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Influence of Excited States of Deep Acceptors on Hole Concentration in SiC

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Abstract. The influence of the excited states of acceptors on the hole concentration in p-type SiC is investigated theoretically and experimentally. Using the temperature dependence of the hole concentration $p(T)$ in Al-doped 6H-SiC wafers, a distribution function suitable for deep acceptors is examined. From the discussion, it is found that we cannot ignore the influence of the excited states on $p(T)$ as well as the ensemble average of the ground and excited state levels of the acceptor when the acceptor level is deep.

Introduction

The excited states of dopants in semiconductors have been theoretically discussed using the hydrogenic dopant model [1], and the existence of the excited states of dopants in Si has been experimentally confirmed using infrared absorption measurements [1]. However, the influence of the excited states on the majority-carrier concentration has not been confirmed because the excited state levels in Si are too shallow. On the other hand, the acceptor levels ΔE_{A} in SiC, measured from the top E_{V} of the valence band, are reported to be deeper than 150 meV [2]. Moreover, according to the hydrogenic dopant model, the first excited state level is calculated to be approximately 35 meV, which is close to normal dopant levels in Si. Therefore, the excited states of acceptors in SiC must affect the hole concentration.

The conventional distribution function for electrons, which includes the influence of the excited states of acceptors, is given by [3]

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

while the Fermi-Dirac distribution function, which does not include the influence, is given by

$$f_{\mathrm{FD}}(\Delta E_{\mathrm{A}}) = \frac{1}{1+4\exp\left(\frac{\Delta E_{\mathrm{A}} - \Delta E_{\mathrm{F}}}{kT}\right)}, \quad (2)$$

where ΔE_{F} is the Fermi level measured from E_{V}, ΔE_r is the difference in energy between the $(r-1)$-th excited state level and E_{V}, which is given by the hydrogenic dopant model [1];

$$\Delta E_r = 13.6 \frac{m^*}{m_0 \varepsilon_{\mathrm{s}}^2} \cdot \frac{1}{r^2} \quad \text{[eV]}, \quad (3)$$

g_1 is the ground-state degeneracy factor, g_r is the $(r-1)$-th excited state degeneracy factor, k is the Boltzmann constant, T is the absolute measurement temperature, m_0 is the free-space electron mass, m^* is the hole effective mass in SiC, and ε_{s} is the dielectric constant of SiC. Moreover, the acceptor level is described as [1]

$$\Delta E_{\mathrm{A}} = \Delta E_1 + E_{\mathrm{CCC}}, \quad (4)$$

where E_{CCC} is the energy induced due to central cell corrections.

In Al-doped SiC, using $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$, 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 neutrality equation to $p(T)$. However, the obtained N_{A} was much higher than the Al concentration determined by secondary ion mass spectroscopy [4], suggesting that this N_{A} should not be reliable. When

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$f_{\mathrm{conv}}(\Delta E_{\mathrm{A}})$ is used, the obtained N_{A} becomes higher than N_{A} obtained using $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$. Therefore, it is necessary to newly introduce a distribution function including the influence of the excited states, which leads N_{A} to be reasonable.

On the other hand, we have proposed and tested a new method for determining the densities and energy levels of several dopant species without any assumption of the number of dopant species, called Free Carrier Concentration Spectroscopy (FCCS) [5, 6]. From each peak of the FCCS signal, it is easy to determine the density and energy level of the corresponding dopant using any distribution function.

In this article, we theoretically derive a distribution function suitable for deep acceptors. Then, by the curve-fitting procedure of $p(T)$ as well as by FCCS using three kinds of distribution functions, we analyze the experimental data obtained by Hall-effect measurements.

Theoretical Consideration of Distribution Function

Electrons and holes in semiconductors are fermions, which obey the Pauli exclusion principle. In the allowed bands, we consider the multiplicity function $W_{\mathrm{B}i}$ for the $n_{\mathrm{h}}(\Delta E_i)$ holes arranged in the $D_{\mathrm{h}}(\Delta E_i)$ degenerate states at some energy level ΔE_i, which is given by [7]

$$W_{\mathrm{B}i} = \frac{D_{\mathrm{h}}(\Delta E_i)!}{[D_{\mathrm{h}}(\Delta E_i) - n_{\mathrm{h}}(\Delta E_i)]! \cdot n_{\mathrm{h}}(\Delta E_i)!}. \tag{5}$$

In a bandgap, on the other hand, we consider the multiplicity function W_{A} for the n_{A} holes arranged in the N_{A} acceptors. When we neglect the spin degeneracy as well as the excited states of acceptors, the multiplicity function W_{A1} for the n_{A} holes arranged in the N_{A} acceptors is given by

$$W_{\mathrm{A1}} = \frac{N_{\mathrm{A}}!}{(N_{\mathrm{A}} - n_{\mathrm{A}})! \cdot n_{\mathrm{A}}!}. \tag{6}$$

In a neutral acceptor, only an excess hole is bound to one state of the ground state and the excited states of the acceptor. Therefore, the multiplicity function W_{A2} is given by [7]

$$W_{\mathrm{A2}} = \left[g_1 + \sum_{r=2} g_r \exp\left(-\frac{\Delta E_{\mathrm{A}} - \Delta E_r}{kT} \right) \right]^{n_{\mathrm{A}}}. \tag{7}$$

On the other hand, the ensemble average $\overline{E_{\mathrm{ex}}}$ of the ground and excited state levels of the acceptor is given by [7]

$$\overline{E_{\mathrm{ex}}} = \frac{\sum_{r=2} (\Delta E_{\mathrm{A}} - \Delta E_r) g_r \exp\left(-\frac{\Delta E_{\mathrm{A}} - \Delta E_r}{kT} \right)}{g_1 + \sum_{r=2} g_r \exp\left(-\frac{\Delta E_{\mathrm{A}} - \Delta E_r}{kT} \right)} \tag{8}$$

and then the average acceptor level $\overline{\Delta E_{\mathrm{A}}}$ is expressed as

$$\overline{\Delta E_{\mathrm{A}}} = \Delta E_{\mathrm{A}} - \overline{E_{\mathrm{ex}}}. \tag{9}$$

Furthermore, the multiplicity function W_{A3} for degenerate spin-up and spin-down states is $2^{n_{\mathrm{A}}}$, while the multiplicity function W_{A4} for degenerate heavy and light hole valence bands is $2^{n_{\mathrm{A}}}$.

Therefore, the multiplicity function for acceptors is $W_{\mathrm{A}} = W_{\mathrm{A1}} W_{\mathrm{A2}} W_{\mathrm{A3}} W_{\mathrm{A4}}$. Finally, the total number W of configurations of the system is obtained as $W = W_A \prod_i W_{\mathrm{B}i}$.

The thermal equilibrium configuration of the system occurs when the entropy

$$S = k \ln W \tag{10}$$

is maximum under the conservation laws of the total number $n_{\mathrm{h,total}}$ of holes and the total energy E_{total} of holes, that is,

$$n_{\mathrm{h,total}} = n_{\mathrm{A}} + \sum_i n_{\mathrm{h}}(\Delta E_i) = \mathrm{const.} \tag{11}$$

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and

$$E_{\mathrm{total}} = \overline{\Delta E_{\mathrm{A}}} n_{\mathrm{A}} + \sum_i \Delta E_i n_{\mathrm{h}}(\Delta E_i) = \mathrm{const.} \tag{12}$$

Under this condition, the distribution functions for electrons are derived as

$$f(\Delta E_i) = 1 - \frac{n_{\mathrm{h}}(\Delta E_i)}{D(\Delta E_i)} = \frac{1}{1+\exp\left(\dfrac{\Delta E_i - \Delta E_{\mathrm{F}}}{kT}\right)} \tag{13}$$

in the allowed bands, and

$$f(\Delta E_{\mathrm{A}}) = 1 - \frac{n_{\mathrm{A}}}{N_{\mathrm{A}}} = \frac{1}{1+4\exp\left(-\dfrac{\overline{E_{\mathrm{ex}}}}{kT}\right)\cdot\left[g_1 \exp\left(\dfrac{\Delta E_{\mathrm{A}} - \Delta E_{\mathrm{F}}}{kT}\right) + \sum_{r=2} g_r \exp\left(\dfrac{\Delta E_r - \Delta E_{\mathrm{F}}}{kT}\right)\right]} \tag{14}$$

in the bandgap.

In the case of the Fermi-Dirac distribution function, Eq. 14 comes to Eq. 2 because the excited states are neglected ($r = 1$, $g_1 = 1$, $\overline{E_{\mathrm{ex}}} = 0$). In the case of the conventional distribution function, on the other hand, Eq. 14 becomes Eq. 1 because of $\overline{E_{\mathrm{ex}}} = 0$.

Experimental

$p(T)$ in a p-type 6H-SiC wafer with the resistivity of approximate 1.4 Ωcm was obtained by Hall-effect measurements at temperatures between 100 K and 380 K and at a magnetic field of 1.4 T. The thickness of the wafer was 0.42 mm, and the size of the sample for measurement was $1\times1\,\mathrm{cm}^2$.

Results and Discussion

The open circles in Fig. 1 show the experimental $p(T)$. Using $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$, the values of ΔE_{A}, N_{A} and N_{comp} determined by the least-squares fit are 182 meV, 3.0×10^{19} cm^{-3} and 8.4×10^{17} cm^{-3}, respectively. The simulated $p(T)$ (dotted curve) is in agreement with the experimental $p(T)$. However, N_{A} is higher than the value ($< 5\times10^{18}\,\mathrm{cm}^{-3}$) to be expected.

Using the experimental $p(T)$, the FCCS signal is defined by [5]

$$H(T, E_{\mathrm{ref}}) \equiv \frac{p(T)^2}{(kT)^{5/2}} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right). \tag{15}$$

The open circles in Fig. 2 represent the experimental $H(T, E_{\mathrm{ref}})$, while the dotted curve shows the $H(T, E_{\mathrm{ref}})$ simulated using ΔE_{A}, N_{A} and N_{comp} obtained in the case of $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$. Although the peak of the simulated $H(T, E_{\mathrm{ref}})$ coincides with the peak of the experimental $H(T, E_{\mathrm{ref}})$, the FCCS signal below the peak temperature is not in agreement with the experimental one at all.

The values of ΔE_{A}, N_{A} and N_{comp} determined from the peak of the experimental $H(T, E_{\mathrm{ref}})$ are 205 meV, 2.2×10^{20} cm^{-3} and 2.7×10^{18} cm^{-3} for $f_{\mathrm{conv}}(\Delta E_{\mathrm{A}})$, and 189 meV, 1.9×10^{18} cm^{-3} and 3.4×10^{16} cm^{-3} for $f(\Delta E_{\mathrm{A}})$. Here, the highest excited state considered in the FCCS analysis is the 9$^{\mathrm{th}}$ excited state. The values of ΔE_{A} in all the cases are considered to be reasonable. The chain and solid curves represent the $H(T, E_{\mathrm{ref}})$ simulated using ΔE_{A}, N_{A} and N_{comp} obtained in the cases of $f_{\mathrm{conv}}(\Delta E_{\mathrm{A}})$ and $f(\Delta E_{\mathrm{A}})$, respectively.

In the case of $f_{\mathrm{conv}}(\Delta E_{\mathrm{A}})$, the simulated $H(T, E_{\mathrm{ref}})$ is not in agreement with the experimental one at all. Moreover, the obtained N_{A} is too high. Therefore, this distribution function is not suitable for deep acceptors.

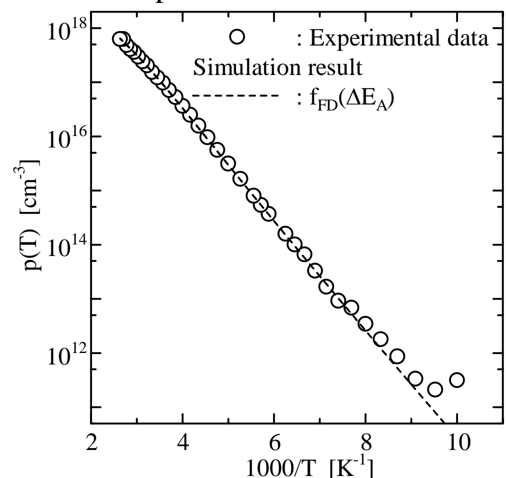

Fig. 1 Experimental and simulated $p(T)$.

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In the case of $f(\Delta E_A)$ proposed here, the simulated $H(T, E_{ref})$ is in better agreement with the experimental $H(T, E_{ref})$ than the others, and N_A is more reliable than the others.

The broken, chain and solid curves in Fig. 3 show the $p(T)$ simulated using ΔE_A, N_A and N_{comp} obtained in the cases of $f_{FD}(\Delta E_A)$, $f_{conv}(\Delta E_A)$ and $f(\Delta E_A)$, respectively. The simulated $p(T)$ for $f(\Delta E_A)$ besides $f_{FD}(\Delta E_A)$ coincides with the experimental $p(T)$.

The value of N_A determined using $f_{FD}(\Delta E_A)$ or $f_{conv}(\Delta E_A)$ is rather high, because $\overline{\Delta E_A}$ is assumed to be ΔE_A. Figure 4 shows the temperature dependences of $\exp(-\overline{E_{ex}}/kT)$, ΔE_F and $\overline{\Delta E_A}$ simulated using ΔE_A, N_A and N_{com} obtained in the case of $f(\Delta E_A)$. Since $\overline{\Delta E_A}$ decreases with T, the value of $\exp(-\overline{E_{ex}}/kT)$ decreases from 1 to 0 rapidly, indicating that almost all acceptors become negatively ionized at moderate temperatures.

Judging from the coincidences between the experimental and simulated $p(T)$ as well as between the experimental and simulated $H(T, E_{ref})$, the proposed $f(\Delta E_A)$ is considered to be more suitable for the acceptor in SiC than the others. This indicates that in the analysis of $p(T)$ in SiC we should consider the influence of the excited states as well as the ensemble average of the ground and excited state levels.

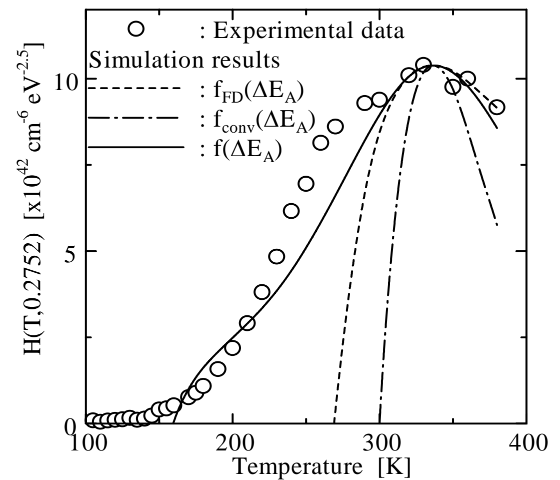

Fig. 2 Experimental and simulated FCCS signals.

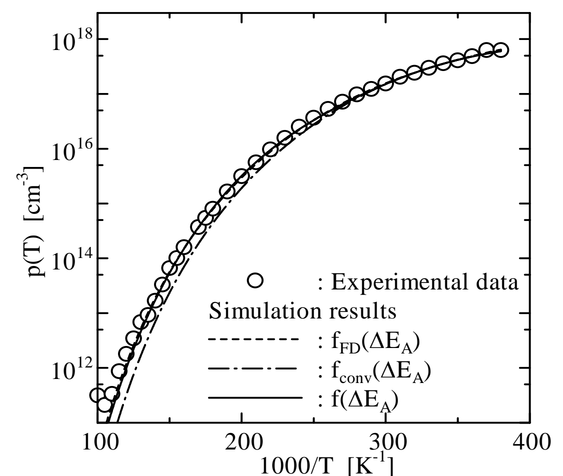

Fig. 3 Experimental and simulated $p(T)$.

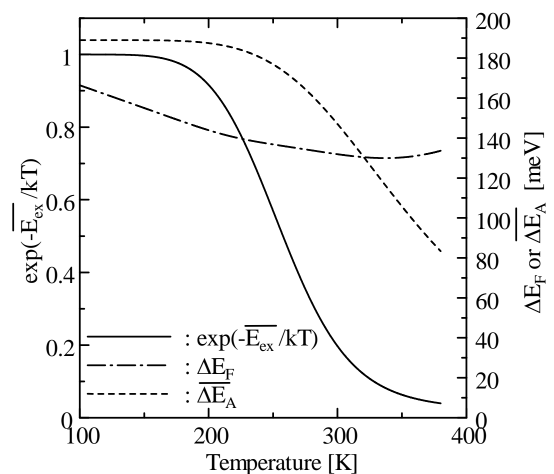

Fig. 4 Temperature dependences of $\exp(-\overline{E_{ex}}/kT)$, ΔE_F and $\overline{\Delta E_A}$.

Summary
We theoretically derived the distribution function considering the influence of the excited states on $p(T)$, in which the ensemble average of the ground and excited state levels of the acceptor was introduced. Using three kinds of distribution functions, we analyzed $p(T)$ in p-type 6H-SiC experimentally obtained by Hall-effect measurements. It is found that FCCS is more suitable for investigating the influence of the excited states of the acceptor in SiC than the least-squares fit of the neutrality equation to $p(T)$, and it is considered that the proposed distribution function is suitable for deep acceptors.

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