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Determination of Donor Densities and Donor Levels in 3C-SiC Grown from $Si_2(CH_3)_6$ Using Hall-Effect Measurements

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Without any assumption of the number of types of impurities, the densities and energy levels of donors in undoped 3C-SiC grown from $Si_2(CH_3)_6$ are precisely determined by the simple graphical method proposed here, using the temperature dependence of the majority-carrier concentration obtained by Hall-effect measurements. We detect at least three types of donors whose energy levels (ΔE_D) are 7–14 meV, 46–54 meV and 97–120 meV as measured from the conduction band, although it was reported that ΔE_D for nitrogen atoms decreased with an increase in the donor density from ~50 meV to ~15 meV. In addition to the ~15 meV donor that was reported in undoped 3C-SiC grown from a mixture of SiH_4 and C_3H_8, at least two donor levels are detected in undoped epilayers grown from $Si_2(CH_3)_6$. From the viewpoints of donor density and compensation ratio, the quality of undoped 3C-SiC grown from $Si_2(CH_3)_6$ is better than that of undoped 3C-SiC grown from a mixture of SiH_4 and C_3H_8.

KEYWORDS: 3C-SiC, donor level, donor density, determination of donor density and donor level, graphical approach, $Si_2(CH_3)_6$, HMDS

1. Introduction

Silicon carbide (SiC) is a semiconductor with a wide band gap, a high electron mobility, a high electron saturation drift velocity and a high thermal conductivity. It is also chemically and thermally stable and extremely hard. As a result, it is regarded as a promising semiconductor for devices operating at high powers, high frequencies and high temperatures. In order to obtain device-quality single crystalline SiC on silicon (Si) or SiC substrates, chemical vapor deposition (CVD) has been conventionally used. In CVD, a mixture of silane (SiH_4), propane (C_3H_8) and hydrogen (H_2) is usually made use of. However, SiH_4 should be avoided because it is highly flammable. Therefore, we have attempted to use non-flammable $Si_2(CH_3)_6$, which is referred to as HMDS, for the epitaxial growth of SiC.

Undoped single crystalline cubic SiC (3C-SiC) films were heteroepitaxially grown on Si substrates using HMDS. Our undoped 3C-SiC films showed n-type conduction, indicating that some donors were unintentionally doped. Thus, we have attempted to determine the densities and energy levels of donors as well as defects using the temperature dependence of the electron concentration $n(T)$ obtained by Hall-effect measurements.

In many papers,[1–7] under the assumption that only one type of donor existed in unintentionally doped 3C-SiC, the density and energy level of the donor and the acceptor (or compensating) density were determined by the curve-fitting method using $n(T)$. Moreover, the donor level corresponding to nitrogen (N) was reported to decrease with an increase in the donor density from ~50 meV to ~15 meV as measured from the bottom of the conduction band (E_C). However, no one knows whether only one type of donor actually exists there. This is why we have proposed and experimentally tested a simple method for graphically determining the densities and energy levels of several types of dopants or traps accurately, using $n(T)$.[8–13]

In N-doped 4H-SiC epilayers, the densities and energy levels of two types of donors could be determined using our method, and the two donor levels were 65 meV and 124 meV.[13] Shallow and deep donors were found to correspond to N atoms at hexagonal and cubic sites in 4H-SiC, respectively. Furthermore, in p-type Si irradiated with a high fluence of 10 MeV protons, this method could determine the densities and energy levels of hole traps induced by irradiation.[12] Their energy levels were in good agreement with those determined by deep level transient spectroscopy (DLTS) in p-type Si irradiated with a low fluence, while DLTS could not accurately determine the densities and energy levels of hole traps induced by a high fluence of 10 MeV protons because these hole trap densities were close to the acceptor density.

In order to obtain the results more easily and with higher reliability, the function to be evaluated has been improved.[14,15] In the improved method, the function is defined as:

$$H(T, E_{\mathrm{ref}}) \equiv \frac{n(T)^2}{(kT)^{2.5}} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right), \tag{1}$$

which has a peak at the temperature corresponding to each energy level, where k is the Boltzmann constant, T is the absolute temperature and E_{ref} is a parameter which can shift the peak temperature of $H(T, E_{\mathrm{ref}})$ within the measurement temperature range. Therefore, from each peak value and peak temperature, the density and energy level of the corresponding dopant or trap can be accurately determined.

In this study, undoped 3C-SiC is heteroepitaxially grown on Si using HMDS, and the Hall-effect measurement is carried out. After the improved method is briefly introduced, the densities and energy levels of several types of donors are determined using $H(T, E_{\mathrm{ref}})$.

2. Theoretical Consideration

In an n-type semiconductor, we consider n types of donors (density $N_{\mathrm{D}i}$ and energy level $\Delta E_{\mathrm{D}i}$ of the i-th donor for $1 \le i \le n$), k types of electron traps (density $N_{\mathrm{TE}i}$ and energy level $\Delta E_{\mathrm{TE}i}$ of the i-th electron trap for $1 \le i \le k$), l types of hole traps (density $N_{\mathrm{TH}i}$ and energy level $\Delta E_{\mathrm{TH}i}$ of the i-th hole trap for $1 \le i \le l$), and m types of acceptors (density $N_{\mathrm{A}i}$ and energy level $\Delta E_{\mathrm{A}i}$ of the i-th acceptor for $1 \le i \le m$), where all energy levels ($\Delta E = E_C - E$) are measured from E_C. Here, $\Delta E_{\mathrm{D}i-1} < \Delta E_{\mathrm{D}i}$, $\Delta E_{\mathrm{TE}i-1} < \Delta E_{\mathrm{TE}i}$,

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$\Delta E_{\mathrm{TH}i-1} > \Delta E_{\mathrm{TH}i}$ and $\Delta E_{\mathrm{A}i-1} > \Delta E_{\mathrm{A}i}$.

In this paper, the definitions of donors, electron traps, hole traps and acceptors are as follows. A donor is positively charged when it emits an electron into the conduction band, while an acceptor is negatively charged when it emits a hole into the valence band. On the other hand, an electron trap is neutral when it emits an electron into the conduction band, while a hole trap is neutral when it emits a hole into the valence band.

From the charge neutrality condition, the free electron concentration $n(T)$ in the conduction band is obtained as[16)]

$$\begin{aligned} n(T) &= \sum_{i=1}^{n} N_{\mathrm{D}i}\left[1 - f_{\mathrm{D}}\left(\Delta E_{\mathrm{D}i}\right)\right] - \sum_{i=1}^{k} N_{\mathrm{TE}i}\, f_{\mathrm{D}}\left(\Delta E_{\mathrm{TE}i}\right) \\ &\quad + \sum_{i=1}^{l} N_{\mathrm{TH}i}\left[1 - f_{\mathrm{A}}\left(\Delta E_{\mathrm{TH}i}\right)\right] - \sum_{i=1}^{m} N_{\mathrm{A}i}\, f_{\mathrm{A}}\left(\Delta E_{\mathrm{A}i}\right) \\ &\quad + p(T), \end{aligned} \tag{2}$$

where $p(T)$ is the free hole concentration in the valence band, and $f_{\mathrm{D}}(\Delta E)$ and $f_{\mathrm{A}}(\Delta E)$ are the Fermi-Dirac distribution functions for donors and acceptors, respectively. These distribution functions are given by[16)]

$$f_{\mathrm{D}}(\Delta E) = \frac{1}{1 + \dfrac{1}{g_{\mathrm{D}}} \exp\left(\dfrac{\Delta E_{\mathrm{F}} - \Delta E}{kT}\right)} \tag{3}$$

and

$$f_{\mathrm{A}}(\Delta E) = \frac{1}{1 + g_{\mathrm{A}} \exp\left(\dfrac{\Delta E_{\mathrm{F}} - \Delta E}{kT}\right)}, \tag{4}$$

where ΔE_{F} is the Fermi level ($E_{\mathrm{C}} - E_{\mathrm{F}}$) measured from E_{C}, and g_{D} and g_{A} are the degeneracy factors of donors and acceptors, respectively.[16,17)]

On the other hand, $n(T)$ is expressed as[16)]

$$n(T) = N_{\mathrm{C}}(T) \exp\left(-\frac{\Delta E_{\mathrm{F}}}{kT}\right), \tag{5}$$

with the effective density of states $N_{\mathrm{C}}(T)$ in the conduction band, which is given by[16)]

$$N_{\mathrm{C}}(T) = (kT)^{1.5} N_{\mathrm{C0}}, \tag{6}$$

where $N_{\mathrm{C0}} = 2(2\pi m_{\mathrm{n}}^{*}/h^{2})^{1.5} M_{\mathrm{C}}$, m_{n}^{*} is the electron effective mass, h is the Planck constant and M_{C} is the number of equivalent minima in the conduction band.

Substituting eq. (2) for one of the $n(T)$ in eq. (1) and substituting eq. (5) for the other $n(T)$ give

$$\begin{aligned} H(T, E_{\mathrm{ref}}) &= \sum_{i=1}^{n} \frac{N_{\mathrm{D}i}}{kT} \exp\left(-\frac{\Delta E_{\mathrm{D}i} - E_{\mathrm{ref}}}{kT}\right) I_{\mathrm{D}}(\Delta E_{\mathrm{D}i}) \\ &\quad + \sum_{i=1}^{k} \frac{N_{\mathrm{TE}i}}{kT} \exp\left(-\frac{\Delta E_{\mathrm{TE}i} - E_{\mathrm{ref}}}{kT}\right) I_{\mathrm{D}}(\Delta E_{\mathrm{TE}i}) \\ &\quad + \sum_{i=1}^{l} \frac{N_{\mathrm{TH}i}}{kT} \exp\left(-\frac{\Delta E_{\mathrm{TH}i} - E_{\mathrm{ref}}}{kT}\right) I_{\mathrm{A}}(\Delta E_{\mathrm{TH}i}) \\ &\quad + \sum_{i=1}^{m} \frac{N_{\mathrm{A}i}}{kT} \exp\left(-\frac{\Delta E_{\mathrm{A}i} - E_{\mathrm{ref}}}{kT}\right) I_{\mathrm{A}}(\Delta E_{\mathrm{A}i}) \\ &\quad - \left(\sum_{i=1}^{k} N_{\mathrm{TE}i} + \sum_{i=1}^{m} N_{\mathrm{A}i}\right) \frac{N_{\mathrm{C0}}}{kT} \exp\left(\frac{E_{\mathrm{ref}} - \Delta E_{\mathrm{F}}}{kT}\right) \\ &\quad + \frac{p(T) N_{\mathrm{C0}}}{kT} \exp\left(\frac{E_{\mathrm{ref}} - \Delta E_{\mathrm{F}}}{kT}\right), \end{aligned} \tag{7}$$

where

$$I_{\mathrm{D}}(\Delta E) = \frac{N_{\mathrm{C0}}}{g_{\mathrm{D}} + \exp\left(\dfrac{\Delta E_{\mathrm{F}} - \Delta E}{kT}\right)} \tag{8}$$

and

$$I_{\mathrm{A}}(\Delta E) = \frac{g_{\mathrm{A}} N_{\mathrm{C0}}}{1 + g_{\mathrm{A}} \exp\left(\dfrac{\Delta E_{\mathrm{F}} - \Delta E}{kT}\right)} \tag{9}$$

and $I_{\mathrm{D}}(\Delta E)$ and $I_{\mathrm{A}}(\Delta E)$ are less temperature-dependent than those in the previous method.[14)]

The function

$$\frac{N_i}{kT} \exp\left(-\frac{\Delta E_i - E_{\mathrm{ref}}}{kT}\right) \tag{10}$$

in the first four terms of the right-hand side in eq. (7) has a peak value of $N_i \exp(-1)/kT_{\mathrm{peak}i}$ at the peak temperature

$$T_{\mathrm{peak}i} = \frac{\Delta E_i - E_{\mathrm{ref}}}{k}, \tag{11}$$

indicating that the peak value and peak temperature provide N_i and ΔE_i. As is clear from eq. (11), E_{ref} can shift the peak of $H(T, E_{\mathrm{ref}})$ within the measurement temperature range even when none of the peaks of $H(T, 0)$ appear within the measurement temperatures. Although each peak temperature of $H(T, E_{\mathrm{ref}})$ is slightly different from the peak temperature calculated by eq. (11) due to the temperature dependence of $I_{\mathrm{D}}(\Delta E_i)$ or $I_{\mathrm{A}}(\Delta E_i)$, we can easily determine the accurate values of N_i and ΔE_i from each peak value and peak temperature of $H(T, E_{\mathrm{ref}})$, using a personal computer.

3. Experimental

3C-SiC films with three thicknesses (8 μm, 16 μm and 32 μm) were grown on (100) Si substrates by atmospheric pressure chemical vapor deposition (AP-CVD). To clean the Si surface, HCl gas of 63.1 sccm and H_2 of 1.5 slm were introduced at 1175°C for 11 min. Then, in order to carbonize the Si surface, C_3H_8 of 1 sccm and H_2 of 1 slm were introduced at 1350°C for 3 min. After the temperature was kept at 1350°C with H_2 of 1 slm at an interval of 30 s, HMDS of 0.5 sccm and H_2 of 2.5 slm were introduced at the same temperature. The growth rate was about 4.3 μm/h. The growth conditions have been reported in detail elsewhere.[18,19)]

Carrier concentrations of the films were measured by the van der Pauw method at temperatures between 85 K and 500 K, at a magnetic field of 5 kG and a current of 1 mA. Each 3C-SiC film was cut into pieces of 5 × 5 mm², and Si substrates were removed by chemical etching. In order to form ohmic contacts, Al of about 0.5 mm diameter was deposited on four corners of the film.

4. Results

The obtained epilayers had a smooth surface, and were light yellow and transparent. According to the observations by atomic force microscopy (AFM), the thicker the epilayer, the broader the antiphase domains (APDs) and also the lower the concentration of the antiphase boundaries (APBs). Reflection high-energy electron diffraction (RHEED) analyses with an acceleration voltage of 75 kV indicated that the grown layers were single crystals of 3C-SiC and that the (100) plane of 3C-SiC was parallel to the substrate surface. Moreover, the intensity of the spot related to 3C-SiC twins decreased with an increase in thickness, and the spot completely disappeared in the 32-μm-thick film. From the results of X-ray diffraction (XRD), the full-width at half maximum (FWHM) of the (200) peak for 3C-SiC was found to decrease with an increase in epilayer thickness. Details of the crystallinity have been reported elsewhere.[18,19)]

Figure 1 shows the temperature dependence of the electron concentration for three thicknesses (open circles: 8 μm, solid triangles: 16 μm, open squares: 32 μm). All the epilayers show n-type conduction. The values of $n(T)$ for the 8-μm-thick 3C-SiC are close to those for the 16-μm-thick 3C-SiC, while the values of $n(T)$ for the thickest 3C-SiC are much less than those for the thinner 3C-SiC films.

Figure 2 shows the temperature dependence of the electron mobility (μ_n) for three thicknesses (open circles: 8 μm, solid triangles: 16 μm, open squares: 32 μm). Judging from the magnitude of μ_n, the band conduction of electrons is dominant over the measurement temperature range. Therefore, $n(T)$ as obtained by Hall-effect measurements is the electron concentration in the conduction band.

Figure 3 shows $n(T)$ and ΔE_F for the 32-μm-thick 3C-SiC film. Open circles represent the experimental $n(T)$, and the solid line is the $n(T)$ interpolated by the cubic smoothing natural spline function. The broken line represents ΔE_F calculated using

$$\Delta E_F = kT \ln\left[\frac{N_C(T)}{n(T)}\right], \qquad (12)$$

where $N_C(T)$ for 3C-SiC is

$$N_C(T) = 3.0 \times 10^{15} T^{3/2}\ \text{cm}^{-3}, \qquad (13)$$

which is calculated using eq. (6), $m_n^* = 0.35 m_0$ and $M_C = 3$.[3–5,7)]

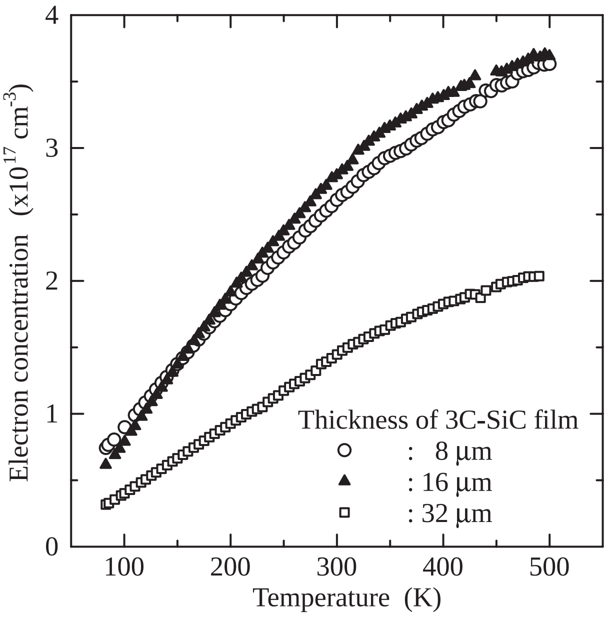

Fig. 1. Dependence of $n(T)$ on the thickness of 3C-SiC film.

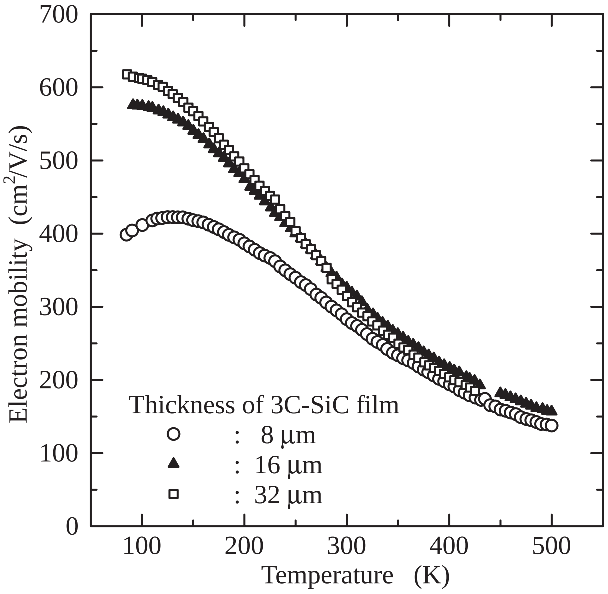

Fig. 2. Temperature dependence of electron mobility.

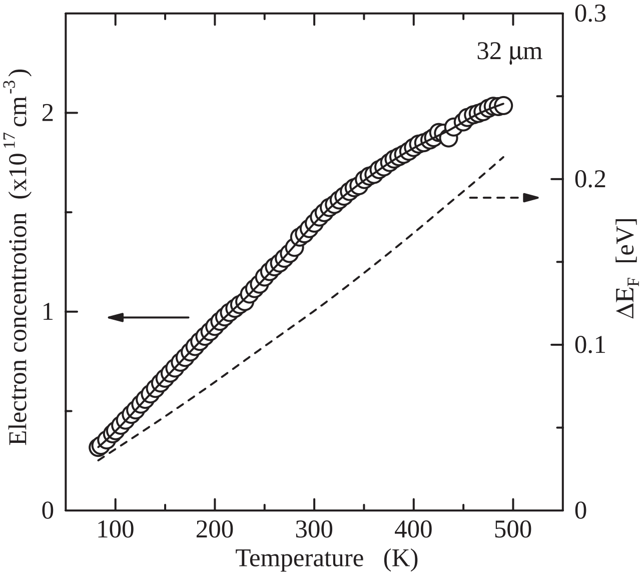

Fig. 3. Temperature dependence of electron concentration and Fermi level. Open circles represent the experimental $n(T)$, and the solid and broken lines represent the $n(T)$ interpolated by the spline function and ΔE_F, respectively.

Figure 4 shows $H(T, E_{\text{ref}})$ with $E_{\text{ref}} = -0.002$ eV calculated using the solid line in Fig. 3 and eq. (1). One peak appears around 160 K, while one shoulder appears around 300 K, indicating that at least two types of donors coexist in this 3C-SiC. Since it is difficult to determine whether each peak corresponds to a donor or an electron trap until the analysis is finished, we tentatively consider the detected energy levels as donor levels. The peak temperature in Fig. 4 is denoted by T_{peak2}, since from later discussion it will be found that there exists another type of donor shallower than the donor corresponding to around 160 K. The peak value $H(T_{\text{peak2}}, -0.002)$ and T_{peak2} are 2.0×10^{38} cm^{-6} eV$^{-2.5}$ and 159.9 K, respectively.

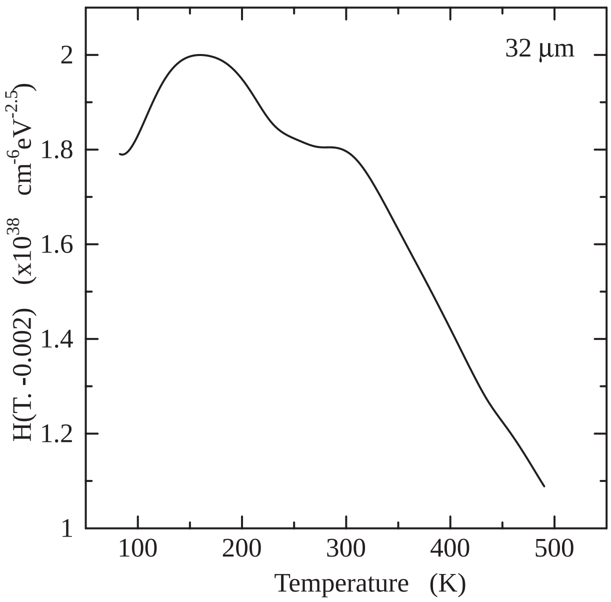

Fig. 4. $H(T, E_{\mathrm{ref}})$ with $E_{\mathrm{ref}} = -0.002$ eV, which is obtained using eq. (1).

When the absolute values of $(\Delta E_{\mathrm{D}i} - \Delta E_{\mathrm{D2}})$ for $i \neq 2$ are large, $f_{\mathrm{D}}(\Delta E_{\mathrm{D1}}) \simeq 0$ and $f_{\mathrm{D}}(\Delta E_{\mathrm{D}i}) \simeq 1$ for $i \geq 3$ around T_{peak2}. Moreover, $p(T) \simeq 0$ and $f_{\mathrm{A}}(\Delta E_{\mathrm{A}i}) \simeq 1$. Therefore, eq. (2) can be approximately expressed around T_{peak2} as

$$n(T) \simeq (N_{\mathrm{D1}} - N_{\mathrm{com}}) + N_{\mathrm{D2}}\left[1 - f_{\mathrm{D}}\left(\Delta E_{\mathrm{D2}}\right)\right], \tag{14}$$

where N_{com} is the compensating density and is given by

$$N_{\mathrm{com}} \equiv \sum_{i=1}^{m} N_{\mathrm{A}i} + \sum_{i=1}^{k} N_{\mathrm{TE}i}, \tag{15}$$

since the energy levels detected here are tentatively considered as donor levels. As a result, $H(T, E_{\mathrm{ref}})$ is approximately expressed as

$$\begin{aligned} H(T, E_{\mathrm{ref}}) \simeq{}& N_{\mathrm{D2}} \cdot \frac{1}{kT} \exp\left(-\frac{\Delta E_{\mathrm{D2}} - E_{\mathrm{ref}}}{kT}\right) I_{\mathrm{D}}(\Delta E_{\mathrm{D2}}) \\ &+ (N_{\mathrm{D1}} - N_{\mathrm{com}}) \cdot \frac{N_{\mathrm{C0}}}{kT} \exp\left(\frac{E_{\mathrm{ref}} - \Delta E_{\mathrm{F}}}{kT}\right). \end{aligned} \tag{16}$$

In order to reduce the number of three unknown parameters $[\Delta E_{\mathrm{D2}}, N_{\mathrm{D2}}$ and $(N_{\mathrm{D1}} - N_{\mathrm{com}})]$ to two $[\Delta E_{\mathrm{D2}}$ and $(N_{\mathrm{D1}} - N_{\mathrm{com}})/N_{\mathrm{D2}}]$, a function is introduced as

$$Z1(T, E_{\mathrm{ref}}) \equiv \frac{H(T, E_{\mathrm{ref}})}{N_{\mathrm{D2}}} \tag{17}$$

$$\begin{aligned} &\simeq \frac{1}{kT} \exp\left(-\frac{\Delta E_{\mathrm{D2}} - E_{\mathrm{ref}}}{kT}\right) I_{\mathrm{D}}(\Delta E_{\mathrm{D2}}) \\ &\quad + \frac{N_{\mathrm{D1}} - N_{\mathrm{com}}}{N_{\mathrm{D2}}} \cdot \frac{N_{\mathrm{C0}}}{kT} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right). \end{aligned} \tag{18}$$

To determine the two values of ΔE_{D2} and $(N_{\mathrm{D1}} - N_{\mathrm{com}})/N_{\mathrm{D2}}$ using eq. (18), two temperature values are required. In addition to T_{peak2}, therefore, T_{R} is introduced as the lower temperature at which the ratio $Z1(T, E_{\mathrm{ref}})/Z1(T_{\mathrm{peak2}}, E_{\mathrm{ref}})$ has a value of R (i.e., $0 < R < 1$), where

$$R = \frac{Z1(T, E_{\mathrm{ref}})}{Z1(T_{\mathrm{peak2}}, E_{\mathrm{ref}})} = \frac{H(T, E_{\mathrm{ref}})}{H(T_{\mathrm{peak2}}, E_{\mathrm{ref}})}. \tag{19}$$

When we select 105.1 K, the value of R is 0.93. Using a personal computer, we can determine ΔE_{D2} and $(N_{\mathrm{D1}} - N_{\mathrm{com}})/N_{\mathrm{D2}}$ that maximize $Z1(T, -0.002)$ at T_{peak2} and make $Z1(T, -0.002)$ 93% of the maximum value at T_{R} in eq. (18). Using $T_{\mathrm{peak2}} = 159.9$ K, $T_{\mathrm{R}} = 105.1$ K and $R = 0.93$, the values of ΔE_{D2} and $(N_{\mathrm{D1}} - N_{\mathrm{com}})/N_{\mathrm{D2}}$ are determined to be 54 meV and 0.44, respectively. The value of $Z1(T_{\mathrm{peak2}}, -0.002)$ is calculated from eq. (18) using the obtained values. From eq. (17), therefore, N_{D2} is estimated to be $8.1 \times 10^{16}\,\mathrm{cm}^{-3}$ using $H(T_{\mathrm{peak2}}, -0.002)$. Since $(N_{\mathrm{D1}} - N_{\mathrm{com}})/N_{\mathrm{D2}}$ is 0.44, the value of $(N_{\mathrm{D1}} - N_{\mathrm{com}})$ is evaluated to be $3.5 \times 10^{16}\,\mathrm{cm}^{-3}$, suggesting that there exist other donors shallower than this donor.

In the above determination, only the selection of T_{R} is ambiguous. When we select $T_{\mathrm{R}} = 115.1$ K, the value of R is 0.95. In this case, ΔE_{D2} and N_{D2} are determined to be 55 meV and $8.0 \times 10^{16}\,\mathrm{cm}^{-3}$, respectively. When we select $T_{\mathrm{R}} = 95.1$ K, on the other hand, the value of R is 0.90. In this case, ΔE_{D2} and N_{D2} are determined to be 53 meV and $8.2 \times 10^{16}\,\mathrm{cm}^{-3}$, respectively. Since the T_{R} dependences of ΔE_{D2} and N_{D2} are rather small, the values of $\Delta E_{\mathrm{D2}} = 54$ meV and $N_{\mathrm{D2}} = 8.1 \times 10^{16}\,\mathrm{cm}^{-3}$ are considered to be reliable.

To evaluate the shallow (first) donor and N_{com}, a function that is not influenced by the second donor is introduced as

$$\begin{aligned} H2(T, E_{\mathrm{ref}}) \equiv{}& \frac{n(T)^2}{(kT)^{2.5}} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right) \\ &- \frac{N_{\mathrm{D2}}}{kT} \exp\left(-\frac{\Delta E_{\mathrm{D2}} - E_{\mathrm{ref}}}{kT}\right) I_{\mathrm{D}}(\Delta E_{\mathrm{D2}}). \end{aligned} \tag{20}$$

Figure 5 shows the experimental $H2(T, -0.01)$ estimated using eq. (20). In the figure, two peaks appear.

Let us determine the density and energy level of the first donor. The values of T_{peak1} and $H2(T_{\mathrm{peak1}}, -0.01)$ are 114.5 K and $6.5 \times 10^{37}\,\mathrm{cm}^{-6}\,\mathrm{eV}^{-2.5}$, respectively. Around T_{peak1},

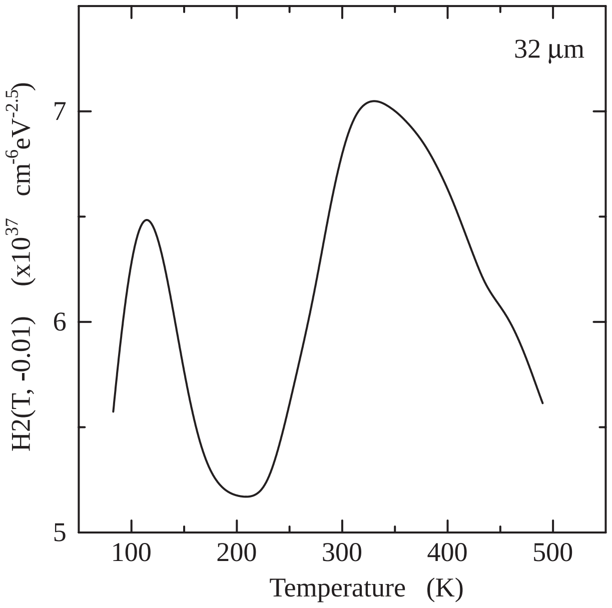

Fig. 5. $H2(T, E_{\mathrm{ref}})$ with $E_{\mathrm{ref}} = -0.01$ eV, which is obtained using eq. (20).

$$H2(T, E_{\mathrm{ref}}) \simeq \frac{N_{\mathrm{D1}}}{kT}\exp\left(-\frac{\Delta E_{\mathrm{D1}}-E_{\mathrm{ref}}}{kT}\right) I_{\mathrm{D}}(\Delta E_1) - N_{\mathrm{com}}\frac{N_{\mathrm{C0}}}{kT}\exp\left(\frac{E_{\mathrm{ref}}-E_{\mathrm{F}}}{kT}\right). \qquad (21)$$

The value of R is 0.86 when $T_{\mathrm{R1}} = 82.7\,\mathrm{K}$. In the same manner as that for the second donor determination, ΔE_{D1} and $N_{\mathrm{com}}/N_{\mathrm{D1}}$ are determined to be 14 meV and 0.12, respectively. Then, N_{D1} and N_{com} are determined to be $4.7 \times 10^{16}\,\mathrm{cm}^{-3}$ and $5.7 \times 10^{15}\,\mathrm{cm}^{-3}$, respectively.

To evaluate the deep (third) donor, a function that is not influenced by the first or second donor or N_{com} is introduced as

$$\begin{aligned} H3(T, E_{\mathrm{ref}}) \equiv{}& \frac{n(T)^2}{(kT)^{2.5}}\exp\left(\frac{E_{\mathrm{ref}}}{kT}\right) \\ &- \frac{N_{\mathrm{D1}}}{kT}\exp\left(-\frac{\Delta E_{\mathrm{D1}}-E_{\mathrm{ref}}}{kT}\right) I_{\mathrm{D}}(\Delta E_{\mathrm{D1}}) \\ &- \frac{N_{\mathrm{D2}}}{kT}\exp\left(-\frac{\Delta E_{\mathrm{D2}}-E_{\mathrm{ref}}}{kT}\right) I_{\mathrm{D}}(\Delta E_{\mathrm{D2}}) \\ &+ N_{\mathrm{com}}\frac{N_{\mathrm{C0}}}{kT}\exp\left(\frac{E_{\mathrm{ref}}-\Delta E_{\mathrm{F}}}{kT}\right). \qquad (22) \end{aligned}$$

Figure 6 shows the experimental $H3(T, 0)$ estimated using eq. (22). In the figure, one peak appears. The values of $H3(T_{\mathrm{peak3}}, 0)$ and T_{peak3} are $5.6 \times 10^{37}\,\mathrm{cm}^{-6}\,\mathrm{eV}^{-2.5}$ and 375.3 K, respectively. Around T_{peak3},

$$H3(T, E_{\mathrm{ref}}) \simeq \frac{N_{\mathrm{D3}}}{kT}\exp\left(-\frac{\Delta E_{\mathrm{D3}}-E_{\mathrm{ref}}}{kT}\right) I_{\mathrm{D}}(\Delta E_{\mathrm{D3}}). \qquad (23)$$

Using $H3(T_{\mathrm{peak3}}, 0)$ and T_{peak3}, the values of ΔE_{D1} and N_{D3} are determined to be 120 meV and $1.0 \times 10^{17}\,\mathrm{cm}^{-3}$, respectively.

In Fig. 6, in addition to the peak at 375.3 K, one shoulder appears around 470 K, suggesting that a deeper (fourth) donor may exist. Unfortunately, it is difficult to determine the density and energy level of the fourth donor using this method, because its density may be much lower than the densities of the other donors.

In order to verify the obtained values that are listed in Table I, we simulate $n(T)$ using the obtained values. The temperature dependence of ΔE_{F} is recalculated using the obtained values and the following two equations:

$$\begin{aligned} n(T) ={}& N_{\mathrm{D1}}\left[1 - f_{\mathrm{D}}(\Delta E_{\mathrm{D1}})\right] + N_{\mathrm{D2}}\left[1 - f_{\mathrm{D}}(\Delta E_{\mathrm{D2}})\right] \\ &+ N_{\mathrm{D3}}\left[1 - f_{\mathrm{D}}(\Delta E_{\mathrm{D3}})\right] - N_{\mathrm{com}} \qquad (24) \end{aligned}$$

and

$$n(T) = N_{\mathrm{C}}(T)\exp\left(-\frac{\Delta E_{\mathrm{F}}}{kT}\right). \qquad (25)$$

Then, $n(T)$, which is shown by the solid line in Fig. 7, is simulated using the calculated ΔE_{F} and eq. (25). In the figure, the open circles represent the experimental $n(T)$. The simulated $n(T)$ is quantitatively in good agreement with the experimental $n(T)$, indicating that the values obtained by $H(T, E_{\mathrm{ref}})$ are reliable.

In the same way, the densities and energy levels of donors for the 8-μm-thick and 16-μm-thick 3C-SiC are determined. The results are listed in Table I. In the 8-μm-thick 3C-SiC, the fourth donor ($\Delta E_{\mathrm{D4}} = 156\,\mathrm{meV}$ and $N_{\mathrm{D4}} = 4.6 \times 10^{16}\,\mathrm{cm}^{-3}$)

Table I. Densities and energy levels of donors in 3C-SiC grown from HMDS.

Thickness (μm)	8	16	32
ΔE_{D1} (meV)	10	7	14
N_{D1} ($\times 10^{16}\,\mathrm{cm}^{-3}$)	11	8.1	4.7
ΔE_{D2} (meV)	46	46	54
N_{D2} ($\times 10^{16}\,\mathrm{cm}^{-3}$)	17	20	8.1
ΔE_{D3} (meV)	107	97	120
N_{D3} ($\times 10^{16}\,\mathrm{cm}^{-3}$)	11	13	10
ΔE_{D4} (meV)	156	—[a]	—[a]
N_{D4} ($\times 10^{16}\,\mathrm{cm}^{-3}$)	4.6	—[a]	—[a]
N_{com} ($\times 10^{16}\,\mathrm{cm}^{-3}$)	1.3	0.99	0.57

a) Density is too small to determine.

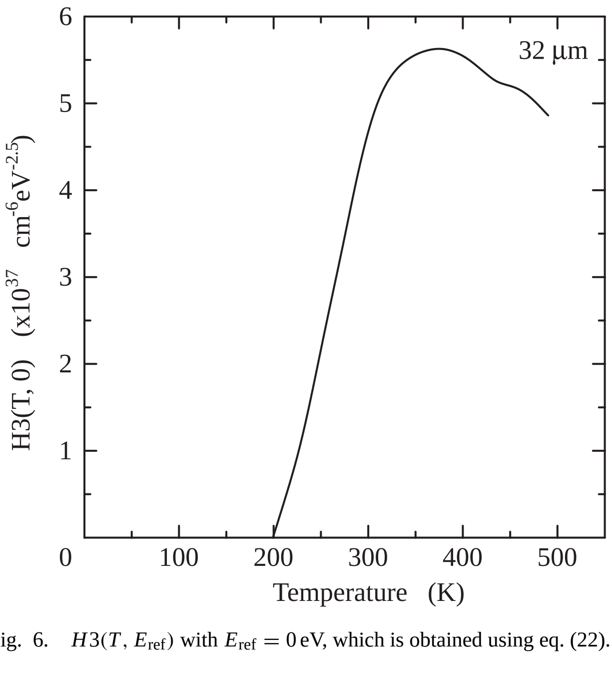

Fig. 6. $H3(T, E_{\mathrm{ref}})$ with $E_{\mathrm{ref}} = 0\,\mathrm{eV}$, which is obtained using eq. (22).

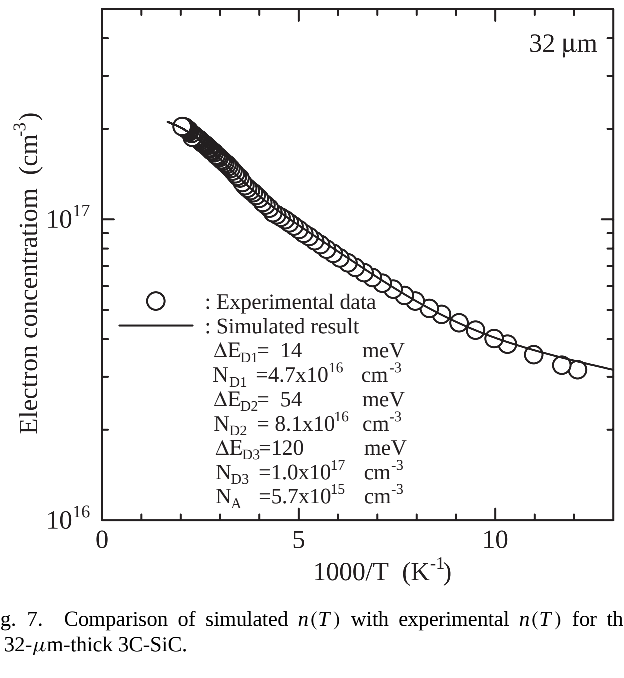

Fig. 7. Comparison of simulated $n(T)$ with experimental $n(T)$ for the 32-μm-thick 3C-SiC.

is detected. In all the cases, the simulated $n(T)$ is quantitatively in good agreement with the experimental $n(T)$. Therefore, the obtained results are considered to be reliable.

The density of the first donor clearly decreases with an increase in thickness. The density of the second donor in the 32-μm-thick film is about one-half of those in the thinner films. On the other hand, the density of the third donor is independent of film thickness. It is only in the 8-μm-thick film that the density and energy level of the fourth donor can be determined. The value of N_{com}, which represents the sum of acceptor densities as well as the densities of electron traps deeper than the energy level detected here, clearly decreases with an increase in thickness.

5. Discussion

5.1 Donors or electron traps

Equation (24) is derived under the assumption that the detected energy levels are donor levels. On the other hand, it happens that one energy level is an electron trap level. For example, the third energy level is assumed to be attributed to an electron trap, and the density and energy level are denoted by N_{TE1} and ΔE_{TE1}, respectively. In this case, eq. (2) can be expressed as

$$n(T) = N_{\mathrm{D1}}\left[1 - f_{\mathrm{D}}(\Delta E_{\mathrm{D1}})\right] + N_{\mathrm{D2}}\left[1 - f_{\mathrm{D}}(\Delta E_{\mathrm{D2}})\right] - N_{\mathrm{TE1}} f_{\mathrm{D}}(\Delta E_{\mathrm{TE1}}) - N'_{\mathrm{com}}, \tag{26}$$

where N'_{com} represents the density of electrons captured by acceptors and electron traps deeper than ΔE_{TE1}, and is given by

$$N'_{\mathrm{com}} = \sum_{i=1}^{m} N_{\mathrm{A}i} + \sum_{i=2}^{k} N_{\mathrm{TE}i}. \tag{27}$$

This equation should coincide with eq. (24), indicating that

$$N'_{\mathrm{com}} = N_{\mathrm{com}} - N_{\mathrm{D3}}, \tag{28}$$

$$N_{\mathrm{TE1}} = N_{\mathrm{D3}} \tag{29}$$

and

$$\Delta E_{\mathrm{TE1}} = \Delta E_{\mathrm{D3}}. \tag{30}$$

In the case of $N'_{\mathrm{com}} > 0$, there is a possibility that the third level is ascribed to an electron trap. In the case of $N'_{\mathrm{com}} < 0$, on the other hand, there are two cases. One case is that some donors shallower than ΔE_{D1} are included and the density of electrons supplied by the shallower donors is higher than the density of electrons captured by acceptors and electron traps. The other case is that the third energy level is attributed to a donor.

In our case, $N'_{\mathrm{com}} < 0$. Moreover, to our knowledge, there are no reports on donors shallower than ΔE_{D1}. Therefore, the third energy level is attributed to a donor. In the same manner, the first and second energy levels are ascribed to donors.

Therefore, when we determine the densities and energy levels of donors and electron traps, we can tentatively consider all energy levels as donor levels. After the determination, we can discuss whether each energy level is attributed to a donor or an electron trap.

5.2 Reported donor levels in 3C-SiC

From photoluminescence (PL) measurements, Freitas *et al.*20) and Kaplan *et al.*21) insisted that ΔE_{D} for N was ~54 meV. Moreover, Freitas *et al.*20) concluded that the ~15 meV donor which dominated the electrical properties of n-type films could not be ascribed to isolated, substitutional N. If N is associated with the ~15 meV donor, it can only be in inhomogeneities in the films where N is incorporated at much higher concentrations or indirectly in the formation of other defects such as defect-impurity complexes or nonstoichiometric defects. Dean *et al.*22) reported that in small high-purity crystals, ΔE_{D} for N was ~54 meV. On the other hand, Choyke and Patrick23) suggested that ΔE_{D} for N was 118 meV.

Also from PL measurements, Padlasov and Mokhov24) found that doping of 3C-SiC with P gave rise to a donor center with $\Delta E_{\mathrm{D}} \simeq 95$ meV.

From Fourier-transform infrared (FT-IR) spectroscopy in 3C-SiC, Moore *et al.*25) reported that the binding energy of the ground state for N was 54.2 meV and that the binding energies of some excited states for N were 15.2 meV, 10.4 meV and 7.0 meV.

From Hall-effect measurements, ΔE_{D} and N_{D} in 3C-SiC were determined under the assumption of only one type of donor in the following reports. Aivazova *et al.*26) reported that in high-purity crystals, ΔE_{D} was ~50 meV, ~40 meV and ~30 meV at $N_{\mathrm{D}} \simeq 10^{15}$ cm^{-3}, $N_{\mathrm{D}} \simeq 10^{16}$ cm^{-3} and $N_{\mathrm{D}} \simeq 10^{17}$ cm^{-3}, respectively. They suggested that this donor was attributed to N by means of electron spin resonance (ESR). On the other hand, Segall *et al.*3,5) reported that in unintentionally doped epilayers grown from a mixture of $\mathrm{SiH_4}$ and $\mathrm{C_3H_8}$, the values of ΔE_{D}, N_{D} and $N_{\mathrm{com}}/N_{\mathrm{D}}$ were ~15 meV, ~2 × 10^{18} cm^{-3} and >0.9, respectively. Similar results were reported.2,4,6,7) However, Sasaki *et al.*1) reported that ΔE_{D} was 40–50 meV on the assumption that $N_{\mathrm{com}} = 0$ cm^{-3}.

Segall *et al.*3,5) concluded that the ~15 meV donor resulted from N, and that a high degree of compensation and a large concentration induced the reduction of the N donor depth. In other words,

$$\Delta E_{\mathrm{D}}(N_{\mathrm{D}}) = \Delta E_{\mathrm{D}}(0) - \alpha N_{\mathrm{D}}^{1/3} \tag{31}$$

with

$$\Delta E_{\mathrm{D}}(0) \simeq 48 \text{ meV} \tag{32}$$

and

$$\alpha \simeq 2.6 \times 10^{-5} \text{ meV}\cdot\text{cm}. \tag{33}$$

On the other hand, Suzuki *et al.*2) insisted that ΔE_{D} for N was determined to be ~35 meV from the study of N-doped 3C-SiC, and that the ~15 meV donors came from nonstoichiometric defects in unintentionally doped films.

5.3 Comparison of our results with others

Using $H(T, E_{\mathrm{ref}})$, four types of donors in undoped 3C-SiC grown from HMDS were detected. The two types of donors (first and second donors) are considered to correspond to the ~15 meV donor and the ~50 meV donor mentioned above, respectively. The origin of the ~110 meV donor is uncertain. Thus, doping of 3C-SiC with P or N is in progress, in order to identify this donor. On the other hand, the fourth donor has not been reported yet.

Since the crystallinity of our epilayers was enhanced as the thickness increased, the density of the first donor is considered to be sensitive to the crystallinity of the epilayer. This coincides with the suggestions of Freitas *et al.*20) and Suzuki *et al.*2) that the ~15 meV donor is attributed to some defect-impurity complex or some nonstoichiometric defect.

Segall *et al.*3,5) suggested that ΔE_D for substitutional N decreased from ~50 meV to ~15 meV with an increase in N_D. From our results, however, the ~15 meV donor and the ~50 meV donors coexist in unintentionally doped 3C-SiC, indicating that in $N_D \leq 10^{17}$ cm^{-3}, the donor level for substitutional N should not be a function of N_D.

From PL and FT-IR measurements, the ~50 meV donor corresponds to substitutional N. This may suggest that the ~50 meV donor density is independent of 3C-SiC thickness. However, its density in 32-μm-thick film was about one-half of that in 16-μm-thick film. Thus, the relationship between N donor density and crystallinity is under investigation.

As is clear from eqs. (15) and (24), N_{com} represents the sum of acceptor densities as well as densities of electron traps deeper than the energy level detected here. Since electron traps result from defects, the thickness dependence of N_{com} is considered to be reasonable.

The ~50 meV and ~110 meV donors, which were detected in epilayers grown from HMDS, were not reported in epilayers grown from a mixture of SiH_4 and C_3H_8. In undoped 3C-SiC grown from a mixture of SiH_4 and C_3H_8, the ~15 meV donor density was about 10^{18} cm^{-3} and the compensation ratio (N_{com}/N_D) was greater than 0.9.3,4,7) On the other hand, in our undoped 3C-SiC grown from HMDS, the sum (N_D) of the donor densities was lower than 5×10^{17} cm^{-3} and N_{com}/N_D was about 0.03. Therefore, the quality of our undoped 3C-SiC is better than that of undoped 3C-SiC grown from a mixture of SiH_4 and C_3H_8.

6. Conclusion

Even if we do not know the number of types of impurities included in the grown semiconductor, we found that $H(T, E_{ref})$ can determine the densities and energy levels of impurities accurately. Since $H(T, E_{ref})$ has a peak at the temperature corresponding to each impurity level, we can easily determine the densities and energy levels of impurities. In undoped 3C-SiC grown from HMDS, we have detected four types of donors whose ΔE_D are 7–14 meV, 46–54 meV, 97–120 meV and 156 meV, while only the ~15 meV donor was reported in undoped 3C-SiC grown from a mixture of SiH_4 and C_3H_8. From the viewpoints of donor density and compensation ratio, the quality of undoped 3C-SiC grown from HMDS is better than that of undoped 3C-SiC grown from a mixture of SiH_4 and C_3H_8.

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