Influence of excited states of a deep substitutional dopant on majority-carrier concentration in semiconductors

Hideharu Matsuura*
Department of Electronic Engineering and Computer Science, Osaka Electro-Communication University, 18-8 Hatsu-cho, Neyagawa, Osaka 572-8530, Japan

(Received 20 June 2006; revised manuscript received 20 October 2006; published 26 December 2006)

The density (N_A) and energy level (E_A) of an acceptor in a p-type wide-band-gap semiconductor (e.g., SiC, GaN, and diamond) are determined by a least-squares fit of the charge neutrality equation to the temperature dependence of the hole concentration $p(T)$ using the Fermi-Dirac distribution function for acceptors that does not consider the influence of the excited states of the acceptor. The N_A obtained this way is, however, much higher than the concentration of acceptor atoms determined by secondary ion mass spectroscopy. Because E_A is far from the valence-band maximum (E_V) and the Fermi level is between E_A and E_V, the influence of the excited states of the acceptor on $p(T)$ should not be ignored. A distribution function including the influence of excited states, which is derived from the viewpoint of the microcanonical ensemble, not the grand canonical ensemble, leads to reliable N_A and E_A. The situation in n-type Te-doped $Al_{0.6}Ga_{0.4}Sb$ is the same, because the Te donor level is far from the conduction-band minimum for large Al mole fraction. Finally, the excited states of a substitutional dopant with a deep energy level are found to enhance the ionization of the dopant, even though they were expected to suppress the ionization because they acted as a trap according to the distribution function derived from the viewpoint of the grand canonical ensemble.

DOI: 10.1103/PhysRevB.74.245216 PACS number(s): 71.55.−i, 73.61.Le

I. INTRODUCTION

The excited states of a substitutional dopant in a semiconductor have been theoretically discussed using the hydrogenic model (or the effective-mass approximation),[1–3] and the existence of excited states of the dopant (e.g., B or P) in Si or Ge was experimentally confirmed from infrared absorption measurements at very low temperatures.[1] However, the influence of the excited states on the majority carrier concentration in Si or Ge was not experimentally confirmed,[2,4] partially because the excited state levels of the dopants in Si or Ge were too shallow and partially because the Fermi level $E_F(T)$ was deeper than the dopant energy level in the temperature range above 77 K. Therefore, by a least-squares fit of the charge neutrality equation to the temperature dependence of the majority-carrier concentration experimentally obtained by Hall-effect measurements, the values of dopant density, dopant energy level, and compensating density can be determined using the Fermi-Dirac (FD) distribution function, which does not include the influence of the excited states of the dopant. The FD distribution functions for donors and acceptors are expressed as[5]

$$f_{\mathrm{FD}}(E_D) = \frac{1}{1 + \frac{1}{g_{D,\mathrm{FD}}} \exp\left(-\frac{E_F(T) - E_D}{kT}\right)} \quad (1)$$

and

$$f_{\mathrm{FD}}(E_A) = \frac{1}{1 + g_{A,\mathrm{FD}} \exp\left(-\frac{E_F(T) - E_A}{kT}\right)}, \quad (2)$$

respectively, where E_D and E_A are the donor and acceptor levels, respectively, $g_{D,\mathrm{FD}}$ and $g_{A,\mathrm{FD}}$ are the degeneracy factors for donors and acceptors, respectively, and k is the Boltzmann constant.

Because in p-type wide-band-gap semiconductors (e.g., SiC, GaN, and diamond) the experimentally obtained values of E_A have been reported to be deep,[6] $E_F(T)$ is often between E_A and the valence-band maximum (E_V). Furthermore, because the excited-state levels of acceptors in these semiconductors are as deep as a B acceptor level (i.e., ground-state level) in Si,[7] $E_F(T)$ is close to the excited-state levels. The excited states of the acceptor must, therefore, affect the temperature dependence of the hole concentration $p(T)$.

Using a distribution function including the influence of the excited states of an acceptor derived from the viewpoint of the grand canonical ensemble,[2,8,9] an acceptor density (N_A) was determined by fitting the simulation $p(T)$ to the experimental $p(T)$. The N_A determined this way was, however, much higher than the concentration of acceptor atoms determined by secondary ion mass spectroscopy (SIMS).[10] This same situation occurred in the case of the FD distribution function.[10–12]

In this paper, we report on our investigation of the optimum distribution function for determining the density and energy level of a deep substitutional dopant in p-type wide-band-gap semiconductors (i.e., B-doped diamond, Al-doped 6H-SiC, Al-implanted 4H-SiC, and Mg-doped GaN) and n-type Te-doped $Al_{0.6}Ga_{0.4}Sb$, where a Te donor level in $Al_{0.6}Ga_{0.4}Sb$ has been reported to be deep.[13]

II. EXPERIMENT

A 1.73-μm-thick single crystalline B-doped p-type diamond epilayer was grown at 830 °C on the (001) surface of a synthesized single-crystal 1b diamond substrate (area of $1.5 \times 2.0\ \mathrm{mm}^2$, thickness of 0.3 mm, and resistivity of

 ©2006 The American Physical Society

$10^{12}-10^{14}$ Ω cm) by a microwave plasma assisted chemical-vapor-deposition method. The B concentration (C_B) in the epilayer, measured by SIMS, was approximately 2×10^{17} cm^{-3}. The details of the sample preparation were reported earlier.[14,15]

A 400-μm-thick heavily Al-doped *p*-type 6*H*-SiC wafer in which the Al concentration (C_{Al}) was approximately 4×10^{18} cm^{-3} is referred to as a heavily doped 6*H*-SiC, while a 4.9-μm-thick Al-doped *p*-type 6*H*-SiC epilayer (C_{Al} of approximately 6×10^{15} cm^{-3}) on an *n*-type 6*H*-SiC substrate is referred to as a lightly doped 6*H*-SiC. These samples were purchased from Cree Res. Inc. The details of these samples were reported earlier.[16]

Al ions were implanted at 1000 °C in a 5-μm-thick *n*-type 4*H*-SiC epilayer with N atoms at 2.5×10^{15} cm^{-3} on an *n*-type 4*H*-SiC {0001} substrate cut 8° off toward the $\langle 11\bar{2}0 \rangle$ direction. To obtain a box profile of the concentration of Al atoms, sevenfold Al ion implantation was carried out at different energies onto the SiC epilayer surface tilted to 7° to normal. After the implantation, the sample was annealed at 1575 °C for 1 h in an Ar atmosphere. The 1.3-μm-thick layer was removed from the surface by reactive ion etching. The C_{Al} in the implanted layer was approximately 1×10^{19} cm^{-3}. The details of the sample preparation were reported earlier.[17]

A 2-μm-thick Mg-doped *p*-type GaN epilayer was grown at 1025 °C by metalorganic chemical vapor deposition on undoped GaN/sapphire, and annealed at 800 °C in N_2 for 20 min. The Mg concentration (C_{Mg}) in the epilayer, measured by SIMS, was approximately 2×10^{19} cm^{-3}. The details of the sample preparation were reported earlier.[18]

A 2-μm-thick Te-doped *n*-type $Al_{0.6}Ga_{0.4}Sb$ epilayer was grown on a semi-insulating GaAs(100) substrate at 470 °C by water-cooled molecular-beam epitaxy. The temperatures of Knudsen cells for Ga and Al were 910 and 1084 °C, respectively, and the temperature of a crystal cell for Sb_4 was 460 °C. For doping Te into the epilayer during the deposition, the temperature of the Knudsen cell for Ga_2Te_3 was 330 °C. The Te concentration (C_{Te}) in the epilayer was approximately 1×10^{17} cm^{-3}. The details of the sample preparation were reported earlier.[13]

The $p(T)$ values for 4*H*-SiC, 6*H*-SiC, diamond, and GaN, and the temperature-dependent electron concentration $n(T)$ for $Al_{0.6}Ga_{0.4}Sb$, were obtained by Hall-effect measurements in the van der Pauw configuration at a magnetic field of 1.4 T using a modified MMR Technologies Hall system.

III. RESULTS

Figure 1 shows $p(T)$ and $E_F(T)$ for the B-doped diamond. Here, $E_F(T)$ was derived from

$$p(T) = N_V(T)\exp\left(-\frac{E_F(T) - E_V}{kT}\right), \quad (3)$$

where $N_V(T)$ is the effective density of states in the valence band, given by

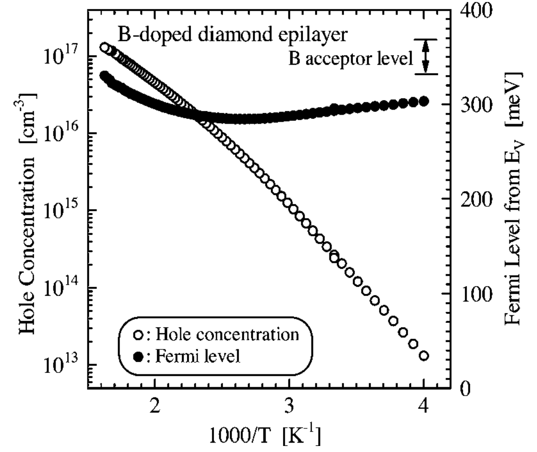

FIG. 1. Temperature dependence of hole concentration and Fermi level for B doped diamond.

$$N_V(T) = 2\left(\frac{2\pi m_h^* kT}{h^2}\right)^{3/2}, \quad (4)$$

m_h^* is the hole effective mass in the semiconductor, and h is Planck's constant. Because the E_A of B in diamond is approximately E_V+0.35 eV, the $E_F(T)$ values were lower than E_A over the measurement temperature range.

N_A and E_A of B acceptors, and a donor density (N_D), can be determined by fitting the simulation $p(T)$ to the experimental $p(T)$ using Eq. (3) and

$$p(T) = N_A F(E_A) - N_D, \quad (5)$$

where $n(T)$ is much less than $p(T)$ over the measurement temperature range, and $F(E_A)$ is the distribution function for acceptors. By replacing $F(E_A)$ with $f_{FD}(E_A)$, the values of N_A, E_A, and N_D were determined and are listed in Table I. In the table, f_{FD}, f_{MC}, and f_{GC} represent the FD distribution function and the distribution functions including the influence of the excited states of a dopant. In the following section, these distribution functions will be derived from the viewpoint of the microcanonical (MC) and grand canonical (GC) ensembles, respectively.

The N_A of 9.7×10^{17} cm^{-3}, which was determined by the curve-fitting procedure described previously, is approximately five times higher than the C_B of approximately 2×10^{17} cm^{-3}. Since N_A is the density of B atoms at the lattice sites, N_A should be less than or equal to C_B. Therefore, $f_{FD}(E_A)$ seems inappropriate to a distribution function for B acceptors in diamond.

Figure 2 depicts $p(T)$ and $E_F(T)$ for the heavily Al-doped 6*H*-SiC wafer, while Fig. 3 shows $p(T)$ and $E_F(T)$ for the lightly Al-doped 6*H*-SiC epilayer. The $E_F(T)$ values for the heavily doped 6*H*-SiC were below E_A over the measurement temperature range, whereas the $E_F(T)$ values for the lightly doped 6*H*-SiC were above E_A over almost all the measurement temperature range.

By the curve-fitting procedure using $f_{FD}(E_A)$, the values of N_A, E_A, and N_D were estimated and are listed in Table I. The N_A obtained for the heavily doped 6*H*-SiC is 2.5

TABLE I. Results for each distribution function.

			B-doped diamond	Heavily doped 6*H*-SiC	Lightly doped 6*H*-SiC	Al-implanted 4*H*-SiC	Mg-doped GaN		Te-doped $Al_{0.6}Ga_{0.4}Sb$
f_{FD}	N_A	(cm^{-3})	9.7×10^{17}	2.5×10^{19}	5.1×10^{15}	4.9×10^{19}	8.5×10^{19}	N_D	3.2×10^{17}
	E_A	(eV)	$E_V+0.34$	$E_V+0.18$	$E_V+0.19$	$E_V+0.16$	$E_V+0.15$	E_D	$E_C-0.09$
	N_D	(cm^{-3})	4.0×10^{16}	7.3×10^{17}	8.1×10^{14}	2.5×10^{18}	2.3×10^{18}	N_A	1.7×10^{17}
f_{MC}	N_A	(cm^{-3})	2.8×10^{17}	3.0×10^{18}	4.4×10^{15}	1.2×10^{19}	6.0×10^{18}	N_D	1.4×10^{17}
	E_A	(eV)	$E_V+0.32$	$E_V+0.18$	$E_V+0.20$	$E_V+0.18$	$E_V+0.16$	E_D	$E_C-0.13$
	N_D	(cm^{-3})	2.0×10^{16}	9.7×10^{16}	3.7×10^{14}	2.2×10^{17}	1.3×10^{17}	N_A	2.5×10^{16}
f_{GC}	N_A	(cm^{-3})	2.1×10^{18}	3.8×10^{20}	5.2×10^{15}	4.9×10^{20}	2.7×10^{20}	N_D	5.0×10^{17}
	E_A	(eV)	$E_V+0.38$	$E_V+0.18$	$E_V+0.19$	$E_V+0.17$	$E_V+0.17$	E_D	$E_C-0.10$
	N_D	(cm^{-3})	1.4×10^{16}	1.2×10^{19}	8.4×10^{14}	1.7×10^{19}	2.6×10^{18}	N_A	2.3×10^{17}
Doping Density	C	(cm^{-3})	$\sim2\times10^{17}$	$\sim4\times10^{18}$	$\sim6\times10^{15}$	$\sim1\times10^{19}$	$\sim2\times10^{19}$		$\sim1\times10^{17}$

$\times10^{19}$ cm^{-3}, which is approximately six times higher than the C_{Al}. On the other hand, the N_A obtained for the lightly doped 6*H*-SiC is 5.1×10^{15} cm^{-3}, which is nearly equal to the C_{Al}. This suggests that $f_{FD}(E_A)$ can be used only in the lightly doped sample. The reason for this is that in the lightly doped case there are few holes located at the excited states of the acceptor due to the large difference in energy between $E_F(T)$ and the excited-state level.

As is clear from Table I, in the Al-implanted 4*H*-SiC layer, the N_A of 4.9×10^{19} cm^{-3} determined by the curve-fitting procedure is approximately five times higher than the C_{Al}, and in the Mg-doped GaN epilayer the N_A of 8.5 $\times10^{19}$ cm^{-3} is approximately four times higher than the C_{Mg}.

The $E_F(T)$ values for the $Al_{0.6}Ga_{0.4}Sb$ epilayer were lower than E_D over almost the entire measurement temperature range. This is because the Te donor in $Al_xGa_{1-x}Sb$ changed from a shallow to a deep donor with the increase in Al mole fraction (x).[13] By the curve-fitting procedure using $f_{FD}(E_D)$, the values of N_D, E_D, and N_A were determined and are listed in Table I. The N_D of 3.2×10^{17} cm^{-3} is approximately three times higher than the C_{Te}. Moreover, the ratio of N_A to N_D is 0.54, which seems too high because the residual acceptor density in our undoped *p*-type $Al_{0.6}Ga_{0.4}Sb$ was of the order of 10^{15} cm^{-3}.[13]

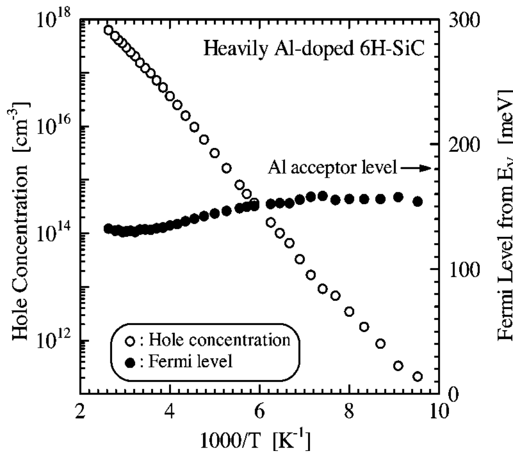

FIG. 2. Temperature dependence of hole concentration and Fermi level for heavily Al-doped 6*H*-SiC.

IV. DISTRIBUTION FUNCTION FOR A DEEP SUBSTITUTIONAL DOPANT

A. The number of configurations of the system

We now consider the microcanonical ensemble. Electrons and holes in semiconductors are fermions, which obey the Pauli exclusion principle. Because of this, in the allowed bands, the multiplicity function $W_B(E_i)$ for $n_e(E_i)$ electrons arranged in $D(E_i)$ states at a given energy (E_i) is expressed as[8]

$$W_B(E_i) = \frac{D(E_i)!}{[D(E_i)-n_e(E_i)]!n_e(E_i)!}, \quad (6)$$

where $D(E_i)$ is the number of degenerate states per unit volume at E_i and $n_e(E_i)$ is the number of electrons per unit volume at E_i.

In a forbidden band, on the other hand, the multiplicity function for n_D electrons arranged in N_D donors is quite dif-

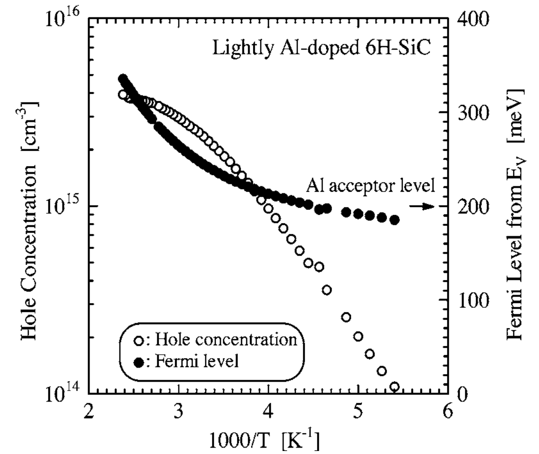

FIG. 3. Temperature dependence of hole concentration and Fermi level for lightly Al doped 6*H*-SiC.

ferent from Eq. (6), where n_D is the number of electrons bound to donors per unit volume. When spin degeneracy as well as 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

$$W_{D1} = \frac{N_D!}{(N_D - n_D)!n_D!}. \quad (7)$$

Each state of the ground and excited states consists of a spin-up state and a spin-down state. When the difference in energy between the two states in a magnetic field is denoted by ΔE_{spin}, the multiplicity function (W_{D2}) is given by

$$W_{D2} = \left[1 + \exp\left(-\frac{\Delta E_{\text{spin}}}{kT}\right)\right]^{n_D}. \quad (8)$$

When the magnetic field is zero or very weak ($\Delta E_{\text{spin}} \cong 0$),

$$W_{D2} \cong 2^{n_D}. \quad (9)$$

In a neutral donor, furthermore, only an electron is located at one state of the ground and excited states of the donor. The multiplicity function (W_{D3}) is given by

$$W_{D3} = \left[g_1 + \sum_{r=2}^{l} g_r \exp\left(-\frac{E_{r,D} - E_D}{kT}\right)\right]^{n_D}, \quad (10)$$

where $E_{r,D}$ is the $(r-1)$th excited-state level ($r \geqslant 2$) of the donor, g_1 is the ground-state degeneracy factor of 1, g_r is the $(r-1)$th excited-state degeneracy factor of r^2, and the value of $(l-1)$ is the highest order of the excited states considered here.

Consequently, the multiplicity function (W_D) for the n_D electrons arranged in the N_D donors is expressed as

$$W_D = W_{D1} W_{D2} W_{D3}. \quad (11)$$

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

$$W = W_D \prod_i W_{Bi}. \quad (12)$$

B. Thermal equilibrium configuration

Thermal equilibrium configuration occurs when the entropy

$$S = k \ln W \quad (13)$$

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

$$n_{\text{total}} = n_D + \sum_i n(E_i) = \text{const}, \quad (14)$$

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

$$E_{\text{total}} = \overline{E_D(T)} n_D + \sum_i E_i n(E_i) = \text{const}, \quad (15)$$

where $\overline{E_D(T)}$ is the average donor level given by

$$\overline{E_D(T)} = E_D + \overline{E_{\text{ex},D}(T)}, \quad (16)$$

and $\overline{E_{\text{ex},D}(T)}$ is the ensemble average of the ground- and excited-state levels of the donor, measured from E_D, and is given by

$$\overline{E_{\text{ex},D}(T)} = \frac{\sum_{r=2}^{l} (E_{r,D} - E_D) g_r \exp\left(-\frac{E_{r,D} - E_D}{kT}\right)}{1 + \sum_{r=2}^{l} g_r \exp\left(-\frac{E_{r,D} - E_D}{kT}\right)}. \quad (17)$$

Under these conditions, the distribution functions for electrons including the influence of the excited states of the donor $f_{\text{MC}}(E_D)$ can be derived,[10]

$$f_{\text{MC}}(E_D) \equiv \frac{n_D}{N_D} = \frac{1}{1 + \frac{1}{g_{D,\text{MC}}(T)} \exp\left(-\frac{E_F(T) - E_D}{kT}\right)}, \quad (18)$$

where $g_{D,\text{MC}}(T)$ is here called the effective degeneracy factor for donors given by

$$g_{D,\text{MC}}(T) = 2\left[1 + \sum_{r=2}^{l} g_r \exp\left(-\frac{E_{r,D} - E_D}{kT}\right)\right] \times \exp\left(-\frac{\overline{E_{\text{ex},D}(T)}}{kT}\right). \quad (19)$$

C. The hydrogenic donor case

A neutral donor can be approximately described as a hydrogen atom, that is, a positively ionized donor with an electron in orbit about the ionized donor. In this case, $E_{r,D}$ is given by[2,3]

$$E_{r,D} = E_C - \frac{q^4 m_e^*}{8h^2 \epsilon_s^2 \epsilon_0^2 r^2} = E_C - \frac{\Delta E_{1,D}}{r^2} \quad (20)$$

and

$$\Delta E_{1,D} = 13.6 \frac{m_e^*}{m_0} \frac{1}{\epsilon_s^2} \quad (\text{eV}), \quad (21)$$

where q is the electron charge, m_0 is the free-space electron mass, ϵ_s is the semiconductor dielectric constant, and ϵ_0 is the free-space permittivity.

Because the Bohr radius (a^*) of the ground state is very small, E_D is expressed as

$$E_D = E_{1,D} - E_{\text{CCC}}, \quad (22)$$

where E_{CCC} is the central cell correction induced due to a strongly localized potential.[1] Therefore, the ground-state level does not obey the hydrogenic model. However, because the wave-function extension of the $(r-1)$th excited state is of the order $r^2 a^*$, the excited-state levels (i.e., $E_{r,D}$ with $r \geqslant 2$) are expected to follow the hydrogenic model.

D. Distribution function for acceptors

In the case of acceptors, different from those in 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. When the density of electrons occupied at acceptors (n_A) is considered, therefore, $f_{\mathrm{MC}}(E_A)$ is derived as[10,16]

$$f_{\mathrm{MC}}(E_A) \equiv \frac{n_A}{N_A} = \frac{1}{1 + g_{A,\mathrm{MC}}(T)\exp\left(-\dfrac{E_F(T) - E_A}{kT}\right)}, \tag{23}$$

where $g_{A,\mathrm{MC}}(T)$ is here called the effective degeneracy factor for acceptors given by

$$g_{A,\mathrm{MC}}(T) = 4\left[1 + \sum_{r=2}^{l} g_r \exp\left(-\frac{E_A - E_{r,A}}{kT}\right)\right]\exp\left(-\frac{\overline{E_{\mathrm{ex},A}(T)}}{kT}\right). \tag{24}$$

Here, $\overline{E_{\mathrm{ex},A}(T)}$ is the ensemble average of the ground- and excited-state levels of the acceptor, measured from E_A, and is given by

$$\overline{E_{\mathrm{ex},A}(T)} = \frac{\displaystyle\sum_{r=2}^{l} (E_A - E_{r,A}) g_r \exp\left(-\frac{E_A - E_{r,A}}{kT}\right)}{1 + \displaystyle\sum_{r=2}^{l} g_r \exp\left(-\frac{E_A - E_{r,A}}{kT}\right)}, \tag{25}$$

$E_{r,A}$ is the $(r-1)$th excited-state level of the acceptor, expressed as

$$E_{r,A} = E_V + \frac{q^4 m_{\mathrm{h}}^*}{8h^2 \epsilon_s^2 \epsilon_0^2 r^2} = E_V + \frac{\Delta E_{1,A}}{r^2}, \tag{26}$$

and

$$\Delta E_{1,A} = 13.6 \frac{m_{\mathrm{h}}^*}{m_0} \frac{1}{\epsilon_s^2} \quad (\mathrm{eV}). \tag{27}$$

The average acceptor level $\overline{E_A(T)}$ and the acceptor level are expressed as

$$\overline{E_A(T)} = E_A - \overline{E_{\mathrm{ex},A}(T)} \tag{28}$$

and

$$E_A = E_{1,A} + E_{\mathrm{CCC}}. \tag{29}$$

E. Distribution function derived from the grand canonical ensemble

The grand canonical ensemble is an ensemble of the same subsystems, and particles can transfer from one subsystem into another subsystem, indicating that the number of particles in the subsystem (N) can change. The partition function (Ξ) for the grand canonical ensemble is given by[19]

$$\Xi = \sum_N z^N Z_N, \tag{30}$$

where

$$z = \exp\left(\frac{E_F(T)}{kT}\right). \tag{31}$$

Z_N is the partition function for the canonical ensemble for a given N, which is expressed as

$$Z_N = \sum \exp\left(-\frac{\sum_j n_j E_j}{kT}\right). \tag{32}$$

This summation is carried out over all the sets of $\{n_j\}$ under the condition

$$N = \sum_j n_j, \tag{33}$$

where E_j and n_j are the energy level and number of electrons at a jth state in the subsystem, respectively.

A donor is a subsystem. Each donor has one electron or no electron (i.e., $N=0$ or 1). The electron is located at one state of the ground and excited states (i.e., $n_j=0$ or 1). Moreover, the number of spin states and degenerate excited states should be taken into account. Therefore,

$$Z_0 = 1 \tag{34}$$

and

$$Z_1 = 2\left[\exp\left(-\frac{E_D}{kT}\right) + \sum_{r=2}^{l} g_r \exp\left(-\frac{E_{r,D}}{kT}\right)\right]. \tag{35}$$

Finally,

$$\Xi = \sum_{N=0}^{1} z^N Z_N = Z_0 + zZ_1 = 1 + 2\left[\exp\left(-\frac{E_D - E_F(T)}{kT}\right) + \sum_{r=2}^{l} g_r \exp\left(-\frac{E_{r,D} - E_F(T)}{kT}\right)\right]. \tag{36}$$

The mean number $\langle N \rangle$ of electrons in the subsystem in thermal equilibrium is given by

$$\langle N \rangle = \frac{\displaystyle\sum_{N=0}^{1} N z^N Z_N}{\Xi}. \tag{37}$$

Therefore, the distribution function including the influence of the excited states of a donor is derived as

$$f_{\mathrm{GC}}(E_D) \equiv \langle N \rangle = \frac{1}{1 + \dfrac{1}{g_{D,\mathrm{GC}}(T)} \exp\left(-\dfrac{E_F(T) - E_D}{kT}\right)}, \tag{38}$$

where

$$g_{D,\mathrm{GC}}(T) = 2\left[1 + \sum_{r=2}^{l} g_r \exp\left(-\frac{E_{r,D} - E_D}{kT}\right)\right], \quad (39)$$

which coincides with the reported distribution functions.[2,4,9] On the other hand, the distribution function for acceptors is derived as

$$f_{\mathrm{GC}}(E_A) = \frac{1}{1 + g_{A,\mathrm{GC}}(T)\exp\left(-\frac{E_F(T) - E_A}{kT}\right)}, \quad (40)$$

where

$$g_{A,\mathrm{GC}}(T) = 4\left[1 + \sum_{r=2}^{l} g_r \exp\left(-\frac{E_A - E_{r,A}}{kT}\right)\right]. \quad (41)$$

F. Comparison between three distribution functions

If the influence of the excited states of a donor or an acceptor could be ignored (i.e., $l=1$), $f_{\mathrm{MC}}(E_D)$ or $f_{\mathrm{MC}}(E_A)$ would coincide with $f_{\mathrm{FD}}(E_D)$ or $f_{\mathrm{FD}}(E_A)$.

The reason why $f_{\mathrm{GC}}(E_D)$ is different from $f_{\mathrm{MC}}(E_D)$ is discussed below. Because an electron can be at a higher excited-state level at elevated temperatures, the energy of an electron bound to a donor increases with increasing T. Therefore, the average donor level should increase with T, which is consistent with Eqs. (16) and (17).

If, on the other hand, electrons were located at the ground-state level at all temperatures, Eq. (15) could be replaced by

$$E_{\mathrm{total}} = E_D n_D + \sum_i E_i n(E_i) = \mathrm{const}. \quad (42)$$

In this case, the distribution function for donors derived from the microcanonical ensemble viewpoint would coincide with $f_{\mathrm{GC}}(E_D)$. This suggests that $f_{\mathrm{GC}}(E_D)$ is correct only under the assumption that all the electrons bound to donors have E_D at all temperatures. In the same way as illustrated for $f_{\mathrm{GC}}(E_D)$, if $\overline{E_A(T)}$ could be assumed to be E_A [i.e., $\overline{E_{\mathrm{ex},A}(T)}=0$], $f_{\mathrm{MC}}(E_A)$ would coincide with $f_{\mathrm{GC}}(E_A)$.

V. DETERMINATION OF RELIABLE DENSITY AND ENERGY LEVEL OF DEEP DOPANT

The ground-state level (i.e., acceptor level of E_A) does not obey the hydrogenic model because a^* is too small. However, the values of $E_{r,A}$ with $r \geqslant 2$ are expected to follow the hydrogenic model, because the wave-function extension of the $(r-1)$th excited state is of the order $r^2 a^*$. In B-doped diamond, by fitting the simulation $p(T)$ to the experimental $p(T)$ using $f_{\mathrm{MC}}(E_A)$ under a simple assumption (i.e., $\Delta E_{1,A}=0.39$ eV), the values of N_A, E_A, and N_D were determined as 2.82×10^{17} cm^{-3}, E_V+0.323 eV, and 1.95×10^{16} cm^{-3}, respectively. The highest excited state considered here was the sixth excited state (i.e., $l=7$), under which the best curve fitting was achieved. Because the radius of the sixth excited state is approximately 15 nm and the lattice constant for diamond is 0.356 nm, the number of C atoms in a sphere of radius 15 nm is approximately 2×10^6. Because the C density is 1.8×10^{23} cm^{-3} and the C_{B} is approximately 2×10^{17} cm^{-3}, there is, on the other hand, one B atom in approximately 10^6 C atoms. These suggest that the condition (i.e., $l=7$) is not so bad.

In the discussion above, $\Delta E_{1,A}$ is ambiguous. When $\Delta E_{1,A}$ was taken as 0.30 eV, N_A, E_A, and N_D were determined as 2.80×10^{17} cm^{-3}, E_V+0.320 eV, and 2.14×10^{16} cm^{-3}, respectively. When $\Delta E_{1,A}$ was taken as 0.50 eV, N_A, E_A, and N_D were determined as 2.88×10^{17} cm^{-3}, E_V+0.327 eV, and 1.72×10^{16} cm^{-3}, respectively. This result suggests that N_A, E_A, and N_D have only a small dependence on the excited-state levels. In Table I, therefore, E_A, N_A, E_D, and N_D are expressed in double figures.

Thonke reported that from their study of photoconductivity, the energy levels of long-lived excited states of B in diamond were 0.200, 0.240, and 0.266 eV from E_A, respectively.[7] On the other hand, the values of $E_A-E_{2,A}$, $E_A-E_{3,A}$, and $E_A-E_{4,A}$ we obtained are 0.22, 0.27, and 0.29 eV, respectively, when $\Delta E_{1,A}=0.39$ eV. Because the values obtained are close to the reported values, the excited-state levels considered here are reasonable.

N_A, E_A, and N_D determined by the curve-fitting procedure using $f_{\mathrm{GC}}(E_A)$ are also shown in Table I. In Table I, all the E_A values determined using three distribution functions seem reasonable. However, the N_A for $f_{\mathrm{GC}}(E_A)$ is highest, while the N_A for $f_{\mathrm{MC}}(E_A)$ is lowest. The N_A obtained using $f_{\mathrm{MC}}(E_A)$ is closest to the C_{B}. Therefore, $f_{\mathrm{MC}}(E_A)$ is suitable for determining N_A from $p(T)$.

Table I shows N_A, E_A, and N_{comp} for the Al-implanted 4*H*-SiC layer determined by the curve-fitting procedure using $f_{\mathrm{MC}}(E_A)$ or $f_{\mathrm{GC}}(E_A)$ for $\Delta E_{1,A}$ of 0.146 eV. The highest excited state considered here was the fourth excited state (i.e., $l=5$), which was less than in the B-doped diamond. This is because the Al-doping density in the 4*H*-SiC layer was higher than the B-doping density in the diamond epilayer. The N_A obtained using $f_{\mathrm{MC}}(E_A)$ is closest to the C_{Al} among the three distribution functions.

As is clear from Table I, only $f_{\mathrm{MC}}(E_A)$ led to reliable N_A, E_A, and N_D for the heavily Al-doped 6*H*-SiC, whereas all three distribution functions led to reasonable values for the lightly Al-doped 6*H*-SiC epilayer. This suggests that the excited states of the Al acceptor do not affect $p(T)$ very much in the lightly Al-doped 6*H*-SiC epilayer whose $E_F(T)$ is far from the excited-state levels. Therefore, $f_{\mathrm{MC}}(E_A)$ is determined to be suitable for both cases.

In Mg-doped GaN or Te-doped $\mathrm{Al_{0.6}Ga_{0.4}Sb}$ where $E_F(T)$ was shallower than the energy level of the dopant, f_{MC} is suitable for determining the density and energy level of the dopant from the temperature dependence of the majority-carrier concentration.

Three valence bands exist close to the Γ point at the center of the Brillouin zone. As discussed in Sec. IV D, in diamond and zinc-blende structures the light-hole and heavy-hole valence bands are degenerated at Γ, and the other valence band is located lower than the degenerate valence bands by spin-orbit splitting (Δ_{SO}). Since Δ_{SO} for Si and GaAs are 43 and 341 meV,[22] respectively, almost all of the holes exist in the two degenerate valence bands at Γ. There-

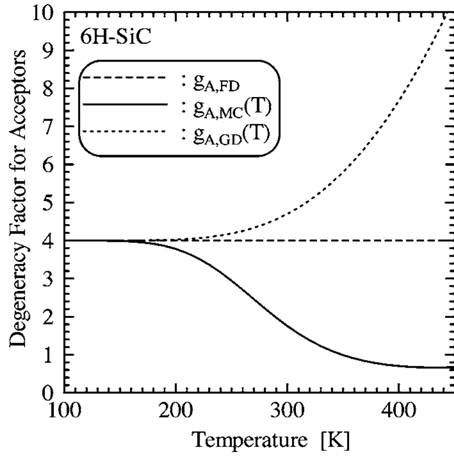

FIG. 4. Temperature dependence of simulated degeneracy factors for acceptors for 6*H*-SiC.

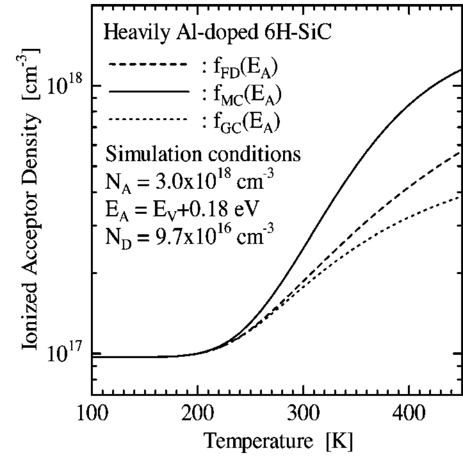

FIG. 5. Temperature dependence of simulated ionized acceptor densities for heavily Al-doped 6*H*-SiC.

fore, $g_{A,\mathrm{FD}}$ of 4 in $f_{\mathrm{FD}}(E_A)$ and a factor of 4 in $g_{A,\mathrm{MC}}(T)$ of $f_{\mathrm{MC}}(E_A)$ are quite reasonable. Δ_{SO} for diamond is, however, 6 meV.[22] If all three valence bands can be assumed to contribute equally to the hole conduction, both $g_{A,\mathrm{FD}}$ and the factor in $g_{A,\mathrm{MC}}(T)$ should be changed from 4 to 6. The values of N_A obtained for the B-doped diamond epilayer using $f_{\mathrm{FD}}(E_A)$ and $f_{\mathrm{MC}}(E_A)$ are 7.9×10^{17} and 2.6×10^{17} cm^{-3}, respectively. The N_A obtained using $f_{\mathrm{MC}}(E_A)$ is close to the C_{B}. Therefore, N_A is probably between 2.6×10^{17} and 2.8×10^{17} cm^{-3}.

In a wurtzite structure and hexagonal polytypes of SiC (e.g., 6*H*-SiC and 4*H*-SiC), three valence bands are all split due to both spin-orbit and crystal-field interactions at Γ.[20,21] The highest valence band is the heavy-hole valence band, and the other valence bands are located lower than the heavy-hole valence band by Δ_{SO} and Δ_{CF}, respectively, where Δ_{CF} is the energy separation due to the crystal-field interaction. The values of Δ_{SO} and Δ_{CF} for 6*H*-SiC are reported to be 7.8 and 48.7 meV, respectively.[21,22] If all the holes can be assumed to exist only in the heavy-hole valence band, both $g_{A,\mathrm{FD}}$ and the factor in $g_{A,\mathrm{MC}}(T)$ should be changed from 4 to 2. In this case, the values of N_A obtained for the heavily Al-doped 6*H*-SiC wafer using $f_{\mathrm{FD}}(E_A)$ and $f_{\mathrm{MC}}(E_A)$ are 1.4×10^{19} and 2.2×10^{18} cm^{-3}, respectively. The N_A obtained using $f_{\mathrm{MC}}(E_A)$ is close to C_{Al}. Therefore, N_A is probably between 2.2×10^{18} and 3.0×10^{18} cm^{-3}. Judging from the above discussions, the distribution function derived from the microcanonical ensemble viewpoint is most appropriate, although the N_A obtained depends slightly on the valence-band structures.

The reason a reasonable dopant density can be obtained using Eq. (18) or Eq. (23) is discussed from the viewpoint of the effective degeneracy factors. Figure 4 shows $g_{A,\mathrm{FD}}$, $g_{A,\mathrm{MC}}(T)$, and $g_{A,\mathrm{GC}}(T)$ for 6*H*-SiC, denoted by broken, solid, and dotted lines, respectively. $g_{A,\mathrm{MC}}(T)$ decreases from 4 with increasing T, whereas $g_{A,\mathrm{GC}}(T)$ increases. As the effective degeneracy factor for acceptors decreases, the distribution function for acceptors approaches 1 at the same T, indicating that in the case of $f_{\mathrm{MC}}(E_A)$, the ionization efficiency of acceptors is highest at elevated temperatures.

Figure 5 depicts the ionized acceptor densities $N_A^-(T)$ simulated using N_A of 3.0×10^{18} cm^{-3}, E_A of E_V+0.18 eV, N_D of 9.7×10^{16} cm^{-3}, and the effective degeneracy factors for acceptors shown in Fig. 4, for $f_{\mathrm{FD}}(E_A)$, $f_{\mathrm{MC}}(E_A)$, and $f_{\mathrm{GC}}(E_A)$, denoted by broken, solid, and dotted curves, respectively. As is clear from the figure, the $N_A^-(T)$ for $f_{\mathrm{MC}}(E_A)$ is highest at elevated temperatures. The $N_A^-(450)$ for $f_{\mathrm{MC}}(E_A)$ is, for example, approximately twice higher than that for $f_{\mathrm{FD}}(E_A)$. In the case of $f_{\mathrm{MC}}(E_A)$, therefore, the N_A required to satisfy the experimentally obtained $p(T)$ is much less than that determined using $f_{\mathrm{FD}}(E_A)$ or $f_{\mathrm{GC}}(E_A)$.

Another interpretation of Fig. 5 is as follows. As the temperature increases, the possibility that a hole bound to the acceptor is located at a higher excited-state level increases. That is why the acceptor can more easily emit a hole to the valence band at elevated temperatures. This coincides with Eq. (28). Therefore, it is clear that the excited states of the acceptor enhance the ionization of the acceptor at elevated temperatures.

Figure 6 shows $N_A^-(T)$ simulations for the lightly Al-doped 6*H*-SiC using the effective degeneracy factors for acceptors shown Fig. 4. Here, N_A, E_A, and N_D used in the simulation

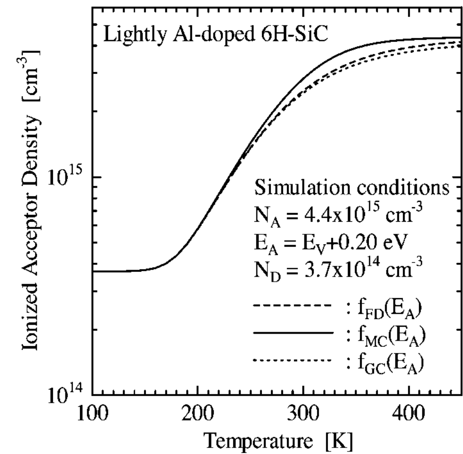

FIG. 6. Temperature dependence of simulated ionized acceptor densities for lightly Al-doped 6*H*-SiC.

were 4.4×10^{15} cm^{-3}, E_V+0.20 eV, and 3.7×10^{14} cm^{-3}, respectively. In the figure, the broken, solid, and dotted lines represent the $N_A^-(T)$ simulations for $f_{FD}(E_A)$, $f_{MC}(E_A)$, and $f_{GC}(E_A)$, respectively. Although the effective degeneracy factors for acceptors in the lightly doped case are the same as those in the heavily doped case, $N_A^-(T)$ for $f_{FD}(E_A)$, $f_{MC}(E_A)$, and $f_{GC}(E_A)$ are similar to each other in the lightly doped case. This is because the effective degeneracy factor for acceptors has little effect on $f_{FD}(E_A)$, $f_{MC}(E_A)$, and $f_{GC}(E_A)$, when $E_F(T)$ is far from the acceptor level, that is,

$$\exp\left(-\frac{E_F(T)-E_A}{kT}\right) \quad (43)$$

in Eqs. (2), (23), and (40) is nearly 0. To determine N_A from $p(T)$, therefore, $f_{MC}(E_A)$ is the most appropriate among them.

VI. CONCLUSION

A distribution function suitable for determining the density of a deep substitutional dopant from the temperature dependence of the majority-carrier concentration was discussed. The following three distribution functions were investigated: (i) the Fermi-Dirac distribution function, which does not consider the influence of the excited states of the dopant, (ii) the distribution function that includes the influence of excited states derived from the microcanonical ensemble viewpoint, and (iii) the distribution function including the influence of excited states derived from the grand canonical ensemble viewpoint.

The distribution function derived from the microcanonical ensemble was determined to be the most appropriate among them for determining the density and energy level of a deep substitutional acceptor in heavily doped *p*-type wide-bandgap semiconductors (e.g., Al-doped SiC, Mg-doped GaN, and B-doped diamond) whose Fermi levels were between E_V and E_A. This was because the excited states of the acceptor enhanced the ionization of the acceptor. This same situation was observed in *n*-type $Al_{0.6}Ga_{0.4}Sb$ with deep Te donors.

ACKNOWLEDGMENTS

The author would like to thank H. Sugimoto of Mitsubishi Electric Corp. for the Al-implanted 4*H*-SiC sample preparation, A. Namba, T. Imai, and T. Takebe of Sumitomo Electric Industries for the diamond sample preparation, T. Suzuki, S.-W. Kim, and T. Shibata of Nippon Institute of Technology for the GaN sample preparation, and W. Susaki of Osaka Electro-Communication University for the $Al_{0.6}Ga_{0.4}Sb$ sample preparation. He would like to acknowledge K. Nishikawa, K. Sugiyama, S. Kagamihara, H. Iwata, and other members of Matsuura Laboratory 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 (MEXT) in 1998–2002 and 2003–2008.

*Electronic address: matsuura@isc.osakac.ac.jp

[1] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors: Physics and Materials Properties*, 2nd ed. (Springer, Berlin, 1999), pp. 156 and 160.
[2] B. Sapoval and C. Hermann, *Physics of Semiconductors* (Springer-Verlag, New York, 1993), pp. 73 and 112.
[3] J. Singh, *Semiconductor Devices: An Introduction* (McGraw-Hill, New York, 1994), p. 110.
[4] R. A. Smith, *Semiconductors*, 2nd ed. (Cambridge University Press, Cambridge, 1978), p. 92.
[5] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981), Chap. 1.
[6] O. Mandelung, *Semiconductors: Data Handbook*, 3rd ed. (Springer, Berlin, 2004), pp. 11, 60, and 103.
[7] K. Thonke, Semicond. Sci. Technol. **18**, S20 (2003).
[8] K. F. Brennan, *The Physics of Semiconductors with Applications to Optoelectronic Devices* (Cambridge University Press, Cambridge, 1999), p. 292.
[9] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt Rinehart and Winston, Philadelphia, 1976), pp. 581 and 586.
[10] H. Matsuura, New J. Phys. **4**, 12.1 (2002) (http://www.njp.org/).
[11] T. Troffer, M. Schadt, T. Frank, H. Itoh, G. Pensl, J. Heindl, H. P. Strunk, and M. Maier, Phys. Status Solidi A **162**, 277 (1997).
[12] N. Schulze, J. Gajowski, K. Semmelroth, M. Laube, and G. Pensl, Mater. Sci. Forum **353–356**, 45 (2001).
[13] H. Matsuura and K. Nishikawa, J. Appl. Phys. **97**, 093711 (2005).
[14] H. Shiomi, Y. Nishibayashi, and N. Fujimori, Jpn. J. Appl. Phys., Part 1 **30**, 1363 (1991).
[15] H. Matsuura, T. Morizono, Y. Inoue, S. Kagamihara, A. Namba, T. Imai, and T. Takebe, Jpn. J. Appl. Phys., Part 1 **45**, 6376 (2006).
[16] H. Matsuura, J. Appl. Phys. **95**, 4213 (2004).
[17] H. Matsuura, K. Sugiyama, K. Nishikawa, T. Nagata, and N. Fukunaga, J. Appl. Phys. **94**, 2234 (2003).
[18] H. Matsuura, D. Katsuya, T. Ishida, S. Kagamihara, K. Aso, H. Iwata, T. Aki, S.-W. Kim, T. Shibata, and T. Suzuki, Phys. Status Solidi C **0**, 2214 (2003).
[19] C. V. Heer, *Statistical Mechanics, Kinetic Theory, and Stochastic Processes* (Academic Press, New York, 1972), p. 224.
[20] H. Morkoç, *Nitride Semiconductors and Devices* (Springer, Berlin, 1999), p. 49.
[21] W. J. Choyke, *Silicon Carbide*, edited by W. J. Choyke, H. Matsunami, and G. Pensl (Springer, Berlin, 2004), p. 417.
[22] S. Adachi, *Properties of Group-IV, III-V and II-VI Semiconductor* (Wiley, Chichester, 2005), p. 119.