERATURE DEPENDENCE OF THE CONCENTRATION AND CONDUCTIVITY

From (2) and (4) we easily see that in contrast to the homogeneous case, the temperature dependence of the concentration of the free carriers has not a constant activation energy but a sliding one, which decreases with decreasing temperature. The physical cause is the presence in the random potential of deep wells that are located at a distance much smaller than from the Fermi level. It can be shown that in accordance with (4) at $T = T_{\min} \equiv \Delta^2/2(\epsilon_i - \lambda_0 \Delta)$ the derivative dn/dT vanishes. But since the region $T \sim T_{\min}$ is simultaneously the degeneracy limit, it follows that formula (4) can be used only at $T > T_{\min}$, i. e., on the rising section of the $n(T)$ plot. At $T \lesssim T_{\min}$ the carrier density in the band ceases to depend on the temperature and is determined by deep potential fluctuations that lie below the Fermi level.

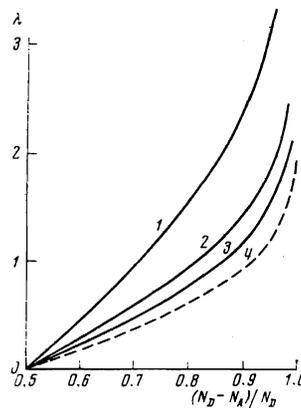


FIG. 1. Dependence of the parameter λ on the degree of compensation. Curves 1, 2, and 3 correspond to $\Delta/T=1$, $\Delta/T=2$ and $\Delta/T=3$. The dashed curve is a plot of λ_0 ($\Delta/T \rightarrow \infty$). At $(N_D - N_A)/N_D < 0.5$ the value of λ is determined from the easily proved identity $\lambda[(N_D - N_A)/N_D] = -\lambda[1 - (N_D - N_A)/N_D]$.

We consider now the conductivity σ of an inhomogeneous semiconductor. If the characteristic dimension of the inhomogeneities exceeds the carrier mean free path, then the presence of inhomogeneities does not change the carrier mobility μ , and only modulates their concentration. Then

$$\sigma \approx n_{\text{eff}} e \mu, \quad (7)$$

where n_{eff} is the density of carriers having an energy exceeding the "percolation energy" ϵ_p .^[3] In a Gaussian random potential we have $\epsilon_p = -0.68 \Delta$ ^[4] and at $\zeta < \epsilon_p$ we have

$$n_{\text{eff}} = N_c \exp(\zeta/T) G(\Delta/T), \quad (8)$$

$$G(x) = \frac{2}{\pi x} \int_0^{\infty} dy \sqrt{y} \int_{-0.68x}^{\infty} dz \exp\left[-0.68x - z - \left(\frac{y-z}{x}\right)^2\right].$$

$G(0) = 1$, and $G \sim 0.1 x^{1/2}$ as $x \rightarrow \infty$, but calculation shows that at $0 \leq x < 6 \cdot 10^2$ the value of G differs from unity by not more than 2.5 times. We can therefore put approximately $G \approx 1$ in (8), all the more since the formula (7) itself is valid only accurate to a pre-exponential factor that has a power-law dependence on the temperature.

Let us analyze the temperature dependence of the conductivity as described by (8). At high temperatures ($T > \Delta$) the role of the inhomogeneities is negligible and the conductivity activation energy E_σ , as in the homogeneous case, is equal to ϵ_i . At low temperatures ($T \ll \Delta$) the activation energy is also constant but differs from ϵ_i (with the exception of the case of half-compensation): $E_0 = \epsilon_i - \lambda_0 \Delta$. Consequently in the general case E depends on the temperature, and, as follows from the figure:

$$E_\sigma \leq \epsilon_i \text{ and } dE_\sigma/dT \geq 0 \text{ for } (N_D - N_A)/N_D \geq 0.5, \text{ and}$$

$$E_\sigma \geq \epsilon_i \text{ and } dE_\sigma/dT \leq 0 \text{ for } (N_D - N_A)/N_D \leq 0.5.$$

We note that in samples with sufficient photoconductivity or with an anomalous temperature dependence of the Hall mobility (i. e., samples that are known to be inhomogeneous) the temperature dependence of the conductivity is quite frequently not a simple exponential, but has a more complicated character, of the type described above, which depends furthermore on the character of the processing (the degree of doping and compensation, the irradiation dose, etc.). However, the

interpretation of these results on the basis of the concepts developed above should be approached with caution. Each case calls for an individual analysis that takes into account the possible existence of other effects, which also alter the character of the $\sigma(T)$ dependence, such as hopping conductivity, the presence of several types of impurity states, or the dependence of the impurity ionization energy on their concentration.

4. THERMAL RELAXATION OF THE CONDUCTIVITY

Besides the unusual temperature dependences of the concentration and the conductivity, inhomogeneous samples have one more feature—abnormally large times of establishment of the equilibrium following abrupt changes of the temperature.^[5-9] The physical nature of such long-time conductivity relaxations was considered by Vul' and Shik.^[10] We present below a rigorous theory of these effects in a randomly-inhomogeneous semiconductor. We describe the distribution of the electrons in a sample by the functions $n(\epsilon)$ and $\nu(\epsilon)$, which constitute the electron density respectively in the conduction band and on the levels, at points where the bottom of the conduction band has an energy ϵ . The processes of electron capture on levels, and of thermal excitation, are described by the equation

$$\frac{\partial \nu(\epsilon)}{\partial t} = \gamma_e n(\epsilon) [N_D - \nu(\epsilon)] - \gamma_e \nu(\epsilon) N_c \exp(-\epsilon/T), \quad (9)$$

where γ_e is the capture coefficient.

If the characteristic time of the electron drift in the random fields of the inhomogeneities is smaller than the time of capture on the levels $(\gamma_e N_D)^{-1}$ then, as shown earlier,^[11] the capture processes can be described by assuming the electrons in the band to be quasi-equilibrium

$$n(\epsilon) = N_c \exp[(\zeta_e - \epsilon)/T], \quad (10)$$

where the quasi-level of the chemical potential ζ_e is determined from the neutrality condition

$$\int d\epsilon F(\epsilon) [n(\epsilon) + \nu(\epsilon)] = N_D - N_A. \quad (11)$$

Eliminating ζ_e and $n(\epsilon)$ from (9)–(11) we arrive at a final equation describing the establishment of equilibrium in the electron system

$$\frac{\partial \nu}{\partial t} = \gamma_e \left\{ (N_D - \nu) \left[N_D - N_A - \int d\epsilon \nu F \right] \exp[-(\epsilon/T) - (\Delta^2/4T^2)] - \nu N_c \exp(-\epsilon/T) \right\}. \quad (12)$$

To calculate with the aid of (12) the kinetics of the variation of the concentration of the free electrons following an abrupt change of temperature from T_1 to T_2 (a quantitative definition of the concept "abrupt" will be given below), we must put in (12) $T = T_2$, and use as the initial condition for this equation

$$\nu(\epsilon, t=0) = \nu_i(\epsilon) = N_D f_1(\epsilon - \epsilon_i), \quad (13)$$

where f_1 is a Fermi function with temperature T_1 . In principle, the solution of (12) would make it possible to determine completely the time dependence of the concentration. Unfortunately, however, this equation cannot be solved analytically. We confine ourselves to calculation of the characteristic time of the thermal relaxation

$$\tau = \left| \frac{1}{(n_1 - n_2)} \left(\frac{dn}{dt} \right)_{t=0} \right|^{-1}, \quad (14)$$

where n_1 and n_2 are the equilibrium concentrations in the band at temperatures T_1 and T_2 . To this end we seek the solution of (12) in the form

$$\nu(\epsilon, t) = \nu_i(\epsilon) + g(\epsilon) t.$$

At $t \rightarrow 0$ we have

$$g = \gamma_e N_D N_c \frac{\mathcal{E}(\epsilon) - \exp(-\epsilon_i/T_2)}{1 + \exp[(\epsilon - \epsilon_i - \zeta_1)/T_1]}, \quad (15)$$

$$\mathcal{E}(\epsilon) = \exp[-(\epsilon/T_2) + (\Delta^2/4T_1^2) - (\Delta^2/4T_2^2) + (\epsilon - \epsilon_i)/T_1].$$

Here ζ_1 is the position of the level of the chemical potential at the temperature T_1 . Multiplying (15) by $F(\epsilon)$ and integrating, we easily obtain the value $dn/dt|_{t=0}$.

A simple analysis shows that the relaxation time calculated in this manner decreases monotonically with increasing compensation of the sample (i. e., when the chemical potential level is lowered). In the case of very strong compensation, when

$$(N_D - N_A)/N_D \ll \exp(-\Delta^2/4T^2),$$

τ tends to $(\gamma_e N_D)^{-1}$, which is the time of capture, in the homogeneous case, and the kinetics of establishment of the thermal equilibrium in the inhomogeneous semiconductor has no specific singularities at all. The same can be demonstrated directly from (12) inasmuch as in the case of strong compensation it is necessary to leave out ν from the factor $N_D - \nu$, after which this equation can be reduced, by multiplying by $F(\epsilon)$ and integrating with respect to ϵ , to the equation for $n(t)$ in a homogeneous semiconductor.

In the opposite limit of weak compensation, when the sample is cooled ($T_1 > T_2$), the first term of (15) predominates and for the characteristic time we have

$$\tau_{\text{cool}} = (\gamma_e N_D)^{-1} \exp[(\Delta^2/2T_1 T_2) - (\Delta^2/4T_1^2) + (\lambda \Delta/T_1)]. \quad (16)$$

In the case of heating ($T_1 < T_2$) the second term predominates in (15) and

$$\tau_{\text{heat}} = (\gamma_e N_D)^{-1} \exp[(\Delta^2/4T_2^2) + (\lambda \Delta/T_2)]. \quad (17)$$

It is seen from (16) and (17) that in weakly compensated inhomogeneous semiconductors the processes of establishment of thermal equilibrium are indeed characterized by an anomalously large relaxation time that depends exponentially on the temperature. The nature of this phenomenon can be easily understood. Let, for example, the sample temperature be lowered. The part

of the electrons from the conduction band should be captured by the centers. But the quasi-equilibrium electrons are localized at the maxima of $V(\mathbf{r})$ whereas free locations on the levels, in the absence of compensation, exist only near the maxima. This leads to the need for activation and to the ensuing exponential slowing down of the process. In the case of strong compensation free places on the levels are available at practically any point, and the capture process can proceed without activation, just as in the homogeneous case. With increasing degree of compensation, the characteristic time of the process decreases smoothly from the value given by (16) to $(\gamma_e N_D)^{-1}$.

Inasmuch as for the existence of long-time thermal relaxations it is necessary to have, besides inhomogeneities, also a low compensation level, the phenomena considered above are less frequently observed than long-time relaxation of the photo-conductivity,^[1] for which the last requirement is not necessary (at least in the case of interband excitation).

We can now define the concept of "abrupt" temperature change. Obviously, the approach used above is valid when the stationary distribution of the temperature in the sample is established within a time much shorter than the characteristic times (16) and (17). As is known from earlier publications,^[5-9] these times were of the order of minutes or even hours, so that our theory cannot be used to interpret these experiments.

For a complete description of the thermal relaxations of the conductivity it is necessary to take into account the fact that the change of temperature gives rise to three relaxation processes: 1) establishment of quasi-equilibrium in the band (fast process); 2) establishment of equilibrium between the band and the levels (slow process); 3) establishment of a new value of mobility. In the course of the first two processes the conductivity varies exponentially, while in the third case in power-law fashion. Consequently, the change of mobility during the course of relaxation will be neglected. Writing down the conductivity in the form

$$\sigma \approx n e \mu \exp(-\Delta^2/4T^2),$$

we easily conclude that the thermal relaxation consists of two parts: a low-inertia jump with amplitude

$$\Delta\sigma = n(T_1) e \mu [\exp(-\Delta^2/4T_1^2) - \exp(-\Delta^2/4T_2^2)] \quad (18)$$

followed by a smooth variation

$$\sigma(t) = n(t) e \mu \exp(-\Delta^2/4T_2^2), \quad (19)$$

where the $n(t)$ dependence is described by the expressions given above.

It can be seen that the investigation of the thermal relaxations of the conductivity can lead to conclusions

on the amplitude of the inhomogeneities, and furthermore by two independent methods, namely, by studying the temperature dependences of the relaxation time τ and of the low-inertia jump.

In analogy with the formulas obtained in the present paper, we can write down expressions for the conductivity relaxations in the case of an abrupt change of the pressure applied to the sample (similar relaxations were observed by Vul' and Shik^[9]). In this case the range of pressure ΔP will be formally described as a shift of the level energy ϵ_i (and consequently of the chemical-potential level (2)) by an amount

$$\Delta\epsilon_i = (\partial\epsilon_i/\partial P)\Delta P.$$

In conclusion, we recall that the drift mobility μ , which enters in the formulas for σ , cannot be determined for inhomogeneous samples from Hall measurements.^[12,14] This must be taken into account when attempts are made to compare the presented theoretical formulas with the experimental results.

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¹⁾Such a model can be used, for example, for semiconductors bombarded by neutrons, where the acceptors are concentrated in individual disordered regions.^[2]

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