

Influence of excited states of deep dopants on majority-carrier concentration in wide bandgap semiconductor

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1. Theoretical consideration of distribution function

1.1. Number of configurations of system

Electrons and holes in semiconductors are fermions, which obey the Pauli exclusion principle. We consider the number $D(E_i)$ of degenerate states per unit volume at some energy E_i in the allowed bands and the number $n(E_i)$ of electrons per unit volume at E_i . The multiplicity function W_{Bi} for the $n(E_i)$ electrons arranged in the $D(E_i)$ states is given by [1]

$$W_{Bi} = \frac{D(E_i)!}{[D(E_i) - n(E_i)]! \cdot n(E_i)!}. \quad (1)$$

In a bandgap, on the other hand, the multiplicity function for the n_D electrons arranged in the N_D donors is different from equation (1), where N_D is the number of donors per unit volume and n_D is the number of electrons bound to donors per unit volume. When the spin degeneracy as well as the existence of the excited states of the donor are neglected, the multiplicity function W_{D1} for the n_D electrons arranged in the N_D donors is given by

$$W_{D1} = \frac{N_D!}{(N_D - n_D)! \cdot n_D!}. \quad (2)$$

In a neutral donor, only an excess electron is bound to some one of the ground state and the excited states of the donor. The partition function for one electron arranged in them is expressed as

$$g_1 + \sum_{r=2} g_r \exp\left(-\frac{E_r - E_D}{k_B T}\right), \quad (3)$$

where E_D is the donor level that is a sum of E_1 and the energy E_{CCC} induced due to central cell corrections [2], E_r is the $(r-1)$ -th excited state level, g is the spin degeneracy factor ($g = 2$) for donors, g_1 is the ground state degeneracy factor, g_r is the $(r-1)$ -th excited state degeneracy factor, k_B is the Boltzmann constant, T is the absolute temperature.

For the n_D electrons, therefore, the multiplicity function W_{D2} is given by

$$W_{D2} = \left[g_1 + \sum_{r=2} g_r \exp\left(-\frac{E_r - E_D}{k_B T}\right) \right]^{n_D}. \quad (4)$$

On the other hand, the ensemble average $\overline{E_{ex}}$ of the ground and excited state levels of the donor is given by

$$\overline{E_{ex}} = \frac{\sum_{r=2} (E_r - E_D) g_r \exp\left(-\frac{E_r - E_D}{k_B T}\right)}{g_1 + \sum_{r=2} g_r \exp\left(-\frac{E_r - E_D}{k_B T}\right)}, \quad (5)$$

and then the average donor level $\overline{E_D}$ is expressed as

$$\overline{E_D} = E_D + \overline{E_{ex}}. \quad (6)$$

Each state of the ground state and the excited states, furthermore, consists of the spin-up state and the spin-down state. When the difference in energy between the two

states under a magnetic field H is denoted by ΔE_{spin} , the partition function for one electron arranged in the two states is expressed as

$$1 + \exp\left(-\frac{\Delta E_{\text{spin}}}{k_{\text{B}}T}\right). \quad (7)$$

For the n_{D} electrons, therefore, the multiplicity function W_{D3} is given by

$$W_{\text{D3}} = \left[1 + \exp\left(-\frac{\Delta E_{\text{spin}}}{k_{\text{B}}T}\right)\right]^{n_{\text{D}}}. \quad (8)$$

In the following sections, since the magnetic field is not applied to the semiconductor ($\Delta E_{\text{spin}} = 0$),

$$W_{\text{D3}} = 2^{n_{\text{D}}}. \quad (9)$$

Therefore, the multiplicity function W_{D} for the n_{D} electrons arranged in the N_{D} donors is expressed as

$$W_{\text{D}} = W_{\text{D1}}W_{\text{D2}}W_{\text{D3}}. \quad (10)$$

Finally, the total number W of configurations of the system is obtained from the product of these multiplicities as

$$W = W_{\text{D}} \cdot \prod_i W_{\text{Bi}}. \quad (11)$$

1.2. Thermal equilibrium configuration

The thermal equilibrium configuration occurs when the entropy

$$S = k_{\text{B}} \ln W \quad (12)$$

is maximum under the following two conditions; (1) the total number n_{total} of electrons in the system is conserved, that is,

$$n_{\text{total}} = n_{\text{D}} + \sum_i n(E_i) = \text{constant} \quad (13)$$

and (2) the total energy E_{total} of electrons in the system is conserved, i.e.,

$$E_{\text{total}} = \overline{E_{\text{D}}}n_{\text{D}} + \sum_i E_i n(E_i) = \text{constant}. \quad (14)$$

We proceed to find the thermal equilibrium configuration by making $\ln W$ extreme under equations (13) and (14). According to the method of Lagrange multipliers, the maximization of $\ln W$ is given by

$$d(\ln W) + \alpha dn_{\text{total}} + \beta dE_{\text{total}} = 0, \quad (15)$$

where α and β are the Lagrange multipliers. When Stirling's approximation

$$\ln N! \sim N(\ln N - 1) \quad (16)$$

is applied to $\ln W$ where N is the large integral number, performing the differentiations of equation (15) gives

$$\left\{ \ln \left\{ 2 \left(\frac{N_D}{n_D} - 1 \right) \cdot \left[g_1 + \sum_{r=2} g_r \exp \left(-\frac{E_r - E_D}{k_B T} \right) \right] \right\} + \alpha + \beta \overline{E_D} \right\} dn_D + \left(\ln \left[\frac{D(E_i)}{n(E_i)} - 1 \right] + \alpha + \beta E_i \right) dn_i = 0, \quad (17)$$

and hence the following equations are obtained;

$$\ln \left[\frac{D(E_i)}{n(E_i)} - 1 \right] + \alpha + \beta E_i = 0 \quad (18)$$

for electrons in the allowed bands, and

$$\ln \left\{ 2 \left(\frac{N_D}{n_D} - 1 \right) \cdot \left[g_1 + \sum_{r=2} g_r \exp \left(-\frac{E_r - E_D}{k_B T} \right) \right] \right\} + \alpha + \beta \overline{E_D} = 0 \quad (19)$$

for electrons bound to donors. Finally, the distribution functions are derived as

$$f(E_i) = \frac{n(E_i)}{D(E_i)} = \frac{1}{1 + \exp(-\alpha - \beta E_i)} \quad (20)$$

for electrons in the allowed bands, and

$$f(E_D) = \frac{n_D}{N_D} = \frac{1}{1 + \frac{1}{2 \exp(\alpha + \beta \overline{E_D}) \cdot \left[g_1 + \sum_{r=2} g_r \exp \left(-\frac{E_r - E_D}{k_B T} \right) \right]}} \quad (21)$$

for electrons bound to donors.

1.3. Determination of α and β

From equation (15), the relationship among $\ln W$, n_{total} and E_{total} is described as

$$d(\ln W) = -\alpha dn_{\text{total}} - \beta dE_{\text{total}}, \quad (22)$$

while the entropy is rewritten as

$$dS = k_B d(\ln W). \quad (23)$$

Therefore, the relationship is derived as follows;

$$dE_{\text{total}} = -\frac{\alpha}{\beta} dn_{\text{total}} - \frac{1}{k\beta} dS. \quad (24)$$

From thermodynamics, on the other hand, the relationship among E_{total} , S and the free energy F is given as

$$dE_{\text{total}} = dF + T dS. \quad (25)$$

By comparing equation (24) with equation (25),

$$\beta = -\frac{1}{k_B T} \quad (26)$$

and

$$\alpha = \frac{1}{k_B T} \cdot \frac{dF}{dn} \quad (27)$$

are then obtained. Since dF/dN_{total} means the chemical potential [3], called the Fermi level E_F in this paper,

$$\alpha = \frac{E_F}{k_B T}. \quad (28)$$

1.4. Distribution function for electrons

Since the energy level E_i in the allowed bands is considered to be approximately continuous, the distribution function is described as

$$f(E) = \frac{1}{1 + \exp\left(-\frac{E_F - E}{k_B T}\right)} \quad (29)$$

for electrons in the allowed bands, which coincides with the Fermi-Dirac distribution function. On the other hand, it is expressed as

$$f(E_D) = \frac{1}{1 + \frac{1}{2 \exp\left(\frac{E_F - E_D}{k_B T}\right) \cdot \left[g_1 + \sum_{r=2} g_r \exp\left(-\frac{E_r - E_D}{k_B T}\right) \right]}} \quad (30)$$

for electrons bound to donors.

1.5. Case of hydrogenic donor

A neutral donor can be approximately described as a hydrogen atom, that is, a positively charged ionized impurity and an electron in orbit about the impurity. In this case, the $(r - 1)$ -th excited state level ΔE_r , measured from the bottom E_C of the conduction band, is given by [2, 4, 5]

$$\begin{aligned} \Delta E_r &= \frac{q^4 m^*}{2 \hbar^2 \epsilon_0^2 \epsilon_s^2 r^2} \\ &= 13.6 \frac{m^*}{m_0 \epsilon_s^2} \cdot \frac{1}{r^2} \quad \text{eV}, \end{aligned} \quad (31)$$

where q is the electron charge, m^* is the electron effective mass in the semiconductor, m_0 is the free-space electron mass, \hbar is the Planck's constant ($\hbar = h/\pi$), ϵ_s is the semiconductor dielectric constant, and ϵ_0 is the free-space permittivity. On the other hand, the donor level ΔE_D , measured from E_C , is given by

$$\Delta E_D = \Delta E_1 + E_{\text{CCC}}. \quad (32)$$

The $(r - 1)$ -th excited state degeneracy factor is given by [2, 6]

$$g_r = r^2. \quad (33)$$

When all the energy levels are measured from E_C (e.g., $\Delta E_F = E_C - E_F$), the distribution functions are rewritten as

$$f(\Delta E) = \frac{1}{1 + \exp\left(\frac{\Delta E_F - \Delta E}{k_B T}\right)} \quad (34)$$

for electrons in the allowed bands, and

$$f(\Delta E_D) = \frac{1}{1 + \frac{1}{2 \exp\left(-\frac{\overline{E_{\text{ex}}}}{k_B T}\right)} \cdot \left[g_1 \exp\left(\frac{\Delta E_D - \Delta E_F}{k_B T}\right) + \sum_{r=2} g_r \exp\left(\frac{\Delta E_r - \Delta E_F}{k_B T}\right) \right]} \quad (35)$$

for electrons bound to donors, where

$$\overline{\Delta E_D} = \Delta E_D - \overline{E_{\text{ex}}}, \quad (36)$$

and

$$\overline{E_{\text{ex}}} = \frac{\sum_{r=2} (\Delta E_D - \Delta E_r) g_r \exp\left(-\frac{\Delta E_D - \Delta E_r}{k_B T}\right)}{g_1 + \sum_{r=2} g_r \exp\left(-\frac{\Delta E_D - \Delta E_r}{k_B T}\right)}. \quad (37)$$

When the influence of the excited states is ignored (i.e., $r = 1$ and $\overline{E_{\text{ex}}} = 0$), equation (35) coincides with the Fermi-Dirac distribution function;

$$f_{\text{FD}}(\Delta E_D) = \frac{1}{1 + \frac{1}{2} \exp\left(\frac{\Delta E_F - \Delta E_D}{k_B T}\right)}. \quad (38)$$

Since according to the conventional distribution function the ensemble average of the ground and excited state levels of the donor is not considered (i.e., $\overline{E_{\text{ex}}} = 0$),

$$f_{\text{con}}(\Delta E_D) = \frac{1}{1 + \frac{1}{2 \left[g_1 \exp\left(\frac{\Delta E_D - \Delta E_F}{k_B T}\right) + \sum_{r=2} g_r \exp\left(\frac{\Delta E_r - \Delta E_F}{k_B T}\right) \right]}}. \quad (39)$$

1.6. Case of hydrogenic acceptor

Different from the conduction band, there are two degenerate valence bands (i.e., the light hole band and the heavy hole band), indicating that there are the acceptor state for the light hole band and the acceptor state for the heavy hole band. Therefore, the multiplicity W_{A4} for one hole arranged in the two acceptor states is given by

$$W_{A4} = 2^{n_A}, \quad (40)$$

where n_A is the number of holes bound to acceptors per unit volume. In the same way as illustrated for the hydrogenic donor, the distribution function $f_h(\Delta E_A)$ for holes is expressed as

$$f_h(\Delta E_A) = \frac{1}{1 + \frac{1}{4 \exp\left(-\frac{\overline{E_{\text{ex}}}}{k_B T}\right)} \cdot \left[g_1 \exp\left(\frac{\Delta E_A - \Delta E_F}{k_B T}\right) + \sum_{r=2} g_r \exp\left(\frac{\Delta E_r - \Delta E_F}{k_B T}\right) \right]}, \quad (41)$$

where all the energy levels are measured from E_V (e.g., $\Delta E_F = E_F - E_V$). Therefore, the distribution function $f(\Delta E_A)$ for electrons is derived as

$$\begin{aligned} f(\Delta E_A) &= 1 - f_h(\Delta E_A) \\ &= \frac{1}{1 + 4 \exp\left(-\frac{\overline{E_{\text{ex}}}}{k_B T}\right) \cdot \left[g_1 \exp\left(\frac{\Delta E_A - \Delta E_F}{k_B T}\right) + \sum_{r=2} g_r \exp\left(\frac{\Delta E_r - \Delta E_F}{k_B T}\right) \right]}, \end{aligned} \quad (42)$$

where

$$\Delta E_A = \Delta E_1 + E_{\text{CCC}}, \quad (43)$$

$$\overline{\Delta E_A} = \Delta E_A - \overline{E_{\text{ex}}}, \quad (44)$$

and

$$\overline{E_{\text{ex}}} = \frac{\sum_{r=2} (\Delta E_A - \Delta E_r) g_r \exp\left(-\frac{\Delta E_A - \Delta E_r}{k_B T}\right)}{g_1 + \sum_{r=2} g_r \exp\left(-\frac{\Delta E_A - \Delta E_r}{k_B T}\right)}. \quad (45)$$

On the other hand, the Fermi-Dirac distribution function for electrons is expressed as

$$f_{\text{FD}}(\Delta E_A) = \frac{1}{1 + 4 \exp\left(\frac{\Delta E_A - \Delta E_F}{k_B T}\right)}, \quad (46)$$

while the conventional distribution function for electrons is described as

$$f_{\text{con}}(\Delta E_A) = \frac{1}{1 + 4 \left[g_1 \exp\left(\frac{\Delta E_A - \Delta E_F}{k_B T}\right) + \sum_{r=2} g_r \exp\left(\frac{\Delta E_r - \Delta E_F}{k_B T}\right) \right]}. \quad (47)$$

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