Investigation of a distribution function suitable for acceptors in SiC

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The distribution function suitable for an acceptor in p-type SiC is investigated using lightly or heavily Al-doped SiC samples. From the temperature dependence of the hole concentration, the density and energy level of the acceptors are estimated using two different distribution functions. The proposed distribution function, which considers the influence of the excited states of acceptors, can be applied to both the samples, while the Fermi–Dirac distribution function, which does not include this influence, can be applied only to the lightly doped sample. In order to elucidate this result theoretically, the dependencies of both distribution functions on the temperature or the acceptor density are simulated. From these simulations, the proposed distribution function is found to be appropriate for determining the density and energy level of dopants with a deep dopant energy level for any dopant density. © 2004 American Institute of Physics. [DOI: 10.1063/1.1655683]

I. INTRODUCTION

Excited states of a substitutional dopant in a semiconductor have been discussed theoretically using the hydrogenic model, and the existence of the excited states in Si or Ge has been experimentally confirmed from infrared absorption measurements. However, the influence of the excited states on the majority-carrier concentration in Si or Ge has not been experimentally confirmed because the excited state levels are too close to the band edge, that is, the valence band maximum (E_V) or the conduction band minimum (E_C). Therefore, the Fermi–Dirac (FD) distribution function, which does not include the influence of the excited states, is considered valid in Si or Ge.

According to the hydrogenic model, the ground-state level of the acceptor (theoretical acceptor level: ΔE_1) in SiC is calculated as ~136 meV. The experimental acceptor level (ΔE_A = E_A − E_V) of Al in SiC was reported to be ~180 meV, which is larger than ΔE_1 due to central cell corrections, where E_A is the acceptor level and all ΔE used here are measured from E_V. Since the theoretical first excited state level (ΔE_2) of acceptors in SiC is close to ΔE_A (~45 meV) of B in Si, the excited states in SiC must affect the hole concentration. This indicates that a distribution function considering the influence of the excited states should be required to investigate the relationship between the acceptor density (N_A) and the temperature dependence of the hole concentration p(T).

Using the FD distribution function f_{FD}(ΔE_A), almost all researchers have determined ΔE_A, N_A and the compensating density (N_{comp}) in heavily Al-doped or Al-implanted SiC by a least-squares fit of the charge neutrality equation to p(T). However, N_A determined using f_{FD}(ΔE_A) has been much higher than the concentration of Al atoms (C_{Al}) determined by secondary ion mass spectroscopy. This result conflicts with the fact that N_A ~ C_{Al} because N_A is the density of Al atoms located at the substitutional sites in SiC. The situation in wide band gap semiconductors such as Mg-doped p-type GaN has also been the same.

In order to determine a reliable value for N_A using p(T) in p-type SiC, the following two attempts have been made: (1) the experimental adjustment of Hall-scattering factor for holes and (2) the theoretical introduction of a distribution function suitable for Al acceptors. Moreover, Al atoms with high density may disturb the valence band structure near E_V, and might form an impurity band. However, the p(T) for these p-type SiC samples exhibit a typical semiconductor behavior. Since the Fermi levels E_F(T) in these p-type SiC samples are located between E_V and E_A, there are a lot of holes at the excited states. Therefore, the distribution function including the influence of the excited states is focused on here.

The conventional distribution function f_{conv,n}(ΔE_A), which includes the influence of the excited states, appears in books. However, N_A determined using f_{conv,n}(ΔE_A) is much higher than N_A determined using f_{FD}(ΔE_A), because the excited states are considered to behave like a hole trap. Therefore, a new distribution function f_n(ΔE_A) including the influence of the excited states has been proposed and tested.

According to Poisson’s equation, moreover, N_A and p(T) significantly influence the shape of the band bending in pn junctions, metal-oxide-semiconductor junctions or Schottky barrier junctions. Since high power SiC devices can be operated in a wide temperature range, the electric characteristics obtained by device simulation should be strongly affected by the distribution function used in simulation. Therefore, the investigation of a distribution function suitable for acceptors in p-type SiC is important.

In lightly Al-doped SiC where E_F(T) is far from both E_V and E_A, f_{FD}(ΔE_A) is assumed to be appropriate for determining N_A using p(T). In heavily Al-doped SiC, on the other hand, f_n(ΔE_A) is considered to be appropriate while f_{FD}(ΔE_A) is not. In this article, in order to obtain a distribu-
tion function suitable for any doping density, we report on our investigation as to whether \( f_a(\Delta E_A) \) is appropriate for lightly Al-doped \( p \)-type SiC.

II. DISTRIBUTION FUNCTION INCLUDING EXCITED STATES OF ACCEPTORS

\[
f_{\text{FD}}(\Delta E_A) = \frac{1}{1 + g_A \exp \left( \frac{E_{\text{ex},n}(T)}{kT} \right) \exp \left( \frac{\Delta E_A - \Delta E_F(T)}{kT} \right) + \sum_{r=2}^{n} g_r \exp \left( \frac{\Delta E_r - \Delta E_F(T)}{kT} \right)}
\]

where \( \Delta E_r \) is the difference in energy between \( E_F \) and the \((r-1)\)th excited state level, \( E_{\text{ex},n}(T) \) is an ensemble average of the ground \((r=1)\) and excited \((r \geq 2)\) levels of the acceptor measured from \( E_A \), and \( g_r \) is the \((r-1)\)th excited state degeneracy factor, which is expressed as \( r^2 \). \( \Delta E_r \) is described as \(^2\)

\[
\Delta E_r = q^4 m_b^* \frac{1}{8 h^2 \varepsilon_0 \varepsilon_r r^2} = 13.6 \frac{m_0^*}{m_0} \varepsilon_0 \varepsilon_r r^2 \text{ (eV)}
\]

and \( E_{\text{ex},n}(T) \) is given by \(^8,9,14,20\)

\[
E_{\text{ex},n}(T) = \frac{\sum_{r=2}^{n} (\Delta E_A - \Delta E_r) g_r \exp \left( \frac{\Delta E_A - \Delta E_r}{kT} \right)}{1 + \sum_{r=2}^{n} g_r \exp \left( \frac{\Delta E_A - \Delta E_r}{kT} \right)}
\]

where \( q \) is the electron charge, \( m_0 \) is the free space electron mass, \( m_b^* \) is the hole effective mass in the semiconductor, \( h \) is Planck’s constant, \( \varepsilon_0 \) is the free space permittivity, and \( \varepsilon_r \) is the dielectric constant for the semiconductor.

Since the Bohr radius \( (a^*) \) of the ground state is very small, \( \Delta E_A \) is larger than \( \Delta E_1 \) due to central cell corrections. \(^1\) Since the wave function extension of the \((r-1)\)th excited state is of order \( r^2 a^* \), \(^2\) however, the excited state levels are assumed not to be affected by central cell corrections. \(^1\)

In order to compare \( f_n(\Delta E_A) \) in Eq. (3) with \( f_{\text{FD}}(\Delta E_A) \) in Eq. (1) easily, \( f_n(\Delta E_A) \) can be rewritten as

\[
f_n(\Delta E_A) = \frac{1}{1 + g_n(T) \exp \left( \frac{\Delta E_A - \Delta E_F(T)}{kT} \right)}
\]

and

\[
g_A = \frac{4}{\Delta E_F(T) = E_F(T) - E_V}, g_A \text{ is the acceptor degeneracy factor, } k \text{ is the Boltzmann constant, and } T \text{ is the absolute temperature.}
\]

On the other hand, the proposed distribution function considering the influence of the excited states is given by \(^9\)

\[
g_n(T) = g_A \exp \left( \frac{-E_{\text{ex},n}(T)}{kT} \right) \times \left[ 1 + \sum_{r=2}^{n} g_r \exp \left( \frac{\Delta E_r - \Delta E_A}{kT} \right) \right].
\]

where \( g_n(T) \) is here called the effective acceptor degeneracy factor, which includes the excited states of acceptors. Although the physically meaningful degeneracy factors \((i.e., g_A, g_r)\) are independent of \( T \), the \( g_n(T) \) defined here strongly depends on \( T \) because the occupation probabilities for holes at excited states change with \( T \). Here, \( f_1(\Delta E_A) = f_{\text{FD}}(\Delta E_A) \) because \( g_1(T) = g_A \).

On the other hand, the effective acceptor degeneracy factor \( g_{\text{conv},n}(T) \) corresponding to \( f_{\text{conv},n}(\Delta E_A) \) is \(^9,16–18\)

\[
g_{\text{conv},n}(T) = g_A \left[ 1 + \sum_{r=2}^{n} g_r \exp \left( \frac{\Delta E_r - \Delta E_A}{kT} \right) \right].
\]

It is clear from Eq. (8) that \( g_{\text{conv},n}(T) \) is always larger than \( g_A \). Therefore, the difference between these distribution functions comes to the difference between \( g_A, g_n(T) \), and \( g_{\text{conv},n}(T) \).

In the following discussion, \( f_{\text{FD}}(\Delta E_A) \) and \( f_a(\Delta E_A) \) are considered because \( f_{\text{conv},n}(\Delta E_A) \) could not lead to a reliable value for \( N_A \) in heavily or lightly Al-doped samples. \(^8,9,14,15\)

III. FREE CARRIER CONCENTRATION SPECTROSCOPY

Free carrier concentration spectroscopy (FCCS) \(^8,9,11,14,15,21–23\) is a graphical peak analysis method for determining the densities and energy levels of acceptor species in a semiconductor using \( p(T) \), even when the number of acceptor species included in the semiconductor is unknown. Using an experimental \( p(T) \), the FCCS signal is defined as \(^22,23\)
\[ H(T,E_{\text{ref}}) = \frac{p(T)}{kT} \exp \left( \frac{E_{\text{ref}}}{kT} \right). \] (9)

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

In order to elucidate the abovementioned feature of FCCS, this method is theoretically discussed. Although FCCS can be applied to any nondegenerate semiconductor, including several types of acceptor species, donor species and traps, we here focus on a \( p \)-type semiconductor doped with one species of acceptor. From the charge neutrality condition, \( p(T) \) is given by

\[ p(T) = N_A f_N(D_{\text{ref}}) - N_{\text{comp}} \] (10)

in the temperature range in which the electron concentration is much less than \( p(T) \), where \( F(\Delta E_A) \) represents \( f_{T_0}(\Delta E_A) \) or \( f_s(\Delta E_A) \). In the case of nondegenerate semiconductors, furthermore, \( p(T) \) is given by \(^{24}\)

\[ p(T) = N_V(T) \exp \left( - \frac{\Delta E_F(T)}{kT} \right), \] (11)

where

\[ N_V(T) = N_{V0} k^{3/2} T^{3/2} \] (12)

and

\[ N_{V0} = 2 \left( \frac{2 \pi m^*_n}{\hbar^2} \right)^{3/2}, \] (13)

because the distribution function for free carriers (i.e., holes) in the valence band is the FD distribution function with the degeneracy factor of 1.

Substituting Eq. (10) for one of the two \( p(T) \) in Eq. (9) and substituting Eq. (11) for the other \( p(T) \) in Eq. (9) yields

\[ H(T,E_{\text{ref}}) = \frac{N_A}{kT} \exp \left( - \frac{\Delta E_A - E_{\text{ref}}}{kT} \right) I(\Delta E_A) \]

\[ - \frac{N_{\text{comp}} N_{V0}}{kT} \exp \left( \frac{E_{\text{ref}} - \Delta E_F(T)}{kT} \right), \] (14)

where

\[ I(\Delta E_A) = N_{V0} \exp \left( \frac{\Delta E_A - \Delta E_F(T)}{kT} \right) F(\Delta E_A). \] (15)

The function

\[ \frac{N_A}{kT} \exp \left( - \frac{\Delta E_A - E_{\text{ref}}}{kT} \right) \] (16)

in Eq. (14) has a peak value of \( N_A \exp(-1)/kT_{\text{peak}} \) at the peak temperature

\[ T_{\text{peak}} = \frac{\Delta E_A - E_{\text{ref}}}{k}. \] (17)

As is clear from Eq. (17), \( E_{\text{ref}} \) can shift the peak of \( H(T,E_{\text{ref}}) \) within the temperature range of the measurement. Although the actual \( T_{\text{peak}} \) of \( H(T,E_{\text{ref}}) \) is slightly different from \( T_{\text{peak}} \) calculated by Eq. (17) due to the temperature dependence of \( I(\Delta E_A) \), we can easily determine the accurate values of \( N_A \) and \( \Delta E_A \) from the peak of the experimental \( H(T,E_{\text{ref}}) \), using a personal computer. The Windows application software for FCCS can be freely downloaded at our web site (http://www.osakac.ac.jp/labs/matsuura/).

**IV. EXPERIMENT**

A 400-\( \mu \)m-thick heavily Al-doped 6H–SiC wafer with a resistivity \( \rho \) of 1.4 \( \Omega \) cm at 300 K is called a heavily doped sample, while a 4.9-\( \mu \)m-thick 6H–SiC epilayer (Al-doping density: \( \sim 6 \times 10^{15} \) cm\(^{-3} \)) on \( n \)-type 6H–SiC substrate \( \rho \) (0.027 \( \Omega \) cm at 300 K) is called a lightly doped sample. The samples were cut to a 1 \( \times \) 1 cm\(^2 \) size. Ohmic metal (Al/Ti) was deposited on four corners of the surface, and the samples were annealed at 900 \( ^\circ \)C for 1 min in an Ar atmosphere in order to form good ohmic contact. The \( p(T) \) was measured by the van der Pauw method in the temperature range of 100–420 K and in a magnetic field of 1.4 T using a modified MMR Technologies’ Hall system.

**V. RESULTS AND DISCUSSION**

Figure 1 shows two experimental \( p(T) \) (open circles: heavily doped sample, open diamonds: lightly doped sample). Both the \( p(T) \) exhibit a typical semiconductor behavior. Therefore, the heavily doped sample is not a degenerate semiconductor, and it does not have an impurity band.

Figure 2 depicts two \( \Delta E_F(T) \) (open circles: heavily doped sample, open diamonds: lightly doped sample), which are calculated using

\[ \Delta E_F(T) = kT \ln \left( \frac{N_V(T)}{p(T)} \right). \] (18)

In order to make symbols regarding energy levels clear, a schematic of the band structure near \( E_V \) is inserted in Fig. 2. Furthermore, the locations of the expected Al acceptor levels are added in the figure. The \( \Delta E_F(T) \) is located between \( E_V \) and \( E_A \) in the heavily doped sample, while it is far from \( E_V \).
in the lightly doped one. Although the $\Delta E_f(T)$ decreases and then increases with increasing $T$ in the heavily doped sample, the $\Delta E_f(T)$ simulation using Eqs. (10) and (11) predicts this phenomenon when $\Delta E_f(T)$ is located between $E_V$ and $E_A$. Since the Al acceptor level in SiC was deep, this phenomenon could be observed in the temperature range of the measurement.

Open circles in Fig. 3 represent the FCCS signal with $E_{\text{ref}}=0.248$ eV in the heavily doped sample. Since there is only one peak in the figure, the sample includes only one species of acceptor. From the peak, the values of $N_A$, $\Delta E_A$, and $N_{\text{comp}}$ are determined using ten different following distribution functions; $f_{\text{FD}}(\Delta E_A)$ corresponding to $n=1$, and nine $f_d(\Delta E_A)$ for $2 \leq n \leq 10$. Using a set of $N_A$, $\Delta E_A$, and $N_{\text{comp}}$ determined using each distribution function as well as $\Delta E_f(T)$ calculated with Eq. (18) from the experimental $p(T)$, the corresponding $H(T,E_{\text{ref}})$ is simulated from Eq. (14). Figure 3 also shows four $H(T,E_{\text{ref}})$ simulations using $f_{\text{FD}}(\Delta E_A)$, $f_d(\Delta E_A)$, $f_7(\Delta E_A)$, and $f_{10}(\Delta E_A)$ (dotted line), $f_3(\Delta E_A)$ (solid line), and $f_{10}(\Delta E_A)$ (chain line). The solid line is in better agreement with the experimental $H(T,E_{\text{ref}})$ than the others. Moreover, the $H(T,E_{\text{ref}})$ simulation for $f_7(\Delta E_A)$ fitted to the experimental $H(T,E_{\text{ref}})$ for most of the nine $H(T,E_{\text{ref}})$ simulations for $f_n(\Delta E_A)$. This indicates that a set of $N_A$, $\Delta E_A$, and $N_{\text{comp}}$ determined using $f_7(\Delta E_A)$ is more reliable than the others. Here, the excited states contained in $f_7(\Delta E_A)$ are $\Delta E_2=34.0$ 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. In the following discussion, therefore, only $f_{\text{FD}}(\Delta E_A)$ and $f_7(\Delta E_A)$ are considered.

The values of $N_A$, $\Delta E_A$, and $N_{\text{comp}}$ determined by FCCS are $3.2 \times 10^{18}$ cm$^{-3}$, $180$ meV and $9.0 \times 10^{16}$ cm$^{-3}$ for $f_7(\Delta E_A)$, respectively, while they are $2.5 \times 10^{19}$ cm$^{-3}$, $180$ meV and $7.3 \times 10^{17}$ cm$^{-3}$ for $f_{\text{FD}}(\Delta E_A)$, respectively, and they are listed in Table I. On the other hand, the value of $N_A-N_{\text{comp}}$, which was determined from the capacitance-voltage characteristics of the Schottky barrier junction formed using this wafer, was $4.2 \times 10^{18}$ cm$^{-3}$. This value indicates that $f_7(\Delta E_A)$ is significantly more appropriate for the distribution function in the heavily doped sample than $f_{\text{FD}}(\Delta E_A)$.

Open diamonds in Fig. 4 represent the FCCS signal with $E_{\text{ref}}=0$ eV in the lightly doped sample. Table I lists $N_A$, $\Delta E_A$ and $N_{\text{comp}}$ determined from the peak. The values determined using $f_7(\Delta E_A)$ are very close to those using $f_{\text{FD}}(\Delta E_A)$. Moreover, both values of $N_A$ are in agreement with the Al-doping density.

**Table I. Dependencies of results on distribution functions.**

<table>
<thead>
<tr>
<th>Distribution Function</th>
<th>Heavily doped $H(T, E_{\text{ref}})$</th>
<th>Lightly doped $H(T, E_{\text{ref}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{\text{FD}}(\Delta E_A)$</td>
<td>$3.2 \times 10^{18}$</td>
<td>$4.1 \times 10^{15}$</td>
</tr>
<tr>
<td>$f_7(\Delta E_A)$</td>
<td>$180$</td>
<td>$212$</td>
</tr>
<tr>
<td>$N_A$ [cm$^{-3}$]</td>
<td>$9.0 \times 10^{16}$</td>
<td>$5.5 \times 10^{14}$</td>
</tr>
</tbody>
</table>

FIG. 2. Temperature dependencies of Fermi levels measured from $E_V$. A schematic of the band structure near the valence band is inserted. The locations of the expected Al acceptor levels are also shown.

FIG. 3. Experimental and simulated FCCS signals of $H(T,0.248)$ in the heavily doped sample.

FIG. 4. Experimental and simulated FCCS signals of $H(T,0)$ in the lightly doped sample.
Figure 4 also shows two $H(T,E_{ref})$ simulations from Eq. (14) with $N_A$, $\Delta E_A$, and $N_{comp}$ shown in Table I. The solid and broken lines represent the $H(T,E_{ref})$ simulations for $f_7(\Delta E_A)$ and $f_{FD}(\Delta E_A)$. Both the lines are in agreement with the experimental $H(T,E_{ref})$. Therefore, it is assumed that both the distribution functions can lead to reliable values for $N_A$ and $\Delta E_A$ in the lightly doped sample.

Figure 5 shows two $p(T)$ simulations from Eqs. (10) and (11) with the values in Table I. In the figure, the open circles and diamonds represent the experimental $p(T)$ in the heavily and lightly doped samples. The solid and broken lines represent $p(T)$ simulated using $f_7(\Delta E_A)$ and $f_{FD}(\Delta E_A)$. From the figure, the $p(T)$ simulations using $f_7(\Delta E_A)$ and $f_{FD}(\Delta E_A)$ coincide with the experimental $p(T)$. From $p(T)$ simulations, therefore, it is difficult to determine which distribution function is suitable for explaining the ionization efficiency of acceptors in SiC.

From the discussion mentioned above, it is concluded that $f_7(\Delta E_A)$ can be applied to both the heavily and lightly doped $p$-type SiC samples while $f_{FD}(\Delta E_A)$ can be applied only to the lightly doped sample. The difference between $f_{FD}(\Delta E_A)$ in Eq. (1) and $f_7(\Delta E_A)$ in Eq. (6) is only the difference between $g_A$ and $g_7(T)$. Figure 6 shows the temperature dependencies of the effective acceptor degeneracy factors (broken line: $g_A$, dotted line: $g_7(T)$, solid line: $g_A(T)$, chain line: $g_{10}(T)$). It is clear from the figure that $g_n(T)$ is $g_A$ at lowered temperatures, indicating that $f_7(\Delta E_A)$ is $f_{FD}(\Delta E_A)$. On the other hand, $g_n(T)$ at elevated temperatures is much less than $g_A$ of 4. For example, the value of $g_7(T)$ at 400 K is 0.70. This small $g_n(T)$ at elevated temperatures makes the ionization efficiency of acceptors high. In the following discussion, we focus on the difference between $g_A$ and $g_7(T)$.

Figure 7 shows the dependencies of $f_7(\Delta E_A)$ and $f_{FD}(\Delta E_A)$ on the value of $E_A - E_F(T)$ at 400 K, which are denoted by the solid and broken lines, where the value of $E_A - E_F(T)$ is positive when $E_F(T)$ is located between $E_V$ and $E_A$. The difference between $g_7(T)$ and $g_A$ at 400 K results in the difference between the solid and broken lines. The ionized acceptor density ($N_A$) is given by $N_A = N_A f_7(\Delta E_A)$ or $N_A = N_A f_{FD}(\Delta E_A)$. Since $E_A - E_F(T)$ is 50 meV in the heavily doped sample, $f_7(\Delta E_A)$ to $f_{FD}(\Delta E_A)$ is 4.5. Therefore, $N_A$ for $f_7(\Delta E_A)$ is higher by 4.5 than $N_A$ for $f_{FD}(\Delta E_A)$. On the other hand, since $E_A - E_F(T) = -110$ meV in the lightly doped sample, $f_7(\Delta E_A)$ to $f_{FD}(\Delta E_A)$ is 1.1, indicating that $N_A$ for $f_7(\Delta E_A)$ is close to $N_A$ for $f_{FD}(\Delta E_A)$.

Figure 8 shows the dependencies of $f_7(\Delta E_A)$ and $f_{FD}(\Delta E_A)$ on the acceptor density at 400 K, which are denoted by the solid and broken lines. These simulations are obtained under the following conditions; $\Delta E_A = 180$ meV and $N_{comp}/N_A = 0.025$. In the lightly doped case, $f_7(\Delta E_A)$ is $f_{FD}(\Delta E_A)$, indicating that $N_A$, $\Delta E_A$, and $N_{comp}$ determined using $f_7(\Delta E_A)$ are similar to those using $f_{FD}(\Delta E_A)$.

It is clear from the abovementioned simulation results that $f_7(\Delta E_A)$ is appropriate for any doping density in $p$-type SiC.
SiC. Since these simulations are not limited to Al acceptors in $p$-type 6H–SiC, moreover, the proposed distribution function including the excited states of dopants is applicable to substitutional dopants with deep dopant energy levels for any dopant density. In other words, this distribution function is applicable to the temperature range where the Fermi level is close to $E_V$ or $E_C$.

VI. CONCLUSION

The Fermi–Dirac distribution function, which does not consider the influence of the excited states of the acceptors, could only be applied to the lightly doped case. On the other hand, the proposed distribution function considering the influence of the excited states led to the reliable acceptor densities and energy levels for the heavily and lightly doped samples, indicating that this distribution function is appropriate for any acceptor density in $p$-type SiC. This result was confirmed from the simulations of the dependencies of two distribution functions on the temperature, the energy level or the acceptor density.

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24. S. M. Sze, in Ref. 18, p. 18.