Jpn. J. Appl. Phys. Vol. 38 (1999) pp. 4013–4016
Part 1, No. 7A, July 1999

Nitrogen Donor Concentrations and Its Energy Levels in 4H-SiC Uniquely Determined by a New Graphical Method Based on Hall-Effect Measurement

Hideharu MATSUURA*, Tsunenobu KIMOTO[1] and Hiroyuki MATSUNAMI[1]

Department of Electronics, Osaka Electro-Communication University, 18-8 Hatsu-cho, Neyagawa, Osaka 572-8530, Japan
[1] *Department of Electronic Science and Engineering, Kyoto University, Yoshida Hon-machi, Sakyo, Kyoto 606-8501, Japan*

(Received January 11, 1999; revised manuscript received February 15, 1999; accepted for publication May 12, 1999)

This is the first report on the experimental results using the precise determination proposed in our previous papers. By means of this analysis, the concentrations and energy levels of dopants in a semiconductor can be uniquely determined using the temperature dependence $n(T)$ of the majority-carrier concentration obtained experimentally from the Hall-effect measurement. In other words, the concentration and energy level of each dopant can be evaluated using the corresponding peak value and temperature of $n(T)/kT$. In nitrogen (N)-doped 4H-SiC, the concentration and energy level of the shallow donor are 6.45×10^{15} cm^{-3} and $E_C - 0.0653$ eV, respectively, and those of the deep donor are 3.04×10^{16} cm^{-3} and $E_C - 0.124$ eV, respectively, where E_C is the bottom of the conduction band. The acceptor concentration is 6.14×10^{13} cm^{-3}. These obtained values are found to be quite reliable.

KEYWORDS: evaluation of dopants, Hall-effect measurement, SiC, 4H-SiC, majority-carrier concentration, temperature dependence, donor concentration, donor level, acceptor concentration, graphical approach

1. Introduction

An accurate evaluation of the concentrations and energy levels of dopants in a semiconductor is essential. In order to determine these concentrations and energy levels, the temperature dependence of the majority-carrier concentration $n(T)$ is usually measured. Although these values are usually determined using the $\ln n(T) - 1/T$ curve, this analysis cannot be applied in the case of semiconductors with more than two types of dopants or compensated semiconductors. Moreover, it is difficult to obtain reliable values by fitting a curve to the experimental data on $n(T)$, since many curve-fitting parameters must be determined at the same time. Though Hoffmann proposed a differential evaluation of $n(T)$,[1)] the differentiation of the experimental data results in an increase in observed errors.

One of the authors has proposed the precise determination without the differentiation of $n(T)$.[2–5)] In this analysis, a function $S(T, E_{\mathrm{ref}})$ is defined as

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

where k is the Boltzmann constant and E_{ref} is a parameter. $S(T, E_{\mathrm{ref}})$ has peaks corresponding to each dopant level. From each peak value and peak temperature, the concentration and energy level of the corresponding dopant can be accurately determined. Even when a peak does not appear in the measurement temperatures with $E_{\mathrm{ref}} = 0$ eV, the peak temperature of $S(T, E_{\mathrm{ref}})$ can be shifted to the range of the measurement temperatures by changing E_{ref}.

4H-SiC has been regarded as a promising semiconductor for power electronic applications owing to its excellent physical properties.[6–8)] When a nitrogen (N) atom is put into 4H-SiC, the atom can be located either at a cubic site or at a hexagonal site in 4H-SiC, indicating that two types of donors with different energy levels are produced. Therefore, N-doped 4H-SiC is a good material for testing our proposed analysis. Using the experimental data on N-doped 4H-SiC, the concentrations and energy levels of donors are uniquely determined.

2. Theoretical Consideration

Let us consider n types of donors (concentration $N_{\mathrm{D}i}$ and energy level $\Delta E_{\mathrm{D}i}$ for $1 \le i \le n$) and one type of acceptor (concentration N_{A}), where $\Delta E_{\mathrm{D}i}$ is measured from the bottom of the conduction band (E_{C}) and $\Delta E_{\mathrm{D}i+1} > \Delta E_{\mathrm{D}i}$. From the electrical neutrality condition, the free electron concentration $n(T)$ is given by[9)]

$$n(T) = \sum_{i=1}^{n} N_{\mathrm{D}i}\left[1 - f(\Delta E_{\mathrm{D}i})\right] - N_{\mathrm{A}}, \tag{2}$$

where

$$f(\Delta E_{\mathrm{D}i}) = \frac{1}{1 + \frac{1}{2}\exp\left(\frac{\Delta E_{\mathrm{F}} - \Delta E_{\mathrm{D}i}}{kT}\right)}, \tag{3}$$

and ΔE_{F} is the Fermi level measured from E_{C}. Using eq. (2), $S(T, E_{\mathrm{ref}})$ can be rewritten as

$$S(T, E_{\mathrm{ref}}) = \sum_{i=1}^{n} \frac{N_{\mathrm{D}i}}{kT} \exp\left(-\frac{\Delta E_{\mathrm{D}i} - E_{\mathrm{ref}}}{kT}\right) F_i(T) - \frac{N_{\mathrm{A}}}{kT}\exp\left(\frac{E_{\mathrm{ref}}}{kT}\right) \tag{4}$$

with

$$F_i(T) = \frac{\exp\left(\frac{\Delta E_{\mathrm{F}}}{kT}\right)}{2 + \exp\left(\frac{\Delta E_{\mathrm{F}} - \Delta E_{\mathrm{D}i}}{kT}\right)}. \tag{5}$$

The term

$$\frac{N_{\mathrm{D}i}}{kT} \exp\left(-\frac{\Delta E_{\mathrm{D}i} - E_{\mathrm{ref}}}{kT}\right) \tag{6}$$

in eq. (4) has a peak value of $N_{\mathrm{D}i} \exp(-1)/kT_{\mathrm{peak}i}$ at $T_{\mathrm{peak}i} = (\Delta E_{\mathrm{D}i} - E_{\mathrm{ref}})/k$. Although $T_{\mathrm{peak}i}$ is shifted to a lower temperature due to the temperature dependence of $F_i(T)$, we can easily determine $N_{\mathrm{D}i}$ and $\Delta E_{\mathrm{D}i}$ from the corresponding peak value and temperature using a personal computer.

---

*Web site: http://www.osakac.ac.jp/labs/matsuura/

3. Experimental

4H-SiC was grown by chemical vapor deposition using gases of 1% SiH_4 and 1% C_3H_8 diluted with H_2 at 1560°C and 760 Torr. After 2-μm-thick p-type 4H-SiC was grown onto a 4H-SiC substrate (off-orientation of about 5° from {0001} toward $\langle 11\bar{2}0\rangle$) prepared by a sublimation method, 5-μm-thick n-type 4H-SiC was grown using a doping gas of N_2. For the growth of the n-type layer, the flow rates of SiH_4, C_3H_8, N_2 and H_2 were 0.30 sccm, 0.20 sccm, 2.5×10^{-2} sccm and 3.0 slm, respectively. The details were reported in the previous papers.[6–8]

4. Results and Discussion

Open circles in Fig. 1 represent the data on $n(T)$ obtained experimentally from the Hall-effect measurement. In the figure, the solid line represents the data on $n(T)$ interpolated by the cubic smoothing natural spline function using the experimental data. The broken line represents ΔE_{F} calculated using

$$\Delta E_{\mathrm{F}} = kT \ln\left[\frac{N_{\mathrm{C}}(T)}{n(T)}\right], \tag{7}$$

where $N_{\mathrm{C}}(T)$ is the effective density of states in the conduction band for 4H-SiC, which is given by[7]

$$N_{\mathrm{C}}(T) = 2.71 \times 10^{15} T^{3/2}\ \mathrm{cm}^{-3}. \tag{8}$$

The solid line in Fig. 2 shows $S(T, 0)$ calculated using the solid line in Fig. 1. One peak appeared around 320 K, while one shoulder appeared around 120 K. Therefore, at least, there exist two types (shallow and deep) of donors in this 4H-SiC. Here, the peak temperatures corresponding to the shallow and deep donors are denoted by T_{peak1} and T_{peak2}, respectively.

First we evaluate the deep donor using the solid line in Fig. 2. The peak value $S(T_{\mathrm{peak2}}, 0)$ and temperature T_{peak2} are $1.04 \times 10^{18}\ \mathrm{cm}^{-3}\mathrm{eV}^{-1}$ and 319 K, respectively. When the absolute values of $\Delta E_{\mathrm{D}i} - \Delta E_{\mathrm{D2}}$ for $i \neq 2$ are large, $f(\Delta E_{\mathrm{D1}}) \simeq 0$ and $f(\Delta E_{\mathrm{D}i}) \simeq 1$ for $i \geq 3$ around T_{peak2}, indicating that eq. (2) can be approximately expressed as

$$n(T) \simeq (N_{\mathrm{D1}} - N_{\mathrm{A}}) + N_{\mathrm{D2}}\left[1 - f(\Delta E_{\mathrm{D2}})\right]. \tag{9}$$

Therefore, $S(T, E_{\mathrm{ref}})$ is approximately expressed as

$$S(T, E_{\mathrm{ref}}) \simeq N_{\mathrm{D2}} \cdot \frac{1}{kT}\exp\left(-\frac{\Delta E_{\mathrm{D2}} - E_{\mathrm{ref}}}{kT}\right) F_2(T) + (N_{\mathrm{D1}} - N_{\mathrm{A}}) \cdot \frac{1}{kT}\exp\left(\frac{E_{\mathrm{ref}}}{kT}\right). \tag{10}$$

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

$$Y1(T, E_{\mathrm{ref}}) \equiv \frac{S(T, E_{\mathrm{ref}})}{N_{\mathrm{D2}}} \tag{11}$$

$$\simeq \frac{1}{kT}\exp\left(-\frac{\Delta E_{\mathrm{D2}} - E_{\mathrm{ref}}}{kT}\right) F_2(T) + \frac{N_{\mathrm{D1}} - N_{\mathrm{A}}}{N_{\mathrm{D2}}} \cdot \frac{1}{kT}\exp\left(\frac{E_{\mathrm{ref}}}{kT}\right). \tag{12}$$

To determine two values of ΔE_{D2} and $(N_{\mathrm{D1}} - N_{\mathrm{A}})/N_{\mathrm{D2}}$ using eq. (12), two temperature values are required. Besides T_{peak2}, therefore, T_{R2} is introduced as the lower temperature at which the ratio $Y1(T, E_{\mathrm{ref}})/Y1(T_{\mathrm{peak2}}, E_{\mathrm{ref}})$ has a value of R (i.e., $0 < R < 1$), where

$$\frac{Y1(T, E_{\mathrm{ref}})}{Y1(T_{\mathrm{peak2}}, E_{\mathrm{ref}})} = \frac{S(T, E_{\mathrm{ref}})}{S(T_{\mathrm{peak2}}, E_{\mathrm{ref}})}. \tag{13}$$

In the solid line of Fig. 2, the shoulder appears around 120 K, suggesting that this shoulder results from a shallow donor. When determining the deep donor concentration and its energy level, we should select T_{R2} from the temperatures at which $f(\Delta E_{\mathrm{D1}}) \simeq 0$ (i.e., the temperature higher than the temperature at which the shoulder appears). When we select $T_{\mathrm{R2}} = 250$ K, the value of R is 0.886. Using a personal computer, we can determine ΔE_{D2} and $(N_{\mathrm{D1}} - N_{\mathrm{A}})/N_{\mathrm{D2}}$ that maximize $Y1(T, 0)$ at T_{peak2} and make $Y1(T, 0)$ 88.6% of the

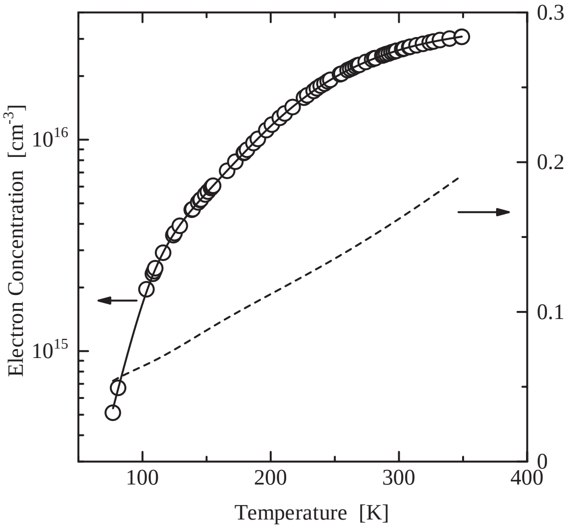

Fig. 1. Temperature dependence of electron concentration and Fermi level in N-doped 4H-SiC. The open circles represent the experimental $n(T)$, and the solid line represents $n(T)$ interpolated by the spline function using the experimental data. The broken line represents the temperature dependence of the Fermi level.

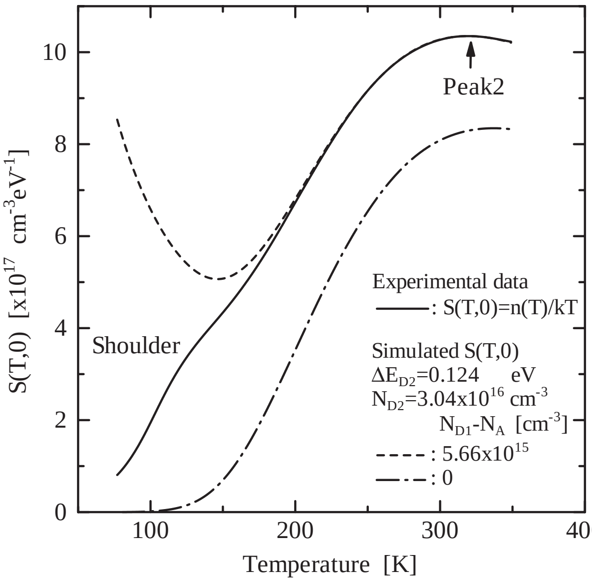

Fig. 2. Experimental $S(T, 0)$ obtained using eq. (1) and $S(T, 0)$ simulated using eq. (10). The solid and broken lines represent experimental and simulated $S(T, 0)$, respectively. Shoulder and Peak2 correspond to the effects of the shallow and deep donors on $S(T, 0)$, respectively.

maximum value at T_{R2} in eq. (12). Using $T_{peak2} = 319\,K$, $T_{R2} = 250\,K$ and $R = 0.886$, the values of ΔE_{D2} and $(N_{D1} - N_A)/N_{D2}$ are determined to be 0.124 eV and 0.186, respectively. The value of $Y1(T_{peak2}, 0)$ is calculated from eq. (12) with the obtained values. From eq. (11), N_{D2} is estimated to be $3.04 \times 10^{16}\,cm^{-3}$ using $S(T_{peak2}, 0) = 1.04 \times 10^{18}\,cm^{-3}eV^{-1}$. Since $(N_{D1} - N_A)/N_{D2}$ is 0.186, the value of $N_{D1} - N_A$ is evaluated to be $5.66 \times 10^{15}\,cm^{-3}$.

In the above determination, only the selection of T_{R2} is ambiguous. When we select $T_{R2} = 200\,K$, the value of R is 0.651. In this case, ΔE_{D2} and N_{D2} are determined to be 0.123 eV and $3.07 \times 10^{16}\,cm^{-3}$, respectively. The difference between ΔE_{D2} for two T_{R2} (200 K and 250 K) is only 0.001 eV and the difference between N_{D2} for two T_{R2} is only $3 \times 10^{14}\,cm^{-3}$. Therefore, as long as we select T_{R2} from the temperatures at which all the shallow donors are considered to be ionized, we can obtain reliable results.

The broken line in Fig. 2 is $S(T, 0)$ simulated using eq. (10) with the obtained values. The broken line coincides with the solid line around T_{peak2}, while it does not coincide with the solid line at low temperatures. This disagreement at low temperatures results from the wrong assumption of $f(\Delta E_{D1}) = 0$ at these low temperatures.

The dashed-dotted line in Fig. 2, which is $S(T, 0)$ simulated using $(N_{D1} - N_A) = 0\,cm^{-3}$, represents $S(T, 0)$ owing to the deep donor without the effect of the shallow donor and the acceptor. Therefore, the difference between the solid line and the dashed-dotted line represents the contribution of the shallow donor and the acceptor to $S(T, E_{ref})$. To evaluate the shallow donor and the acceptor, a function that is not influenced by the deep donor is introduced from eq. (4) as

$$\begin{aligned} S2(T, E_{ref}) &\equiv S(T, E_{ref}) \\ &\quad - \frac{N_{D2}}{kT} \exp\left(-\frac{\Delta E_{D2} - E_{ref}}{kT}\right) F_2(T) \qquad (14) \\ &\simeq \frac{N_{D1}}{kT} \exp\left(-\frac{\Delta E_{D1} - E_{ref}}{kT}\right) F_1(T) \\ &\quad - \frac{N_A}{kT} \exp\left(\frac{E_{ref}}{kT}\right). \qquad (15) \end{aligned}$$

The solid line in Fig. 3 represents the experimental $S2(T, 0)$ estimated using eq. (14). $S2(T_{peak1}, 0)$ and T_{peak1} are $3.65 \times 10^{17}\,cm^{-3}eV^{-1}$ and 154 K, respectively, and R is 0.251 when $T_{R1} = 80.1\,K$. In the same manner of the deep donor determination, ΔE_{D1} and N_A/N_{D1} are determined to be 0.0653 eV and 9.52×10^{-3}, respectively. Then, N_{D1} and N_A are determined to be $6.45 \times 10^{15}\,cm^{-3}$ and $6.14 \times 10^{13}\,cm^{-3}$, respectively.

The broken line in Fig. 3 is $S2(T, 0)$ simulated using eq. (15) with the obtained values (ΔE_{D1}, N_{D1}, N_A). The broken line coincides with the solid line very well, indicating that there are no more donors in this 4H-SiC.

Let us simulate $n(T)$ using the obtained values. The temperature dependence of ΔE_F is recalculated using the following two equations:

$$n(T) = N_{D1}\left[1 - f(\Delta E_{D1})\right] + N_{D2}\left[1 - f(\Delta E_{D2})\right] - N_A \qquad (16)$$

and

$$n(T) = N_C(T) \exp\left(-\frac{\Delta E_F}{kT}\right). \qquad (17)$$

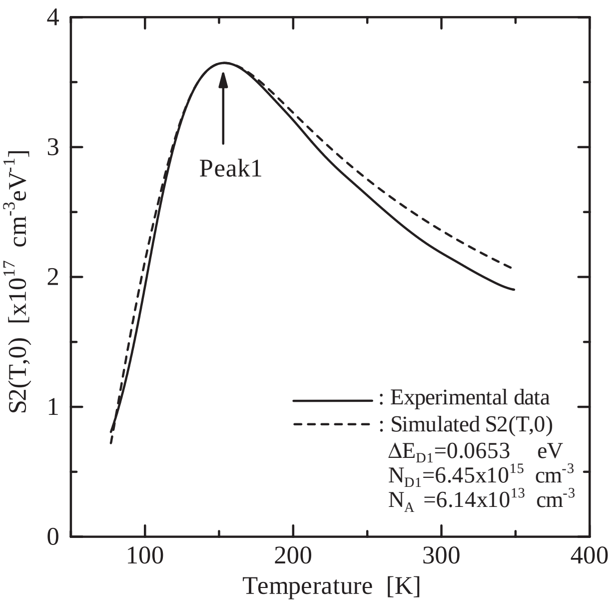

Fig. 3. Experimental $S2(T, 0)$ obtained using eq. (14) and $S2(T, 0)$ simulated using eq. (15). Peak1 corresponds to the effect of the shallow donor on $S2(T, 0)$.

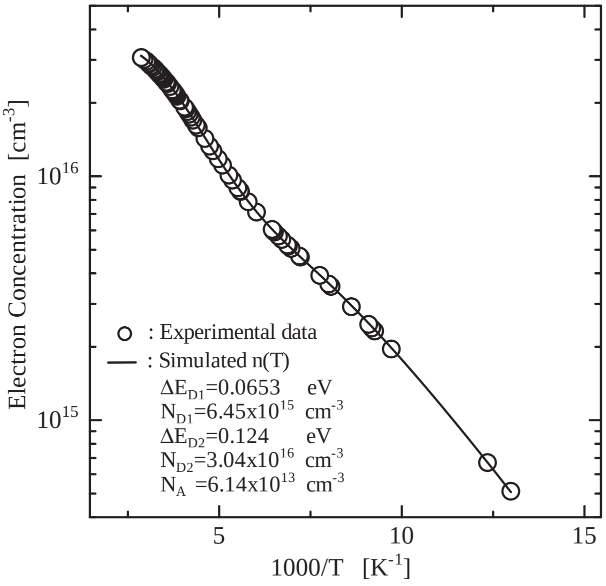

Fig. 4. Temperature dependence of electron concentration (open circle: experimental $n(T)$ and solid line: $n(T)$ simulated with results determined by our analysis).

Then, $n(T)$, which is shown in the solid line of Fig. 4, is calculated using eq. (17) and the obtained ΔE_F. In the figure, the open circles represent the experimental $n(T)$. The simulated $n(T)$ is quantitatively in very good agreement with the experimental $n(T)$. Since two donor levels of N in 4H-SiC are reported to be 45–66 meV and 92–124 meV,[10,11)] the donor levels obtained here are reliable.

5. Comparison with Other Analyses

5.1 *Graphical method using* $\ln n(T) - 1/T$ *curve*

In the $n(T) - 1/T$ characteristics, the donor concentration is equal to $n(T)$ in the saturation region.[9)] The donor level is evaluated from the slope of the $\ln n(T) - 1/T$ curve in the freeze-out region, because $n(T)$ in this region is approximately proportional to[9)]

$$\exp\left(-\frac{\Delta E_{\mathrm{D}i}}{2kT}\right). \tag{18}$$

The experimental $\ln n(T) - 1/T$ curve is shown as the open circles in Fig. 4. Since there are no clear saturation regions in Fig. 4, it is difficult to determine the donor concentrations. From the range $8.62\ \mathrm{K}^{-1} \le 1000/T \le 13.0\,\mathrm{K}^{-1}$, ΔE_{D1} is calculated to be 0.0693 eV, while from the range $4.24\,\mathrm{K}^{-1} \le 1000/T \le 5.59\,\mathrm{K}^{-1}$, ΔE_{D2} is estimated to be 0.0901 eV. In this analysis, it is also difficult to determine the acceptor concentration. In our analysis, on the other hand, the donor concentrations, the donor levels and the acceptor concentration can be determined.

5.2 *Curve-fitting method*

When the values of $\Delta E_{\mathrm{D}i}$, $N_{\mathrm{D}i}$ and N_{A} are determined by fitting a curve to the experimental data for the $n(T) - 1/T$ curve, it is necessary to determine how many types of donors exist in the semiconductor before the curve-fitting procedure is carried out. Therefore, it is difficult to apply this analysis when we do not know how many types of donors exist there. Moreover, because so many curve-fitting parameters are determined at the same time to fit a curve to the experimental data, it is difficult to evaluate the concentrations and energy levels accurately. In our analysis, on the other hand, each donor level can be determined using the corresponding peak temperature, and each donor concentration can be estimated using the corresponding peak value.

5.3 *Differential method*

According to the differential evaluation of $n(T)$ proposed by Hoffmann,[1)] for small temperature difference $T_{j+1} - T_j$, the derivative $-kT[\mathrm{d}n(T)/\mathrm{d}\Delta E_{\mathrm{F}}]$ as a function of ΔE_{F} can be approximated by[2)]

$$\frac{T_{j+1}+T_j}{2}\cdot\frac{n(T_{j+1})-n(T_j)}{T_{j+1}\ln\left[\dfrac{N_{\mathrm{C}}(T_{j+1})}{n(T_{j+1})}\right]-T_j\ln\left[\dfrac{N_{\mathrm{C}}(T_j)}{n(T_j)}\right]} \tag{19}$$

as a function of

$$\frac{k}{2}\left\{T_{j+1}\ln\left[\frac{N_{\mathrm{C}}(T_{j+1})}{n(T_{j+1})}\right]+T_j\ln\left[\frac{N_{\mathrm{C}}(T_j)}{n(T_j)}\right]\right\}. \tag{20}$$

The $-kT[\mathrm{d}n(T)/\mathrm{d}\Delta E_{\mathrm{F}}]$ curve has a maximum at $\Delta E_{\mathrm{F}} = \Delta E_{\mathrm{D}i} + kT_{\mathrm{m}i}\ln 2$, where $T_{\mathrm{m}i}$ is the temperature corresponding to the i-th maximum. The ordinate of the i-th maximum equals $N_{\mathrm{D}i}/4$.

When the $-kT[\mathrm{d}n(T)/\mathrm{d}\Delta E_{\mathrm{F}}]$ vs ΔE_{F} was calculated using the experimental $n(T)$, it was quite difficult to determine $\Delta E_{\mathrm{D}i}$ and $N_{\mathrm{D}i}$ because of a large fluctuation of $-kT[\mathrm{d}n(T)/\mathrm{d}\Delta E_{\mathrm{F}}]$. When the curve was calculated using the data on $n(T)$ that were interpolated using the cubic smoothing natural spline function, the values of ΔE_{D1} and N_{D1} were evaluated to be 0.0614 eV and $6.90\times10^{15}\,\mathrm{cm}^{-3}$, respectively, and ΔE_{D2} and N_{D2} were estimated to be 0.115 eV and $2.83\times10^{16}\,\mathrm{cm}^{-3}$, respectively. However, the acceptor concentration cannot be evaluated by Hoffmann's analysis at all. On the other hand, since all the values that are necessary to simulate $n(T)$ can be determined by our analysis, the reliability of the obtained values can be checked. Moreover, because the data on $n(T)$ are differentiated in Hoffmann's analysis, donor concentrations and donor levels are apt to depend on the type of interpolation function. In our analysis where the data are not differentiated, however, these are much less dependent on the type of interpolation function.

6. Summary

The graphical method to uniquely determine the concentrations and energy levels of dopants in a semiconductor has been discussed theoretically. Using the $n(T)$ of N-doped 4H-SiC, for the first time, we have experimentally elucidated the reliability and accuracy of our analysis in comparison with other analyses.

1) H. J. Hoffmann: Appl. Phys. **19** (1979) 307.
2) H. Matsuura and K. Sonoi: Jpn. J. Appl. Phys. **35** (1996) L555.
3) H. Matsuura: Jpn. J. Appl. Phys. **35** (1996) 5297.
4) H. Matsuura: Jpn. J. Appl. Phys. **35** (1996) 5680.
5) H. Matsuura: Jpn. J. Appl. Phys. **36** (1997) 3541.
6) A. Itoh, H. Akita, T. Kimoto and H. Matsunami: Appl. Phys. Lett. **65** (1994) 1400.
7) A. Itoh: Dr. Thesis, Faculty of Engineering, Kyoto University, Kyoto, 1995.
8) T. Kimoto, A. Itoh, H. Matsunami, S. Sridhara, L. L. Clemen, R. P. Devaty, W. J. Choyke, T. Dalibor, C. Peppermüller and G. Pensl: Appl. Phys. Lett. **67** (1995) 2833.
9) S. M. Sze: *Physics of Semiconductor Devices* (Wiley, New York, 1981) 2nd ed., p.22.
10) M. Ikeda, H. Matsunami and T. Tanaka: Phys. Rev. B **22** (1980) 2842.
11) W. Götz, A. Schöner, G. Pensl, W. Suttrop, W. J. Choyke, R. Stein and S. Leibenzeder: J. Appl. Phys. **73** (1993) 3332.