New Journal of Physics
An Institute of Physics and Deutsche Physikalische Gesellschaft Journal

The influence of excited states of deep dopants on majority-carrier concentration in a wide-bandgap semiconductor

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New Journal of Physics **4** (2002) 12.1–12.15 (http://www.njp.org/)
Received 22 November 2001
Published 6 March 2002

Abstract. The influence of the excited states of a substitutional dopant (donor or acceptor) on the majority-carrier concentration in a wide-bandgap semiconductor is investigated theoretically and experimentally, because acceptor levels ΔE_A in SiC, GaN and diamond were reported to be deeper than 150 meV. In order to accurately determine the values of ΔE_A, the acceptor density N_A and the compensating density N_{comp} in Al-doped p-type 4H–SiC using the temperature dependence $p(T)$ of the hole concentration obtained from Hall-effect measurements, a distribution function including this influence is theoretically derived. Here, an ensemble average $\overline{E_{ex}}$ of the ground and excited state levels of the acceptor is newly introduced into the distribution function. It is found that a curve-fitting procedure, in which we proceed to search for N_A, ΔE_A and N_{comp} to fit a curve to the experimental $p(T)$ by a method of least squares, is not suitable for investigating this influence. It is experimentally demonstrated that free-carrier concentration spectroscopy (FCCS), which we have proposed, can investigate this influence in detail. By using FCCS and the distribution function proposed here, the reliable values of N_A, ΔE_A and N_{comp} can be obtained.

1. Introduction

Excited states of a substitutional dopant (donor or acceptor) in a semiconductor have been theoretically discussed using the hydrogenic dopant model [1]–[3], and the existence of the excited states of the dopants (e.g., B, P) in Si or Ge has been experimentally confirmed using

PII: S1367-2630(02)31098-X
1367-2630/02/000012+15$30.00
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infrared absorption measurements [1, 4, 5]. However, the influence of the excited states on the majority-carrier concentration in Si or Ge has not been confirmed because the excited state levels of the dopants in Si or Ge are too shallow.

Since the dielectric constants of wide-bandgap semiconductors such as SiC, GaN and diamond are lower than those of Si and Ge, the energy levels of substitutional dopants become deep according to the hydrogenic dopant model. For example, the energy levels ΔE_A of acceptors (e.g., B or Al in SiC, Mg in GaN and B in diamond), measured from the top E_V of the valence band, were reported to be deeper than 150 meV from photoluminescence (PL) studies [6]–[9]. Moreover, the theoretical first excited state level of the acceptor in the wide-bandgap semiconductor is expected to be close to the acceptor level (45 meV) of B in Si, indicating that the excited states of the acceptor in the wide-bandgap semiconductor must affect the hole concentration.

The conventional occupation probability function $f_{\mathrm{conv}}(E_D)$ for electrons bound to donors in a forbidden band, which includes the influence of the excited states of the donor, is given by [10]–[12]

$$f_{\mathrm{conv}}(E_D) = \frac{1}{1 + \frac{1}{g\left[g_1 \exp\left(\frac{E_F - E_D}{k_B T}\right) + \sum_{r=2} g_r \exp\left(\frac{E_F - E_r}{k_B T}\right)\right]}}, \quad (1)$$

while the Fermi–Dirac (FD) occupation probability function $f_{\mathrm{FD}}(E_D)$ for electrons bound to donors in the forbidden band, which does not include the influence of the excited states of the donor, is given by

$$f_{\mathrm{FD}}(E_D) = \frac{1}{1 + \frac{1}{g}\exp\left(-\frac{E_F - E_D}{k_B T}\right)}, \quad (2)$$

where E_D is the donor level that is the sum of the theoretical ground-state level E_1 and the energy E_{CCC} induced due to central cell corrections (CCC) [13], 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 and T is the absolute temperature. In the following sections, the occupation probability function is called a distribution function. In n-type semiconductors, by comparing equation (1) with (2), the electron concentration $n(T)$ simulated using $f_{\mathrm{conv}}(E_D)$ should become lower than $n(T)$ using $f_{\mathrm{FD}}(E_D)$. As is clear from equation (1), $f_{\mathrm{conv}}(E_D)$ makes the ionization efficiency of the dopant lower even at high temperatures than $f_{\mathrm{FD}}(E_D)$ does. This situation in p-type semiconductors is also the same.

In Al-doped SiC [14]–[17], using the FD distribution function, the values of ΔE_A, the acceptor density N_A and the compensating density N_{comp} were determined by a least-squares fit of the charge neutrality equation to the temperature dependence $p(T)$ of the hole concentration experimentally obtained from Hall-effect measurements, referred to as a conventional curve-fitting procedure here. However, N_A values determined by the conventional curve-fitting procedure were much higher than the Al concentrations determined by secondary ion mass spectroscopy (SIMS) [14]–[16], suggesting that N_A determined by the conventional curve-fitting procedure are not reliable. The situation in Mg-doped p-type GaN was also the same [18]. When the influence of the excited states of the acceptor on $p(T)$ is considered using the conventional distribution function, the N_A value required to meet the experimental $p(T)$ is higher than N_A obtained using the FD distribution function. Therefore, when we consider the influence of the

excited states of the acceptor on $p(T)$, it is necessary to newly introduce a distribution function including this influence, which leads N_A to be appropriate.

On the other hand, we have proposed and tested a graphical peak analysis method for determining the densities and energy levels of several dopant species and traps without any assumption regarding dopant species and traps, called free-carrier concentration spectroscopy (FCCS) [17]–[23]. Since the FCCS signal obtained from the experimental $p(T)$ has a peak at the temperature corresponding to each energy level, from each peak the density and energy level of the corresponding dopant or trap can be determined accurately. By FCCS using the FD distribution function, the densities of a 95 meV hole trap and a 191 meV hole trap could be determined in p-type Si irradiated with 10 MeV protons [20], while those of a 65 meV donor and a 124 meV donor could be determined in N-doped n-type 4H–SiC [21]. Moreover, it is easy to make use of any distribution function in the FCCS analysis.

In this paper, we theoretically derive a distribution function suitable for deep dopants, and then shortly describe the conventional curve-fitting procedure and the FCCS analysis. Then, we analyse $p(T)$ in Al-doped p-type 4H–SiC experimentally obtained from Hall-effect measurements, using the distribution function proposed here as well as the FD distribution function and the conventional distribution function.

2. Theoretical consideration of the distribution function

2.1. The number of configurations of the 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 a given energy E_i in 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 [24]

$$W_{Bi} = \frac{D(E_i)!}{[D(E_i) - n(E_i)]! \cdot n(E_i)!}. \tag{3}$$

In a forbidden band, on the other hand, the multiplicity function for n_D electrons arranged in N_D donors is quite different from equation (3), 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 spin degeneracy as well as the existence of the excited states of the donor is neglected, the multiplicity function W_{D1} for the n_D electrons arranged in the N_D donors is given by

$$W_{D1} = \frac{N_D!}{(N_D - n_D)! \cdot n_D!}. \tag{4}$$

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

$$g_1 + \sum_{r=2} g_r \exp\left(-\frac{E_r - E_D}{k_B T}\right). \tag{5}$$

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

$$W_{D2} = \left[g_1 + \sum_{r=2} g_r \exp\left(-\frac{E_r - E_D}{k_B T}\right)\right]^{n_D}. \tag{6}$$

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

$$\overline{E_{\mathrm{ex}}} = \frac{\sum_{r=2}(E_r - E_{\mathrm{D}})g_r \exp\left(-\frac{E_r - E_{\mathrm{D}}}{k_{\mathrm{B}}T}\right)}{g_1 + \sum_{r=2} g_r \exp\left(-\frac{E_r - E_{\mathrm{D}}}{k_{\mathrm{B}}T}\right)}, \quad (7)$$

and then an average donor level $\overline{E_{\mathrm{D}}}$ is expressed as

$$\overline{E_{\mathrm{D}}} = E_{\mathrm{D}} + \overline{E_{\mathrm{ex}}}. \quad (8)$$

Each state of the ground state and the excited states, furthermore, consists of a spin-up state and a spin-down state. When the difference in energy between the two states under a magnetic field is denoted by ΔE_{spin}, the partition function for one electron arranged in the two states is expressed as

$$1 + \exp\left(-\frac{\Delta E_{\mathrm{spin}}}{k_{\mathrm{B}}T}\right). \quad (9)$$

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

$$W_{\mathrm{D3}} = \left[1 + \exp\left(-\frac{\Delta E_{\mathrm{spin}}}{k_{\mathrm{B}}T}\right)\right]^{n_{\mathrm{D}}}. \quad (10)$$

When the magnetic field is not applied to the semiconductor ($\Delta E_{\mathrm{spin}} = 0$),

$$W_{\mathrm{D3}} = 2^{n_{\mathrm{D}}}. \quad (11)$$

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

$$W_{\mathrm{D}} = W_{\mathrm{D1}} W_{\mathrm{D2}} W_{\mathrm{D3}}. \quad (12)$$

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

$$W = W_{\mathrm{D}} \prod_i W_{\mathrm{B}i}. \quad (13)$$

2.2. *Thermal equilibrium configuration*

The thermal equilibrium configuration occurs when the entropy

$$S = k_{\mathrm{B}} \ln W \quad (14)$$

becomes a maximum value under the following two conservation laws; (1) the total number n_{total} of electrons in the system is conserved, that is,

$$n_{\mathrm{total}} = n_{\mathrm{D}} + \sum_i n(E_i) = \mathrm{const} \quad (15)$$

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

$$E_{\mathrm{total}} = \overline{E_{\mathrm{D}}} n_{\mathrm{D}} + \sum_i E_i n(E_i) = \mathrm{const}. \quad (16)$$

We proceed to find the thermal equilibrium configuration by making $\ln W$ extreme under equations (15) and (16). According to the method of Lagrange multipliers, the maximization of $\ln W$ is given by

$$\mathrm{d}(\ln W) + \alpha\, \mathrm{d}n_{\mathrm{total}} + \beta\, \mathrm{d}E_{\mathrm{total}} = 0, \quad (17)$$

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

$$\ln N! \sim N(\ln N - 1) \tag{18}$$

is applied to $\ln W$ where N is the large integral number, performing the differentiations of equation (17) gives

$$\left\{\ln\left\{2\left(\frac{N_\mathrm{D}}{n_\mathrm{D}} - 1\right)\left[g_1 + \sum_{r=2} g_r \exp\left(-\frac{E_r - E_\mathrm{D}}{k_\mathrm{B}T}\right)\right]\right\} + \alpha + \beta\overline{E_\mathrm{D}}\right\}\mathrm{d}n_\mathrm{D} + \sum_i\left(\ln\left[\frac{D(E_i)}{n(E_i)} - 1\right] + \alpha + \beta E_i\right)\mathrm{d}n(E_i) = 0, \tag{19}$$

and hence the following equations are obtained:

$$\ln\left[\frac{D(E_i)}{n(E_i)} - 1\right] + \alpha + \beta E_i = 0 \tag{20}$$

for electrons in the allowed bands, and

$$\ln\left\{2\left(\frac{N_\mathrm{D}}{n_\mathrm{D}} - 1\right)\left[g_1 + \sum_{r=2} g_r \exp\left(-\frac{E_r - E_\mathrm{D}}{k_\mathrm{B}T}\right)\right]\right\} + \alpha + \beta\overline{E_\mathrm{D}} = 0 \tag{21}$$

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

$$f(E_i) = \frac{n(E_i)}{D(E_i)} = \frac{1}{1 + \exp(-\alpha - \beta E_i)} \tag{22}$$

for electrons in the allowed bands, and

$$f(E_\mathrm{D}) = \frac{n_\mathrm{D}}{N_\mathrm{D}} = \frac{1}{1 + \frac{1}{2\exp(\alpha + \beta\overline{E_\mathrm{D}})\left[g_1 + \sum_{r=2} g_r \exp\left(-\frac{E_r - E_\mathrm{D}}{k_\mathrm{B}T}\right)\right]}} \tag{23}$$

for electrons bound to donors in the forbidden band.

2.3. *Determination of α and β*

From equation (17), the relationship between $\ln W$, n_total and E_total is described as

$$\mathrm{d}(\ln W) = -\alpha\,\mathrm{d}n_\mathrm{total} - \beta\,\mathrm{d}E_\mathrm{total}, \tag{24}$$

while the entropy is rewritten as

$$\mathrm{d}S = k_\mathrm{B}\,\mathrm{d}(\ln W). \tag{25}$$

Therefore, the relationship is derived as follows:

$$\mathrm{d}E_\mathrm{total} = -\frac{\alpha}{\beta}\,\mathrm{d}n_\mathrm{total} - \frac{1}{k\beta}\,\mathrm{d}S. \tag{26}$$

From thermodynamics, on the other hand, the relationship between E_total, S and the free energy F is given as

$$\mathrm{d}E_\mathrm{total} = \mathrm{d}F + T\,\mathrm{d}S. \tag{27}$$

By comparing equation (26) with (27),

$$\beta = -\frac{1}{k_\mathrm{B}T} \tag{28}$$

and

$$\alpha = \frac{1}{k_{\mathrm{B}}T}\frac{\mathrm{d}F}{\mathrm{d}n_{\mathrm{total}}} \tag{29}$$

are then obtained. Since $\mathrm{d}F/\mathrm{d}n_{\mathrm{total}}$ is the chemical potential [25], called the Fermi level E_{F} in this paper,

$$\alpha = \frac{E_{\mathrm{F}}}{k_{\mathrm{B}}T}. \tag{30}$$

2.4. Distribution function for electrons

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

$$f(E) = \frac{1}{1+\exp\left(-\frac{E_{\mathrm{F}}-E}{k_{\mathrm{B}}T}\right)} \tag{31}$$

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

$$f(E_{\mathrm{D}}) = \frac{1}{1+\frac{1}{2\exp\left(\frac{E_{\mathrm{F}}-E_{\mathrm{D}}}{k_{\mathrm{B}}T}\right)\left[g_1+\sum_{r=2} g_r \exp\left(-\frac{E_r-E_{\mathrm{D}}}{k_{\mathrm{B}}T}\right)\right]}} \tag{32}$$

for electrons bound to donors in the forbidden band.

2.5. The hydrogenic donor case

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 [1]–[3]:

$$\begin{aligned}\Delta E_r &= \frac{q^4 m^*}{8h^2\epsilon_0^2\epsilon_{\mathrm{s}}^2 r^2}\\ &= 13.6\frac{m^*}{m_0\epsilon_{\mathrm{s}}^2}\frac{1}{r^2}\ \mathrm{eV},\end{aligned} \tag{33}$$

where q is the electron charge, m^* is the electron effective mass in the semiconductor, m_0 is the free-space electron mass, h is Planck's constant, ϵ_{s} is the semiconductor dielectric constant and ϵ_0 is the free-space permittivity. On the other hand, a donor level ΔE_{D}, measured from E_{C}, is given by

$$\Delta E_{\mathrm{D}} = \Delta E_1 + E_{\mathrm{CCC}}. \tag{34}$$

The $(r-1)$th excited state degeneracy factor is given by [1, 12]

$$g_r = r^2. \tag{35}$$

When all the energy levels are measured from E_{C} (e.g., $\Delta E_{\mathrm{F}} = E_{\mathrm{C}} - E_{\mathrm{F}}$), the distribution functions are rewritten as

$$f(\Delta E) = \frac{1}{1+\exp\left(\frac{\Delta E_{\mathrm{F}}-\Delta E}{k_{\mathrm{B}}T}\right)} \tag{36}$$

for electrons in the allowed bands, and

$$f(\Delta E_{\rm D}) = \frac{1}{1 + \frac{1}{2\exp\left(-\frac{\overline{E_{\rm ex}}}{k_{\rm B}T}\right)\left[g_1\exp\left(\frac{\Delta E_{\rm D}-\Delta E_{\rm F}}{k_{\rm B}T}\right)+\sum_{r=2} g_r\exp\left(\frac{\Delta E_r-\Delta E_{\rm F}}{k_{\rm B}T}\right)\right]}} \tag{37}$$

for electrons bound to donors in the forbidden band, where

$$\overline{E_{\rm ex}} = \frac{\sum_{r=2}(\Delta E_{\rm D} - \Delta E_r) g_r \exp\left(-\frac{\Delta E_{\rm D}-\Delta E_r}{k_{\rm B}T}\right)}{g_1 + \sum_{r=2} g_r \exp\left(-\frac{\Delta E_{\rm D}-\Delta E_r}{k_{\rm B}T}\right)}. \tag{38}$$

Therefore, an average donor level $\overline{\Delta E_{\rm D}}$ is expressed as

$$\overline{\Delta E_{\rm D}} = \Delta E_{\rm D} - \overline{E_{\rm ex}}. \tag{39}$$

When the influence of the excited states is ignored (i.e. $r = 1$ and $\overline{E_{\rm ex}} = 0$), equation (37) coincides with the FD distribution function for electrons bound to donors in the forbidden band:

$$f_{\rm FD}(\Delta E_{\rm D}) = \frac{1}{1 + \frac{1}{2}\exp\left(\frac{\Delta E_{\rm F}-\Delta E_{\rm D}}{k_{\rm B}T}\right)}. \tag{40}$$

When the ensemble average of the ground and excited state levels of the donor is not considered (i.e. $\overline{E_{\rm ex}} = 0$), equation (37) coincides with the conventional distribution function

$$f_{\rm conv}(\Delta E_{\rm D}) = \frac{1}{1 + \frac{1}{2\left[g_1\exp\left(\frac{\Delta E_{\rm D}-\Delta E_{\rm F}}{k_{\rm B}T}\right)+\sum_{r=2} g_r\exp\left(\frac{\Delta E_r-\Delta E_{\rm F}}{k_{\rm B}T}\right)\right]}}. \tag{41}$$

2.6. The hydrogenic acceptor case

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

$$W_{\rm A4} = 2^{n_{\rm A}}, \tag{42}$$

where $n_{\rm A}$ is the number of holes bound to acceptors per unit volume. In the same way as illustrated for the hydrogenic donor, the distribution function $f_{\rm h}(\Delta E_{\rm A})$ for holes bound to acceptors in the forbidden band is expressed as

$$f_{\rm h}(\Delta E_{\rm A}) = \frac{1}{1 + \frac{1}{4\exp\left(-\frac{\overline{E_{\rm ex}}}{k_{\rm B}T}\right)\left[g_1\exp\left(\frac{\Delta E_{\rm A}-\Delta E_{\rm F}}{k_{\rm B}T}\right)+\sum_{r=2} g_r\exp\left(\frac{\Delta E_r-\Delta E_{\rm F}}{k_{\rm B}T}\right)\right]}}, \tag{43}$$

where all the energy levels are measured from $E_{\rm V}$ (e.g., $\Delta E_{\rm F} = E_{\rm F} - E_{\rm V}$),

$$\Delta E_{\rm A} = \Delta E_1 + E_{\rm CCC}, \tag{44}$$

and

$$\overline{E_{\rm ex}} = \frac{\sum_{r=2}\left(\Delta E_{\rm A} - \Delta E_r\right) g_r \exp\left(-\frac{\Delta E_{\rm A}-\Delta E_r}{k_{\rm B}T}\right)}{g_1 + \sum_{r=2} g_r \exp\left(-\frac{\Delta E_{\rm A}-\Delta E_r}{k_{\rm B}T}\right)}. \tag{45}$$

Therefore, the distribution function $f(\Delta E_{\mathrm{A}})$ for electrons in the forbidden band, which corresponds to acceptors, is derived as

$$f(\Delta E_{\mathrm{A}}) = 1 - f_{\mathrm{h}}(\Delta E_{\mathrm{A}})$$
$$= \frac{1}{1 + 4\exp\left(-\frac{\overline{E_{\mathrm{ex}}}}{k_{\mathrm{B}}T}\right)\left[g_1 \exp\left(\frac{\Delta E_{\mathrm{A}} - \Delta E_{\mathrm{F}}}{k_{\mathrm{B}}T}\right) + \sum_{r=2} g_r \exp\left(\frac{\Delta E_r - \Delta E_{\mathrm{F}}}{k_{\mathrm{B}}T}\right)\right]}. \quad (46)$$

On the other hand, an average acceptor level $\overline{\Delta E_{\mathrm{A}}}$ is expressed as

$$\overline{\Delta E_{\mathrm{A}}} = \Delta E_{\mathrm{A}} - \overline{E_{\mathrm{ex}}}. \quad (47)$$

The FD distribution function for electrons in the forbidden band, which corresponds to acceptors, is expressed as

$$f_{\mathrm{FD}}(\Delta E_{\mathrm{A}}) = \frac{1}{1 + 4\exp\left(\frac{\Delta E_{\mathrm{A}} - \Delta E_{\mathrm{F}}}{k_{\mathrm{B}}T}\right)}, \quad (48)$$

while the conventional distribution function for electrons in the forbidden band, which corresponds to acceptors, is described as

$$f_{\mathrm{conv}}(\Delta E_{\mathrm{A}}) = \frac{1}{1 + 4\left[g_1 \exp\left(\frac{\Delta E_{\mathrm{A}} - \Delta E_{\mathrm{F}}}{k_{\mathrm{B}}T}\right) + \sum_{r=2} g_r \exp\left(\frac{\Delta E_r - \Delta E_{\mathrm{F}}}{k_{\mathrm{B}}T}\right)\right]}. \quad (49)$$

3. Procedures for determining the dopant density and dopant level

3.1. Conventional curve-fitting procedure

Since p-type 4H–SiC is discussed in the following sections, the majority carriers are holes. In nondegenerate semiconductors including one sort of acceptor, the following simple curve-fitting procedure can be applied.

Using ΔE_{F} and the effective density $N_{\mathrm{V}}(T)$ of states in the valence band, $p(T)$ is given by

$$p(T) = N_{\mathrm{V}}(T)\exp\left(-\frac{\Delta E_{\mathrm{F}}}{k_{\mathrm{B}}T}\right), \quad (50)$$

where

$$N_{\mathrm{V}}(T) = N_{\mathrm{V0}} k_{\mathrm{B}}^{3/2} T^{3/2} \quad (51)$$

and

$$N_{\mathrm{V0}} = 2\left(\frac{2\pi m^*}{h^2}\right)^{3/2}. \quad (52)$$

When the distribution function in the forbidden band is considered to be $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$, $p(T)$ is given by

$$p(T) = \frac{N_{\mathrm{A}}}{1 + 4\exp\left(\frac{\Delta E_{\mathrm{A}} - \Delta E_{\mathrm{F}}}{k_{\mathrm{B}}T}\right)} - N_{\mathrm{comp}}, \quad (53)$$

which is called the charge neutrality equation, where N_{comp} is the compensating density including the donor densities and hole trap densities. Here, we consider the temperature range in which the

minority carrier concentration $n(T)$ is much less than the majority carrier concentration $p(T)$. When the value y is defined as

$$y \equiv \frac{1}{T^{3/2}} \frac{p(T)[p(T)+N_{\rm comp}]}{(N_{\rm A}-N_{\rm comp})-p(T)}, \tag{54}$$

the following relationship is obtained from equations (50) and (53):

$$y = \frac{N_{\rm V0} k_{\rm B}^{3/2}}{4} \exp\left(-\frac{\Delta E_{\rm A}}{k_{\rm B}T}\right). \tag{55}$$

We proceed to find the values of $(N_{\rm A}-N_{\rm comp})$ and $N_{\rm comp}$ by making the $\ln y - 1/T$ curve straight. Using equation (55), $\Delta E_{\rm A}$ is then determined from the slope of the straight $\ln y - 1/T$ line. The software for this curve-fitting procedure is included in the Windows application software for FCCS freely downloaded from our web site (http://www.osakac.ac.jp/labs/matsuura/).

3.2. Free-carrier concentration spectroscopy

Using experimental $p(T)$, the FCCS signal is defined as [22, 23]

$$H(T, E_{\rm ref}) \equiv \frac{p(T)^2}{(k_{\rm B}T)^{5/2}} \exp\left(\frac{E_{\rm ref}}{k_{\rm B}T}\right). \tag{56}$$

The FCCS signal has a peak at the temperature corresponding to each acceptor level or hole trap level, where $E_{\rm ref}$ is the parameter which can shift the peak temperature of $H(T, E_{\rm ref})$ within the temperature range of the measurement. From each peak value and peak temperature, therefore, the density and energy level of the corresponding acceptor or hole trap can be accurately determined.

Although FCCS can be applied in any nondegenerate semiconductor including several acceptor species, donor species and traps, we focus on a p-type semiconductor doped with one sort of acceptor. Since $p(T)$ is given by

$$p(T) = N_{\rm A} F(\Delta E_{\rm A}) - N_{\rm comp} \tag{57}$$

in the temperature range in which $n(T)$ is much less than $p(T)$, substituting equation (50) for one of the two $p(T)$ in equation (56) and substituting equation (57) for the other $p(T)$ in equation (56) yield

$$H(T, E_{\rm ref}) = \frac{N_{\rm A}}{k_{\rm B}T} \exp\left(-\frac{\Delta E_{\rm A} - E_{\rm ref}}{k_{\rm B}T}\right) I(\Delta E_{\rm A}) - \frac{N_{\rm comp} N_{\rm V0}}{k_{\rm B}T} \exp\left(\frac{E_{\rm ref} - \Delta E_{\rm F}}{k_{\rm B}T}\right), \tag{58}$$

where

$$I(\Delta E_{\rm A}) = N_{\rm V0} \exp\left(\frac{\Delta E_{\rm A} - \Delta E_{\rm F}}{k_{\rm B}T}\right) F(\Delta E_{\rm A}) \tag{59}$$

and $F(\Delta E_{\rm A})$ represents $f_{\rm FD}(\Delta E_{\rm A})$ or $f_{\rm conv}(\Delta E_{\rm A})$ or $f(\Delta E_{\rm A})$.

The function

$$\frac{N_{\rm A}}{k_{\rm B}T} \exp\left(-\frac{\Delta E_{\rm A} - E_{\rm ref}}{k_{\rm B}T}\right) \tag{60}$$

in equation (58) has a peak value of $N_{\rm A}\exp(-1)/kT_{\rm peak}$ at the peak temperature

$$T_{\rm peak} = \frac{\Delta E_{\rm A} - E_{\rm ref}}{k_{\rm B}}. \tag{61}$$

As is clear from equation (61), $E_{\rm ref}$ can shift the peak of $H(T, E_{\rm ref})$ within the temperature range of the measurement. Although the peak temperature of $H(T, E_{\rm ref})$ is slightly different from the peak temperature calculated by equation (61) due to the temperature dependence of $I(\Delta E_{\rm A})$, we can easily determine the accurate values of $N_{\rm A}$ and $\Delta E_{\rm A}$ from the peak of the experimental $H(T, E_{\rm ref})$, using a personal computer. The Windows application software for FCCS can be freely downloaded from our web site (http://www.osakac.ac.jp/labs/matsuura/).

When $f_{\rm FD}(\Delta E_{\rm A})$ is substituted for $F(\Delta E_{\rm A})$ in equation (59), the values of $N_{\rm A}$, $\Delta E_{\rm A}$ and $N_{\rm comp}$ determined from the peak value and peak temperature of $H(T, E_{\rm ref})$ coincides with those determined by the conventional curve-fitting procedure. In the following sections, therefore, FCCS is applied to determine $N_{\rm A}$, $\Delta E_{\rm A}$ and $N_{\rm comp}$ for all the distribution functions.

4. Experimental

In order to form a p-type 4H–SiC layer, Al ions were implanted at room temperature to the 5 μm thick n-type 4H–SiC epilayer with N atoms of 2.5×10^{15} cm^{-3} on n-type 4H–SiC $\{0001\}$ substrate with 8° off to $\langle 11\bar{2}0\rangle$ direction. In order to obtain a box profile of the Al concentration, seven-fold Al ion implantation was carried out with different energies onto the SiC epilayer surface tilted to 7° to normal. Each dose of Al ions was 3.0×10^{14} cm^{-2}, and the implantation energies were 1.0, 1.6, 2.4, 3.3, 4.4, 5.6 and 7.0 MeV. After the implantation, the sample was annealed at 1575 °C for 1 h in an Ar atmosphere (post-annealing). The Rutherford backscattering spectroscopy (RBS) spectrum of the post-annealed sample was close to the RBS spectrum of the pre-implanted SiC epilayer, indicating that the damage due to the ion implantation was almost annealed out. Figure 1 shows the profile of the Al concentration measured by SIMS. From figure 1, the mean Al concentration in the box profile is approximately 5×10^{18} cm^{-3}.

The 1.3 μm thick layer from the surface was removed by reactive ion etching using a mixture of CF_4 and O_2, and then the sample was cut into a square 4×4 mm^2 in size. Ohmic metal (Al/Ti) was deposited on four corners of the etched surface, and the sample was annealed. The hole concentration $p(T)$ of the p-type layer formed by Al implantation was measured by the van der Pauw method at temperatures between 100 and 420 K and in a magnetic field of 1.4 T. In order to estimate $p(T)$ from the results of the Hall-effect measurements, the thickness of p-type layer was assumed to be 2 μm.

5. Results and discussion

Figure 2 shows the temperature dependences of the hole concentration (open circles) and the Fermi level (open triangles), where $\Delta E_{\rm F}$ is calculated using

$$\Delta E_{\rm F} = k_{\rm B} T \ln\left[\frac{N_{\rm V}(T)}{p(T)}\right] \qquad (62)$$

and m^* is assumed to be m_0 in order to calculate $N_{\rm V}(T)$ using equation (51). The value of $p(T)$ at room temperature is 2.5×10^{17} cm^{-3}, while it exceeds 10^{18} cm^{-3} above 390 K. Since the series of the open circles in figure 2 seem straight, the thermal activation energy can be tentatively obtained from the slope of the Arrhenius plot. The thermal activation energy is estimated to be 0.33 eV, which corresponds to $\Delta E_{\rm A}$ only when one sort of acceptor exists and $N_{\rm comp} = 0$ cm^{-3}. In order to meet the $p(T)$ experimentally obtained, $N_{\rm A}$ is suggested to be 3.6×10^{21} cm^{-3}, indicating that it is too high. Therefore, this estimation is not good.

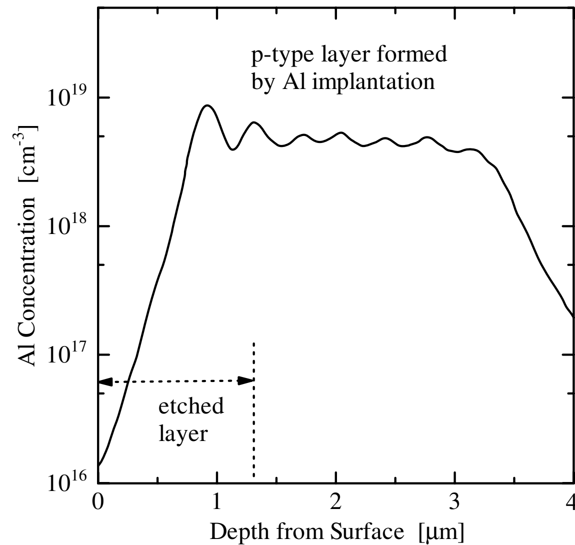

Figure 1. Depth profile of implanted Al concentration measured by SIMS. The thickness of n-type epilayer is $5\ \mu$m. In order to form the sample for Hall-effect measurements, the $1.3\ \mu$m thick layer from the surface is etched.

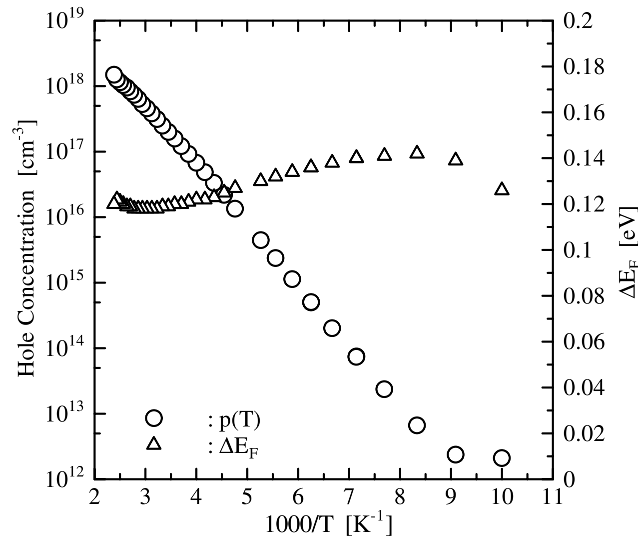

Figure 2. Temperature dependences of hole concentration (open circles) and Fermi level (open triangles).

Since ΔE_{F} is between 0.12 and 0.14 eV in figure 2, the Fermi level is closer to E_{V} than the Al acceptor level of ~ 0.18 eV obtained from PL [6]. Therefore, it is impossible to ignore the influence of the excited states of the Al acceptor on $p(T)$.

In the FCCS analyses, $H(T, E_{\mathrm{ref}})$ is calculated by interpolating $p(T)$ with a cubic smoothing natural spline function at intervals of 0.1 K. The peak temperature and peak value of $H(T, 0.219)$ are 366.8 K and $3.62 \times 10^{42}\ \mathrm{cm}^{-6}\,\mathrm{eV}^{-2.5}$, respectively. Since only one peak appears in the

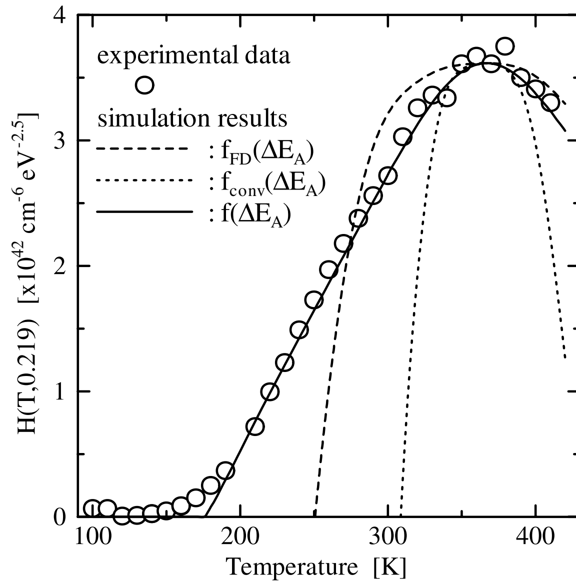

Figure 3. Experimental $H(T, E_{\mathrm{ref}})$ (open circles), and a set of three $H(T, E_{\mathrm{ref}})$ simulated with the values determined by FCCS using $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$ (broken curve), $f_{\mathrm{conv}}(\Delta E_{\mathrm{A}})$ (dotted curve) and $f(\Delta E_{\mathrm{A}})$ (solid curve).

Table 1. Results determined by FCCS.

Distribution function type	N_{A} (cm^{-3})	ΔE_{A} (eV)	N_{comp} (cm^{-3})
FD distribution: $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$	3.51×10^{19}	0.162	1.28×10^{18}
Conventional distribution: $f_{\mathrm{conv}}(\Delta E_{\mathrm{A}})$	6.03×10^{20}	0.176	1.36×10^{19}
Proposed distribution: $f(\Delta E_{\mathrm{A}})$	5.46×10^{18}	0.177	7.42×10^{16}

experimental $H(T, E_{\mathrm{ref}})$ with $E_{\mathrm{ref}} = 0.219$ eV (open circles) in figure 3, it is considered that only one acceptor level may be included in the semiconductor. Table 1 shows the values of N_{A}, ΔE_{A} and N_{comp} determined by FCCS using $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$, $f_{\mathrm{conv}}(\Delta E_{\mathrm{A}})$ and $f(\Delta E_{\mathrm{A}})$ from this peak. Here, the values determined by FCCS using $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$ are in good agreement with those determined by the conventional curve-fitting procedure. In the case of $f_{\mathrm{conv}}(\Delta E_{\mathrm{A}})$ or $f(\Delta E_{\mathrm{A}})$, the highest excited state considered in the FCCS analysis is the sixth excited state. When ϵ_{s} is 10, the ground-state level is calculated to be $\Delta E_1 = 136.0$ meV, and the excited state levels are calculated to be $\Delta E_2 = 34.0$ meV, $\Delta E_3 = 15.1$ meV, $\Delta E_4 = 8.5$ meV, $\Delta E_5 = 5.4$ meV, $\Delta E_6 = 3.8$ meV and $\Delta E_7 = 2.8$ meV. Since the experimental excited state levels were uncertain, these calculated excited state levels were used in the analyses. All the ΔE_{A} shown in table 1 are close to ΔE_{A} determined from PL.

Figure 3 also shows a set of three $H(T, E_{\mathrm{ref}})$ simulated using equation (58) with N_{A}, ΔE_{A} and N_{comp} determined by FCCS for $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$ (broken curve), $f_{\mathrm{conv}}(\Delta E_{\mathrm{A}})$ (dotted curve) and $f(\Delta E_{\mathrm{A}})$ (solid curve). Although all the peaks of the three simulated FCCS signals coincide with the peak of the experimental $H(T, E_{\mathrm{ref}})$, the FCCS signal (solid curve) simulated using $f(\Delta E_{\mathrm{A}})$ is in better agreement with the experimental FCCS signal (open circles) than the other

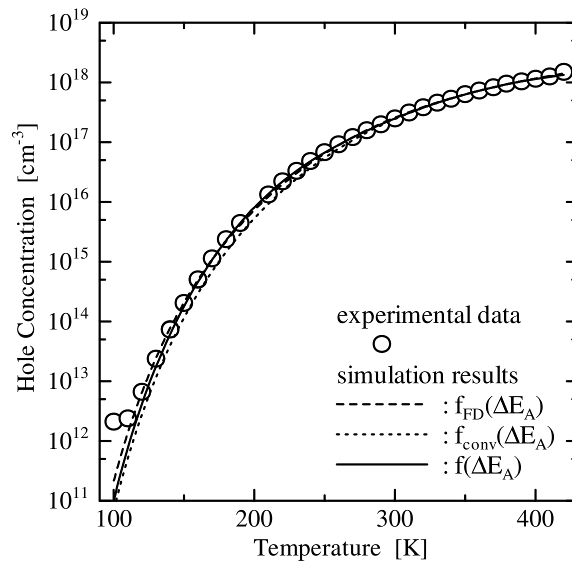

Figure 4. Experimental $p(T)$ (open circles) and a set of three $p(T)$ simulated using $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$ (broken curve), $f_{\mathrm{conv}}(\Delta E_{\mathrm{A}})$ (dotted curve) and $f(\Delta E_{\mathrm{A}})$ (solid curve).

signals (dotted and broken curves) are. This indicates that N_{A}, ΔE_{A} and N_{comp} determined using $f(\Delta E_{\mathrm{A}})$ are more reliable than the others.

Figure 4 shows the experimental $p(T)$ (open circles) and a set of three $p(T)$ simulated by equations (50) and (57) using N_{A}, ΔE_{A} and N_{comp} shown in table 1. The broken, dotted and solid curves represent the $p(T)$ simulated using $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$, $f_{\mathrm{conv}}(\Delta E_{\mathrm{A}})$ and $f(\Delta E_{\mathrm{A}})$, respectively. All the simulated $p(T)$ are in good agreement with the experimental $p(T)$. This indicates that it is difficult to investigate the influence of the excited states of the acceptor on $p(T)$ by the curve-fitting procedure of $p(T)$.

As is clear from figure 1, N_{A} should be lower than approximately 5×10^{18} cm^{-3}. This indicates that N_{A} of 5.46×10^{18} cm^{-3} obtained using the proposed distribution function $f(\Delta E_{\mathrm{A}})$ is more reliable than the others. N_{comp} determined by FCCS is higher than the density of N atoms with which the n-type epilayer was doped, because N_{comp} determined by FCCS includes the donor density owing to N atoms as well as deep hole traps created by ion implantation.

Since the excited states are considered to behave like hole traps according to the conventional distribution function model, $p(T)$ simulated using $f_{\mathrm{conv}}(\Delta E_{\mathrm{A}})$ becomes lower than $p(T)$ simulated using $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$ in the case of the same N_{A}. This indicates that N_{A} required to meet the experimental $p(T)$ in the case of $f_{\mathrm{conv}}(\Delta E_{\mathrm{A}})$ becomes higher than N_{A} in the case of $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$. Since N_{A} obtained using $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$ is already higher than the Al concentration determined by SIMS, it is necessary to introduce $\overline{E_{\mathrm{ex}}}$ when the influence of the excited states of the acceptor is considered.

In figure 5, the solid, dotted and chain curves represent $\exp(-\overline{E_{\mathrm{ex}}}/k_{\mathrm{B}}T)$, $\overline{\Delta E_{\mathrm{A}}}$ and ΔE_{F}, respectively, which are simulated using N_{A}, ΔE_{A} and N_{comp} determined using $f(\Delta E_{\mathrm{A}})$. $\overline{\Delta E_{\mathrm{A}}}$ decreases with T, and then $\overline{\Delta E_{\mathrm{A}}}$ above 356 K becomes lower than ΔE_{F}, indicating that the ionization efficiency of the Al acceptor increases rapidly with T. Since $\exp(-\overline{E_{\mathrm{ex}}}/k_{\mathrm{B}}T)$ decreases rapidly with T, the holes bound to acceptors are expected to decrease rapidly with T.

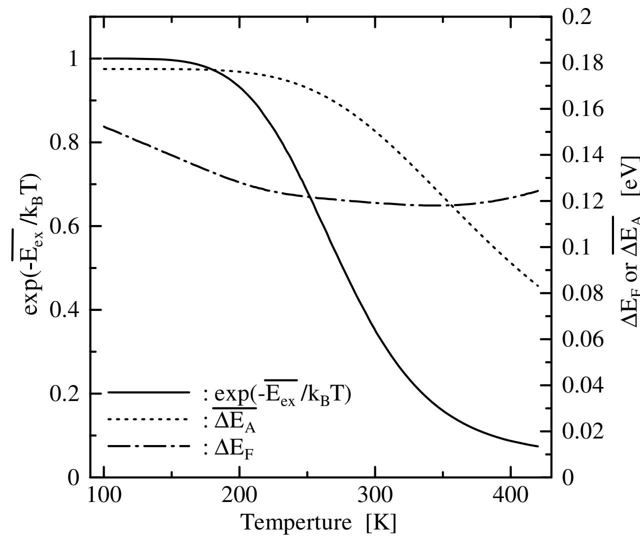

Figure 5. Temperature dependence of $\exp(-\overline{E_{\rm ex}}/k_{\rm B}T)$ (solid curve), $\overline{\Delta E_{\rm A}}$ (dotted curve) and $\Delta E_{\rm F}$ (chain curve), which are simulated with $N_{\rm A}$, $\Delta E_{\rm A}$ and $N_{\rm comp}$ determined using $f(\Delta E_{\rm A})$.

Therefore, $N_{\rm A}$ required to meet the experimental $p(T)$ becomes appropriate. In other words, the acceptor behaves as a shallow acceptor at the operative temperatures of SiC devices, although it acts as a deep acceptor at room temperature.

When the simulated $H(T, E_{\rm ref})$ can be fitted to the experimental $H(T, E_{\rm ref})$, the simulated $p(T)$ is always fitted to the experimental $p(T)$. However, the opposite is not always true. This indicates that the conventional curve-fitting procedure of $p(T)$ is not suitable for investigating the influence of the excited states on the majority-carrier concentration. Moreover, it is found that the influence of the excited states as well as the ensemble average of the ground and excited state levels of the acceptor should be considered in the analysis of $p(T)$.

6. Conclusion

The distribution function considering the influence of the excited states of a substitutional dopant on the majority-carrier concentration was theoretically discussed. In the discussion, an ensemble average of the ground and excited state levels of the dopant was introduced. Using the experimental $p(T)$ in Al-doped p-type 4H–SiC, the influence of the excited states of the Al acceptor on $p(T)$ was investigated. It was found that FCCS, which we have proposed, was suitable for investigating this influence more than the curve-fitting procedure of $p(T)$ was. In the FCCS analysis, the values of $N_{\rm A}$, $\Delta E_{\rm A}$ and $N_{\rm comp}$ determined using the proposed distribution function were considered to be reliable. It was demonstrated that in the analysis of $p(T)$ the influence of the excited states of the acceptor as well as the ensemble average of the excited state levels should be considered.

Acknowledgments

The author would like to thank Dr H Sugimoto of the Mitsubishi Electronic Corporation for the sample preparation, and SIMS and RBS measurements. He is also grateful for Mr K Nishikawa, Mr T Mizukoshi and the other members at the Matsuura laboratory of Osaka

Electro-Communication University for the Hall-effect measurements. This work was partially supported by the Academic Frontier Promotion Projects of the Ministry of Education, Culture, Sports, Science and Technology, and it was also partially supported by the R & D Association of Future Electron Devices (FED) and the New Energy and Industrial Technology Development Organization (NEDO).

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