

IMPURITY IONIZATION BY HOT ELECTRONS*

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ABSTRACT:

The ionization of impurities by hot electrons is examined. Several expressions for the occupancy number of impurities are calculated using different assumptions on the form of the ionization cross section. The displaced Maxwellian distribution is used throughout. The expressions are applied to p-Ge with shallow and deep impurities in order to calculate the electron temperature under high electric field.

I. INTRODUCTION

At low temperature, before the so called exhaustion region in semiconductors, there is an important residual part of the impurities of donor or

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acceptor type that have not been ionized. The action of an electric field applied to the semiconductor is to accelerate the electrons (or holes) in the conduction (or valence) band so that they are able to ionize new impurities. Hence, we expect the number of electrons to increase with the applied field. The most dramatic example of this effect is given by the so called low-temperature reversible breakdown¹. A semiconductor at 4 or 5°K has only a few electrons in the conduction band. When a field of a few volts per cm is applied, these electrons are able to ionize a large number of shallow impurities and an enormous increase in the conductivity is observed. At a somewhat higher temperature the shallow impurities are almost fully ionized and such a large increase is not observed, but if the sample has deep impurities an increase in conductivity is observed again at a larger field². For p-Ge the field is of the order of 10^3 volts/cm.

The above phenomena can be described using hot electron theory, together with various assumptions commonly employed therein, to calculate the number of ionized impurities as a function of the applied field.

II. THE IONIZATION TERM IN THE BOLTZMANN EQUATION

The Boltzmann Equation for the problem takes the form³:

$$-\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_F + \left(\frac{\partial f}{\partial t}\right)_{Ph} + \left(\frac{\partial f}{\partial t}\right)_{Im} + \left(\frac{\partial f}{\partial t}\right)_{e-e} + \left(\frac{\partial f}{\partial t}\right)_{I_0} \quad (\text{II.1})$$

where the different terms represent changes in the distribution function f due to field, phonons, elastic collision with impurities, electron-electron collisions and ionization of impurities, respectively.

The first four terms in the right hand side of the equation represent particle-preserving interactions. The last one takes the explicit form:

$$\begin{aligned} \left(\frac{\partial f}{\partial t}\right)_{I_0} = & \int d^3p' d^3p'' \{ -f(p) n_n P_I(p; p', p'') + f(p') f(p'') n_i P_R(p', p''; p) \\ & + 2f(p') n_n P_I(p'; p, p'') - 2f(p) f(p') n_i P_R(p, p'; p'') \} \quad (\text{II.2}) \end{aligned}$$

where $P_I(p; p', p'')$ is the probability per unit time that an electron with

momentum \mathbf{p} collides with a neutral impurity and as a result of the collision there appear electrons with momenta \mathbf{p}' and \mathbf{p}'' ; n_n and n_i are the densities of neutral and ionized impurities, respectively. $P_R(\mathbf{p}', \mathbf{p}''; \mathbf{p})$ is the probability per unit time of the reverse Auger recombination process. We have used the properties:

$$P_I(\mathbf{p}; \mathbf{p}', \mathbf{p}'') = P_I(\mathbf{p}; \mathbf{p}'', \mathbf{p}') \quad (\text{II.3})$$

$$P_R(\mathbf{p}', \mathbf{p}''; \mathbf{p}) = P_R(\mathbf{p}'', \mathbf{p}'; \mathbf{p}).$$

Using equation (II.2) to describe the thermodynamic equilibrium between conduction band and an impurity level with an energy E_D below the bottom of the band one finds the elementary results:

$$\frac{n_n \exp[-E_D/kT_0]}{C_0 n_i^0} = 1 \quad (\text{II.4a})$$

and

$$P_R(\mathbf{p}', \mathbf{p}''; \mathbf{p}) = P_I(\mathbf{p}; \mathbf{p}', \mathbf{p}'') . \quad (\text{II.4b})$$

To obtain these results we have used:

$$f_0(\mathbf{p}) = C_0 \exp[-E(\mathbf{p})/kT_0] \quad (\text{II.5a})$$

and

$$E(\mathbf{p}) = E(\mathbf{p}') + E(\mathbf{p}'') + E_D . \quad (\text{II.5b})$$

The index zero indicates quantities in thermodynamic equilibrium.

Using our previous statements in the Boltzmann equation (II.1) we obtain the conservation relations. For the details of the calculation reference may be made to the Lecture Notes by de Alba³. We obtain

$$\frac{dn}{dt} \equiv \int \frac{\partial f}{\partial t} d^3 p = \int G(\mathbf{p}; \mathbf{p}', \mathbf{p}'') d^3 p d^3 p' d^3 p'' \quad (\text{II.6})$$

$$\frac{dE}{dt} \equiv \int E(\mathbf{p}) \frac{\partial f}{\partial t} d^3 p = \int \left[\left(\frac{\partial f}{\partial t_F} \right) + \left(\frac{\partial f}{\partial t_{Ph}} \right) \right] E(\mathbf{p}) d^3 p + E_D \frac{dn}{dt} \quad (\text{II.7})$$

$$\begin{aligned} \frac{d\mathbf{p}}{dt} \equiv \int \mathbf{p} \frac{\partial f}{\partial t} d^3 p = \int \left[\left(\frac{\partial f}{\partial t_F} \right) + \left(\frac{\partial f}{\partial t_{Ph}} \right) + \left(\frac{\partial f}{\partial t_{Im}} \right) \right] \mathbf{p} d^3 p \\ + \int (2\mathbf{p}' - \mathbf{p}) G(\mathbf{p}; \mathbf{p}', \mathbf{p}'') d^3 p d^3 p' d^3 p'' \end{aligned} \quad (\text{II.8})$$

where

$$G(\mathbf{p}; \mathbf{p}', \mathbf{p}'') = G(\mathbf{p}; \mathbf{p}'', \mathbf{p}') = \{ f(\mathbf{p}) n_n - f(\mathbf{p}') f(\mathbf{p}'') n_i \} P_I(\mathbf{p}; \mathbf{p}', \mathbf{p}'').$$

In the steady state situation, energy conservation for each collision implies that the conservation equation (II.7) remains unaltered with respect to a situation in which the ionization process is not present.

Up to here, we have found results that are of general applicability, we now make some usual assumptions to treat the problem in greater detail.

III. CALCULATIONS

In order to do explicit calculations of the ionization term we have to consider explicit forms for the probability rate P_I . Exact expressions are very difficult to treat and not very well known for electrons in solids. We can use two extreme simplifying assumptions.

1) Isotropic collisions:

$$P_I(\mathbf{p}; \mathbf{p}', \mathbf{p}'') = B_1(p) \delta [E - E' - E'' - E_D] \quad (\text{III.1})$$

2) Momentum conservation:

$$P_I(\mathbf{p}; \mathbf{p}', \mathbf{p}'') = B_2(p) \delta(\mathbf{p} - \mathbf{p}' - \mathbf{p}'') \delta(E - E' - E'' - E_D) \quad (\text{III.2})$$

where $B_1(p)$ and $B_2(p)$ are the squares of the interaction matrix elements, and $E \equiv E(\mathbf{p})$, $E' \equiv E(\mathbf{p}')$, $E'' \equiv E(\mathbf{p}'')$.

The first assumption implies that there is no angular correlation between the particles, and the probability depends only on the energy of the incoming particle (an isotropic energy band is assumed). The second assumption is likely to be valid for fast conduction electrons and shallow impurities.

In certain circumstances approximate forms of the distribution function are justifiable and these are now considered in turn.

a) Linear theories in the drift.

When dealing with situations in which the ratio of drift to thermal energy is small, we can develop the distribution function in spherical harmonics and keep only the zero and first order terms. In this case, all theories imply the general form²

$$f(\mathbf{p}) = c \exp[-E(\mathbf{p})/kT_e] + f_1(\mathbf{p}) \cos \theta \quad (\text{III.3})$$

where $c = nb^3/2(2\pi mkT_e)^{3/2}$, T_e is the electron temperature under field, n is the electron density, $f_1(\mathbf{p})$ is the drift component to be calculated from the theory and θ is the angle between \mathbf{p} and the field direction.

Keeping only terms linear in the first harmonic we obtain, using (III.1) and (III.3) in equation (II.6) (steady state situation, isotropic case):

$$\int \{ c \exp[-E(\mathbf{p})/kT_e] n_n - c^2 \exp[-(E(\mathbf{p}') + E(\mathbf{p}''))/kT_e] n_i \} B_1(\mathbf{p}) \\ \times \delta(E - E' - E'' - E_D) p^2 p'^2 p''^2 dp dp' dp'' = 0 .$$

Hence, the population of the impurity level is simply that of equilibrium between the level and electrons in the conduction band at a temperature T_e :

$$\frac{n_n \exp[-E_D/kT_e]}{Cn_i} = 1. \quad (\text{III.4})$$

b) General case.

There are several substances (p -Ge⁵, polar semiconductors⁶ for which, at intermediate and high electric fields, the assumption of small drift

versus thermal energy ratio is not valid. For these situations either the distribution function must be specified numerically or, if strong interelectronic scattering is present, a shifted Maxwellian distribution⁷ may be assumed. If we restrict ourselves to the latter case then, for parabolic bands,

$$f(p) = C \exp \left[- \left| p - p_0 \right| / 2mkT_e \right]. \quad (\text{III.5})$$

Complete knowledge of the steady state situation is given by the simultaneous equations

$$\frac{dn}{dt} = 0; \quad \frac{dE}{dt} = 0 \quad \text{and} \quad \frac{dp}{dt} = 0$$

in the parameters n , T_e and p_0 .

When the assumption of conservation of momentum (III.2) is used, the set of equations for T_e and p_0 reduces identically to those obtained when impact ionization is not present. Hence the mobility as a function of field is not modified by the impact ionization mechanism and the population can be independently calculated by means of the equation (II.6):

$$\int G(p; p', p'') d^3p d^3p' d^3p'' = 0 \quad (\text{III.6})$$

where we have to use the form (III.5) of the distribution function.

After some calculation, equation (III.6) reduces to:

$$\frac{n_n \exp \left[- \left(E_D - \frac{p_0^2}{2m} \right) / kT_e \right]}{Cn_i} = 1. \quad (\text{III.7})$$

That is, the electron population is that of electrons in the conduction band in equilibrium at temperature T_e with impurity levels at a pseudo-energy

$$E_{ps} = E_D - \frac{p_0^2}{2m} = E_D - \frac{m}{2} [\mu(F) F]^2 \quad (\text{III.8})$$

where $\mu(F)$ represent the carrier mobility and F the electric field strength.

In many cases the lowering of the effective ionization energy is small, but non-zero.

Now, when instead the isotropic assumption (III.1) is made, equation (III.6) reduces to:

$$\frac{n_n}{Cn_i} = \mathcal{J}(x_0^2, \gamma) \tag{III.9}$$

where

$$\begin{aligned} \mathcal{J}(x_0^2, \gamma) = & \frac{4}{x_0} \left\{ \iint dx' dx x^2 x' B(x) \left[e^{-\frac{(x'-x_0)^2}{x_0^2}} - e^{-\frac{(x'+x_0)^2}{x_0^2}} \right] \right. \\ & \left. \left[e^{-\frac{\{\sqrt{x^2-x'^2} \cdot \gamma - x_0\}^2}{x_0^2}} - e^{-\frac{\{\sqrt{x^2-x'^2} \cdot \gamma + x_0\}^2}{x_0^2}} \right] \right\} \\ & \times \left\{ \int x(x^2 - \gamma)^2 B(x) \left[e^{-\frac{(x-x_0)^2}{x_0^2}} - e^{-\frac{(x+x_0)^2}{x_0^2}} \right] dx \right\}^{-1} \end{aligned}$$

The function $B(x)$ appearing in $\mathcal{J}(x_0^2, \gamma)$ is defined as the square of the interaction matrix element and $x_0 = p_0 (2mkT_e)^{-1/2}$; $\gamma = E_D/kT_e$. The result is a complicated expression in the hot-electron parameters p_0 and T_e .

In order to see the differences between results (III.7) and (III.9), let us develop $\mathcal{J}(x_0^2, \gamma)$ up to the second order in x_0 , that is, the first significant correction to "linear in the drift" theories. After some manipulation, we find:

$$\frac{n_n}{Cn_i} \approx (1 - 2x_0^2) e^\gamma$$

or, valid to the same order,

$$\frac{n_n}{Cn_i} = \exp \left[\left(E_D - \frac{2p_0^2}{2m} \right) / kT_e \right]$$

The pseudo-level has now an ionization energy reduced by twice the drift energy of the distribution.

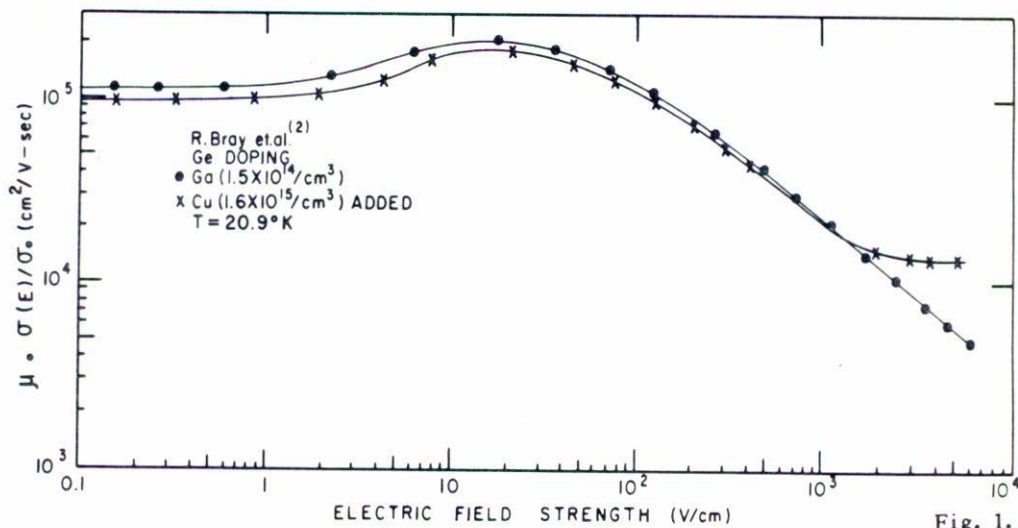
On the other hand, in the isotropic case the ionization mechanism gives a non zero contribution to the momentum balance and hence the mobility

is directly dependent on the cross section for this mechanism.

IV. A SIMPLE APPLICATION

In this paragraph we will apply the previous results to calculate the electron temperature of p-Ge at 20.9°K for fields higher than 1400 V/cm.

The graphs of figure 1, show the results of Bray et al² for the conductivity of p-Ge as function of electric field at 20.9°K. One of the samples has Ga ($1.5 \times 10^{14}/\text{cm}^3$) as shallow impurity and the other sample is the same crystal with Cu ($1.6 \times 10^{15}/\text{cm}^3$) added as deep impurity.



Except for the discrepancies due to added impurities at low electric fields both curves behave similarly up to 1700 V/cm. For small fields an increase in conductivity is observed due to exhaustion of shallow impurities. When the shallow impurities have been exhausted (~ 17 V/cm) a decay in the mobility with field forces produces a decay in the conductivity. The conductivity curves for both samples remain together from this field up to 1400 V/cm, where the ionization of deep impurities begins to play a role. From this field up to 6000 V/cm the deep impurities are ionized and the conductivities of the two samples diverge.

It has been shown⁶ that collisions with ionized impurities tend to be less important when the field is increased; hence, we assume that at these large fields the variation in conductivity is due only to the variation in the number of carriers.

The behavior of the conductivity in the presence of only shallow impurities gives us the values for combining the result with the different behavior in the higher region in the presence of deep impurities; we are then able to calculate T_0 and n_i using previously described formulae.

In figure 2 we show the variation in the number of carriers versus electric field in the region of interest. In this region we can see that

$$E_D \gg kT \gg \frac{1}{2} m [\mu(F) F]^2$$

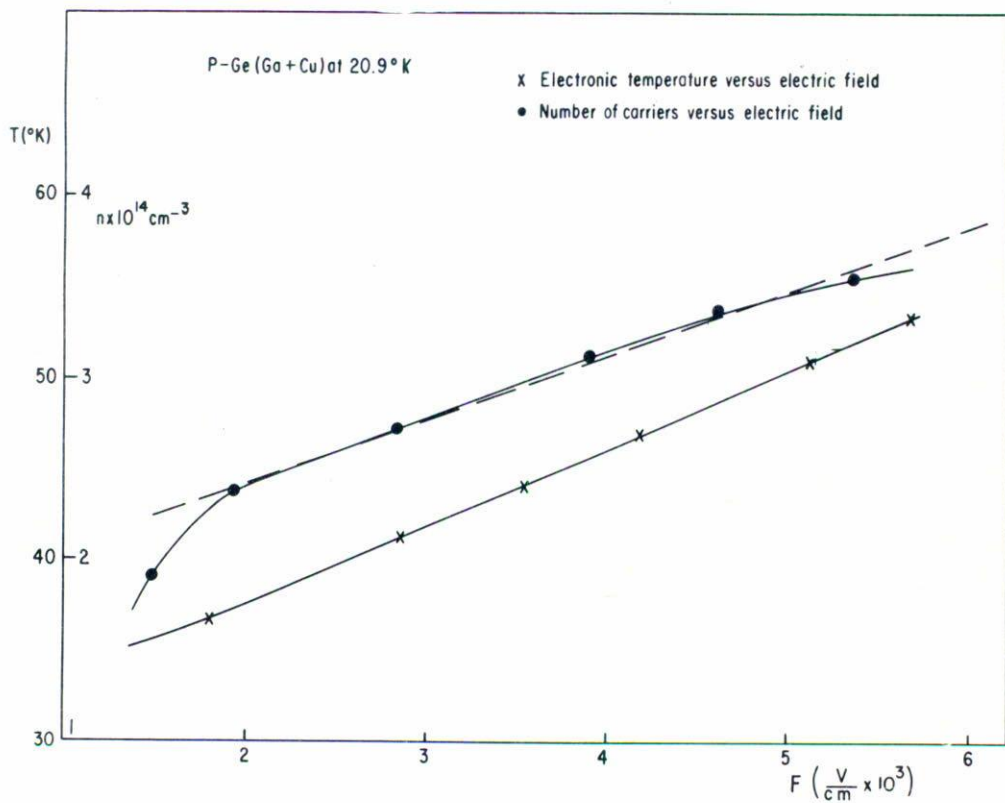


Fig. 2.

where F is the electric field; hence, all our previously treated forms for the variation of number of carriers with field, reduce to the equilibrium form at a temperature T_e (equation III.4).

Applying this formula to the present situation we calculate the temperature of the electrons versus field obtaining the results shown in figure 2.

Our semi-empirical results based on deep impurity ionization, originates electron temperatures that are lower than those obtained from calculations using hot electron theory without impact ionization. The difference gives additional support to the view that the tail of the distribution functions with larger energy than the optical phonon threshold has a different temperature than that of the bulk distribution that is found on the usual calculation procedures.

V. CONCLUSIONS

The number of carriers in the conduction band in the presence of ionizable impurities and high electric fields can be calculated by means of the thermodynamic formula:

$$\frac{n_i}{Cn_i} = \exp [E_D / kT_e] \quad (\text{III.4})$$

provided that: *The ratio of drift to thermal energy is small.*

When this ratio is not small, we have calculated two possible situations:

a) If momentum conservation is a reasonable approximation, so

$$\frac{n_i}{Cn_i} = \exp \left[\left(E_D - \frac{1}{2} m (\mu F)^2 \right) / kT_e \right] \quad (\text{III.7})$$

b) If the isotropic assumption is the most reasonable one, we have:

$$\frac{n_i}{Cn_i} = \mathcal{J}(x_0^2, \gamma) \quad (\text{III.9})$$

where \mathcal{J} is given in the text.

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RESUMEN

En este artículo se examina la ionización de impurezas por medio de electrones calientes. Se calculan varias expresiones para el número de ocupación de impurezas, utilizando diferentes suposiciones sobre la sección transversal de ionización. La distribución de Maxwell desplazada se usa en todos los casos. Las expresiones resultantes se aplican al caso p-Ge con impurezas profundas y poco profundas para calcular la temperatura electrónica en un campo eléctrico intenso.