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Brief Communication

Accurate Determination of Density and Energy Level of B Acceptor in Diamond from Temperature Dependence of Hole Concentration

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The density (N_A) and energy level (E_A) of a B acceptor in B-doped p-type diamond epilayers are usually determined from the temperature dependence of hole concentration, $p(T)$, using the Fermi–Dirac distribution function for acceptors, which does not consider the effect of the excited states of the B acceptor. However, in samples whose Fermi levels, $E_F(T)$, are located between the valence band maximum (E_V) and E_A in a measurement temperature range, the obtained N_A is much higher than the concentration of B atoms determined by secondary ion mass spectroscopy. Because the B acceptor level in diamond is deep, the effect of the excited states of the B acceptor on $p(T)$ should not be ignored. When $E_F(T)$ is between E_V and E_A, the reasonable N_A and E_A are obtained by fitting a curve to $p(T)$ using the distribution function including the effect of its excited states. [DOI: 10.1143/JJAP.45.6376]

KEYWORDS: B-doped diamond, B acceptor density, B acceptor level, distribution function, determination of density, temperature dependence of hole concentration, excited states

Diamond has been an attractive semiconductor because of its wide band gap, high electron mobility, highest electron-saturation-drift velocity and highest thermal conductivity.[1,2] Therefore, it has been regarded as a promising semiconductor for devices operating at high powers, high frequencies, and high temperatures, and superior to SiC.[2]

Because presently the appropriate acceptor species in diamond is considered to be B, B acceptors in p-type diamond epilayers have been investigated by several methods.[3–6] In particular, the density (N_A) and energy level (E_A) of acceptors have been investigated using the temperature dependence of hole concentration, $p(T)$, obtained by Hall-effect measurements.

In p-type wide-band-gap semiconductors (e.g., SiC, GaN, and diamond), experimentally obtained E_A was reported to be deep.[1,3–6] Consequently, the Fermi level $E_F(T)$ is often between E_A and the valence band maximum (E_V). Moreover, the excited state levels (E_r; $r \geq 2$) are close to the E_A of B in Si.[4]

The excited states of a substitutional dopant in a semiconductor have been theoretically investigated using the hydrogenic model,[7–9] and the existence of the excited states of a dopant (e.g., B, P) in Si or Ge was experimentally confirmed by infrared absorption measurements at very low temperatures.[7] On the other hand, the effect of excited states on majority-carrier concentration in Si or Ge was not experimentally confirmed,[8,10] partially because the excited state levels of a dopant in Si or Ge were too shallow and partially because $E_F(T)$ was deeper than the dopant level in the measurement temperature range. However, $E_F(T)$ in p-type wide-band-gap semiconductors is often between E_V and E_A in the measurement temperature range. Therefore, the effect of the excited states of acceptors on $p(T)$ cannot be ignored.

Using the Fermi–Dirac distribution function $f_{FD}(E_A)$, the values of E_A, N_A and total donor density (N_D) in Al-doped or Al-implanted SiC were determined by the least-squares fitting of the charge neutrality equation to $p(T)$ experimentally obtained by Hall-effect measurements.[11,12] $f_{FD}(E_A)$ does not include the effect of the excited states of an acceptor, which is given by[13]

$$f_{FD}(E_A) = \frac{1}{1 + 4\exp\left(-\frac{E_F(T) - E_A}{kT}\right)}, \qquad (1)$$

where k is the Boltzmann constant and T is the absolute temperature. In the case that $E_F(T)$ is between E_V and E_A, however, N_A determined using $f_{FD}(E_A)$ was much higher than the concentration of Al atoms (C_{Al}), which was determined by secondary ion mass spectroscopy (SIMS).[11,12,14] Because N_A means the density of Al atoms located at Si sublattice sites, N_A must be less than or equal to C_{Al}. This suggests that the obtained N_A is not reliable. The situation in Mg-doped p-type GaN is also the same.[15] Although $Al_{0.6}Ga_{0.4}Sb$ is not a wide-band-gap semiconductor, the situation in Te-doped n-type $Al_{0.6}Ga_{0.4}Sb$ is the same,[16] because Te acts as a deep donor. These indicate that a suitable distribution function including the effect of the excited states of a deep dopant, $f(E_A)$, should replace $f_{FD}(E_A)$. On the other hand, it was reported that both $f(E_A)$ and $f_{FD}(E_A)$ can be applied to lightly Al-doped SiC whose $E_F(T)$ is far from E_A.[18]

In this paper, we report on our investigation of the optimum distribution function for determining the density and energy level of B acceptors in a single crystalline B-doped p-type diamond epilayer whose $E_F(T)$ is located between E_V and E_A in a measurement temperature range.

A 1.73-μm-thick single crystalline diamond epilayer was grown on the (001) surface of a synthesized single crystal 1b diamond substrate (area, $1.5 \times 2.0\,\mathrm{mm}^2$; thickness, 0.3 mm; resistivity, 10^{12}–10^{14} Ω cm) by a microwave-plasma-assisted chemical-vapor-deposition method. H_2 and CH_4 were used as source gases at a CH_4 concentration of $CH_4/H_2 = 1\%$, and 10 ppm B_2H_6 diluted with H_2 was used as the doping gas at a B_2H_6 concentration of $B_2H_6/CH_4 = 10$ ppm. The gas pressure was 40 Torr, and the substrate temperature was

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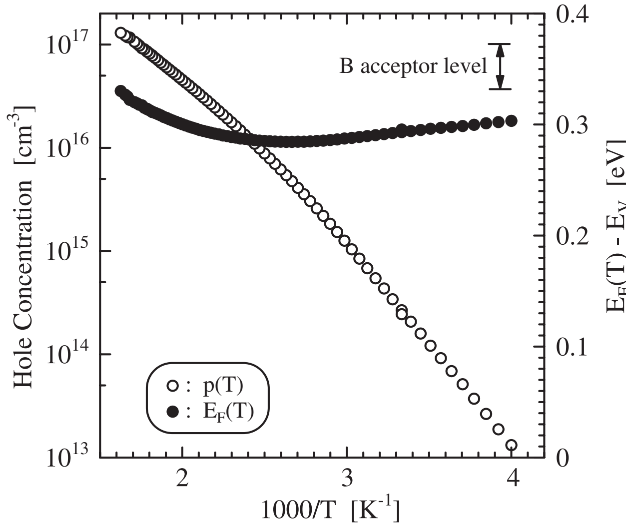

Fig. 1. Temperature dependence of hole concentration and Fermi level in B-doped p-type diamond epilayer.

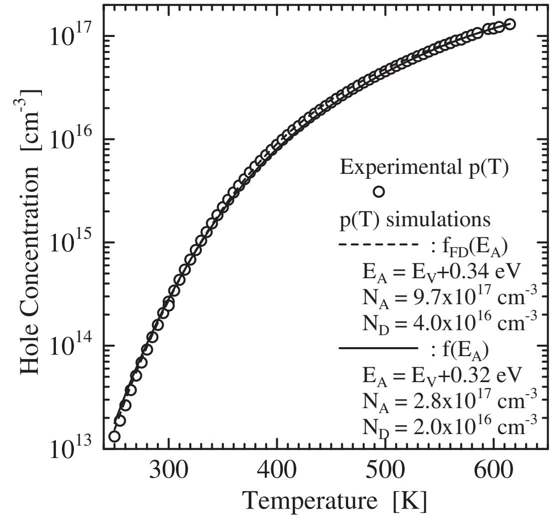

Fig. 2. $p(T)$ simulation with values determined by curve-fitting procedure using $f_{\mathrm{FD}}(E_{\mathrm{A}})$ or $f(E_{\mathrm{A}})$. Because $p(T)$ simulation using $f(E_{\mathrm{A}})$ is very close to $p(T)$ simulation using $f_{\mathrm{FD}}(E_{\mathrm{A}})$, the solid line overlaps with the broken line.

830 °C. The details of growth conditions were reported earlier.[17] The concentration of B atoms (C_{B}) in this epilayer measured by SIMS was $\sim 2\times10^{17}$ cm^{-3}.

Ohmic metal (Ti) was deposited on the four corners of the surface of the sample at 400 °C by an electron-beam evaporation method, and then Pt/Au was deposited. The $p(T)$ and temperature dependence of the hole mobility $\mu_{\mathrm{p}}(T)$ were obtained by Hall-effect measurements in the van der Pauw configuration in a temperature range from 250 to 620 K at a magnetic field of 1.4 T and a current of 10 µA using a modified MMR Technologies' Hall system.

Figure 1 shows $p(T)$ and $E_{\mathrm{F}}(T)$ in the B-doped p-type diamond epilayer, which are denoted by ○ and ●, respectively. Here $E_{\mathrm{F}}(T)$ is given by[13]

$$E_{\mathrm{F}}(T) = E_{\mathrm{V}} + kT\ln\left[\frac{N_{\mathrm{V}}(T)}{p(T)}\right], \quad (2)$$

where $N_{\mathrm{V}}(T)$ is the effective density of states in the valence band, which is expressed as[13]

$$N_{\mathrm{V}}(T) = 2\left(\frac{2\pi m_{\mathrm{h}}^{*}kT}{h^2}\right)^{3/2}, \quad (3)$$

where m_{h}^{*} is the hole effective mass and h is Planck's constant.

In Fig. 1, moreover, the expected E_{A} of B acceptors is included. The experimental $E_{\mathrm{F}}(T)$ was located between E_{V} and E_{A}, indicating that it should be impossible to ignore the effect of the excited states of the B acceptor on $p(T)$.

The $p(T)$ and $\mu_{\mathrm{p}}(T)$ were 2.4×10^{14} cm^{-3} and 6.2×10^{2} cm^2 V^{-1} s^{-1} at 300 K, and 1.3×10^{13} cm^{-3} and 7.4×10^{2} cm^2 V^{-1} s^{-1} at 250 K, respectively. At >415 K, $\mu_{\mathrm{p}}(T)$ was expressed as

$$\mu_{\mathrm{p}}(T) = 4.0\times10^{10}T^{-3.1} \quad (\mathrm{cm^2\,V^{-1}\,s^{-1}}). \quad (4)$$

$p(T)$ and $\mu_{\mathrm{p}}(T)$ exhibited a typical semiconductor behavior, indicating that this epilayer is not a degenerate semiconductor and the band conduction of holes is dominant in this epilayer within the measurement temperature range.

By fitting a curve to $p(T)$ using $f_{\mathrm{FD}}(E_{\mathrm{A}})$, the values of N_{A}, E_{A}, and N_{D} were determined as 9.7×10^{17} cm^{-3}, $E_{\mathrm{V}}+0.34$ eV, and 4.0×10^{16} cm^{-3}, respectively. Figure 2 shows the experimental $p(T)$ denoted by ○ and $p(T)$ simulation (– –) with the obtained values. The $p(T)$ simulation is in good agreement with the experimental $p(T)$. However, the determined N_{A} is ~ 5 higher than the C_{B} of 2×10^{17} cm^{-3}, indicating that it is not reliable.

The distribution function for acceptors, $f(E_{\mathrm{A}})$, which includes the effect of the excited states of an acceptor, is derived as[14,18]

$$f(E_{\mathrm{A}}) = \frac{1}{1 + g_{\mathrm{A}}(T)\exp\left(-\dfrac{E_{\mathrm{F}}(T)-E_{\mathrm{A}}}{kT}\right)}, \quad (5)$$

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

$$g_{\mathrm{A}}(T) = 4\left[1 + \sum_{r=2} g_r \exp\left(\frac{E_r - E_{\mathrm{A}}}{kT}\right)\right] \times \exp\left(-\frac{\overline{E_{\mathrm{ex,A}}(T)}}{kT}\right), \quad (6)$$

$\overline{E_{\mathrm{ex,A}}(T)}$ is the ensemble average energy of holes at the ground and excited state levels at T, measured from E_{A}, which is given by

$$\overline{E_{\mathrm{ex,A}}(T)} = \frac{\sum_{r=2}(E_{\mathrm{A}}-E_r)g_r\exp\left(-\dfrac{E_{\mathrm{A}}-E_r}{kT}\right)}{1+\sum_{r=2}g_r\exp\left(-\dfrac{E_{\mathrm{A}}-E_r}{kT}\right)}, \quad (7)$$

and g_r is the $(r-1)$th excited state degeneracy factor of r^2.[7,8]

The ground state level (i.e., E_{A}) does not obey the hydrogenic model because the Bohr radius (a^*) of the ground state is very small. However, because the wave function extension of the $(r-1)$th excited state is of the order r^2a^*, the values of E_r with $r \geq 2$ are expected to follow the hydrogenic model. By fitting a curve to $p(T)$ using $f(E_{\mathrm{A}})$ under simple assumptions of its excited states

(i.e., $E_r - E_V = \Delta E/r^2$, $\Delta E = 0.39$ eV and $2 \leq r \leq 7$), the values of N_A, E_A and N_D were determined as 2.8×10^{17} cm^{-3}, $E_V + 0.32$ eV and 2.0×10^{16} cm^{-3}, respectively. The solid line in Fig. 2 shows $p(T)$ simulation with the obtained values. The $p(T)$ simulation is in good agreement with the experimental $p(T)$. Furthermore, the determined N_A is nearly equal to C_B. On the other hand, the determined N_A, E_A and N_D were almost independent of ΔE between 0.3 and 0.5 eV, similar to other semiconductors.[16] This suggests that reliable N_A and E_A can be obtained using the approximate excited state levels of the B acceptor. Therefore, $f(E_A)$ is appropriate for the analysis of $p(T)$ in B-doped diamond whose $E_F(T)$ is located between E_V and E_A.

Thonke reported that from the study of photoconductivity, the energy levels of long-lived excited states of B in diamond are 0.200, 0.240, and 0.266 eV from the ground state.[4] On the other hand, the first, second and third excited state levels measured from E_A were obtained as 0.22, 0.27, and 0.29 eV, respectively, which are close to the reported values.

The reason a reasonable N_A was obtained using $f(E_A)$ is discussed. Because to date they are considered to act as a hole trap, the excited states of an acceptor are expected to suppress the ionization efficiency of acceptors.[19–21] According to eq. (7), however, the average acceptor level, $\overline{E_A(T)}$, can approximately be expressed as

$$\overline{E_A(T)} = E_A - \overline{E_{ex,A}(T)}, \tag{8}$$

indicating that $\overline{E_A(T)}$ decreases with increasing temperature. This is, as temperature increases, the possibility that a hole bound to the acceptor is located at a higher excited state level becomes higher. That is why the acceptor can more easily emit a hole to the valence band at high temperatures. On the other hand, $g_A(T)$ decreases from 4 with increasing temperature,[18] suggesting that $f(E_A)$ becomes closer to 1 than $f_{FD}(E_A)$ at high temperatures. Therefore, the excited states of an acceptor enhance its ionization at elevated temperatures. Finally, N_A required to satisfy the experimentally obtained $p(T)$ is much lower than that required for $f_{FD}(E_A)$.

In conclusion, from $p(T)$ in the B-doped p-type diamond epilayer whose $E_F(T)$ was located between E_V and E_A, the values of E_A and N_A were determined by a curve-fitting procedure using the Fermi–Dirac distribution function or the distribution function including the effect of the excited states of an acceptor. To obtain N_A close to the concentration of B atoms determined by SIMS, it was found that the effect of its excited states on $p(T)$ should not be ignored at least when $E_F(T)$ is located between E_V and E_A in the measurement temperature range.

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