Jpn. J. Appl. Phys. Vol. 36 (1997) pp. 3541–3547
Part 1, No. 6A, June 1997

A Simple Graphical Method for Determining Densities and Energy Levels of Donors and Acceptors in Semiconductor from Temperature Dependence of Majority Carrier Concentration

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(Received January 24, 1997; accepted for publication March 24, 1997)

The purpose of this study is to propose a simple graphical method for accurately determining the densities and energy levels of donors and acceptors with different energy levels in a semiconductor from the temperature dependence of majority carrier concentration $n(T)$. For this purpose, a function $S(T, E_{\mathrm{ref}})$ is defined as $S(T, E_{\mathrm{ref}}) \equiv n(T)\exp(E_{\mathrm{ref}}/kT)/kT$, where k is the Boltzmann constant and E_{ref} is a parameter which varies a peak temperature of $S(T, E_{\mathrm{ref}})$. Since $S(T, E_{\mathrm{ref}})$ has peaks corresponding to the energy levels of impurities which produce majority carriers, the density and energy level can be evaluated using each peak in the $S(T, E_{\mathrm{ref}})$ curve. This method can be used to investigate how many kinds of impurities, which produce majority carriers, exist in a semiconductor. Moreover, the density of all impurities, which produce minority carriers, can be determined, since we can simulate the dependence of $S(T, E_{\mathrm{ref}})$ on this density.

KEYWORDS: donor level, donor density, acceptor level, acceptor density, compensated semiconductor, graphical evaluation of densities and energy levels of impurities, Hall effect measurement

1. Introduction

Semiconductors usually include several kinds of impurities. For example, 6H-SiC is reported to often include both acceptors (Al and/or B)[1,2] and N atoms which act as donors with two sets of energy levels.[1] In Si, oxygen-related donors are reported to be formed by annealing.[3,4] Besides conventional dopants, impurities are sometimes intentionally doped into Si or III–V compound semiconductors. For instance, rare-earth metals are used as dopants, because near-infrared light can be obtained from these materials.[4,5]

Since the majority carrier concentration (n or p) is very sensitive to impurities, an accurate evaluation of the densities and energy levels of impurities is very important. In order to determine the densities and energy levels of donors and/or acceptors in semiconductors, many methods have been used.[3,4,6–9] The dependence ($\ln n - 1/T$ or $\ln p - 1/T$) of the majority carrier concentration on the temperature (T) is usually used to determine the impurity density and the impurity level. The impurity density is equal to the majority carrier concentration in the saturation region, and the impurity level is evaluated from the slope of the $\ln n - 1/T$ or $\ln p - 1/T$ curve in the freeze-out region. As pointed out by Hoffmann,[6] however, it is difficult to evaluate the densities and energy levels of impurities with different energy levels in a semiconductor using this method. Although Hoffmann proposed a differential evaluation of the temperature dependence of the majority carrier concentration,[6] the differential evaluation of experimental data probably results in an increase in the number of observational errors, indicating that it is difficult to evaluate the densities and energy levels accurately. On the other hand, it is difficult to obtain reliable values by fitting a curve to experimental data for $n - 1/T$ (or $p - 1/T$), partly because it is necessary to determine how many kinds of impurities exist in a semiconductor before carrying out the curve-fitting procedure and partly because so many curve-fitting parameters (i.e., the densities and energy levels of several kinds of donors and acceptors) are required to fit a curve to experimental data.

We have proposed a simple graphical method in which, from each peak in the curve representing the product of n (or p) and $1/kT$, the corresponding density and energy level can be determined,[10] where k is the Boltzmann constant. The smallest difference between energy levels (i.e., the energy resolution) of two impurities, whose densities and energy levels can be determined accurately using this method, is about 0.05 eV.[10] Although this energy resolution is comparable to that for Hoffmann's method,[10] it is necessary to improve the energy resolution. Moreover, it is difficult to evaluate the densities and energy levels of donors and acceptors in a compensated semiconductor using this method. Therefore, we have aimed to modify the previously proposed method[10] in order to obtain more accurate results.[11,12]

The expression $(N_{\mathrm{D}}/kT)\exp[-(\Delta E_{\mathrm{D}} - E_{\mathrm{ref}})/kT]$ plays an important roll in the analysis, where E_{ref} is a given parameter and N_{D} and ΔE_{D} are unknown parameters. Since this function has a maximum value of $N_{\mathrm{D}}\exp(-1)/(\Delta E_{\mathrm{D}} - E_{\mathrm{ref}})$ at $T = (\Delta E_{\mathrm{D}} - E_{\mathrm{ref}})/k$, the values of ΔE_{D} and N_{D} can be evaluated using the peak of the function. In this paper, the author proposes a simple graphical method whose energy resolution is about 0.006 eV and by which the densities and energy levels of donors and acceptors can be accurately evaluated in a compensated semiconductor.

2. Theoretical Consideration

To simplify the following arguments, the temperature dependence of the free electron concentration $n(T)$ in an n-type semiconductor is considered. Instead of $n(T)/kT$,[10] a new function is defined as

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

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where E_{ref} is the newly introduced parameter. The value of $n(T)$ is theoretically given by[7]

$$n(T) = \sum_i N_{\mathrm{D}i}\,[1 - f(E_{\mathrm{D}i})] - \sum_j N_{\mathrm{A}j} f(E_{\mathrm{A}j}) + p(T), \tag{2}$$

where $f(E)$ is the Fermi-Dirac distribution function, $N_{\mathrm{D}i}$ and $E_{\mathrm{D}i}$ are the density and energy level of the i–th donor, respectively, $N_{\mathrm{A}j}$ and $E_{\mathrm{A}j}$ are the density and energy level of the j–th acceptor, respectively, and $p(T)$ is the free hole concentration. Since an n-type semiconductor is considered in this study, all $f(E_{\mathrm{A}j})$ are nearly equal to 1 and $p(T)$ is nearly equal to zero. Therefore,

$$n(T) \simeq \sum_i N_{\mathrm{D}i} \cdot F_i(T) \exp\left(-\frac{\Delta E_{\mathrm{D}i}}{kT}\right) - N_{\mathrm{A}} \tag{3}$$

with

$$F_i(T) = \frac{\exp\left(\dfrac{\Delta E_{\mathrm{F}}}{kT}\right)}{g_{\mathrm{D}i} + \exp\left(\dfrac{\Delta E_{\mathrm{F}} - \Delta E_{\mathrm{D}i}}{kT}\right)}, \tag{4}$$

$$N_{\mathrm{A}} = \sum_j N_{\mathrm{A}j}, \tag{5}$$

and

$$\Delta E_{\mathrm{D}i} = E_{\mathrm{C}} - E_{\mathrm{D}i}, \tag{6}$$

where ΔE_{F} and $\Delta E_{\mathrm{D}i}$ are the Fermi level and the i–th donor level measured from the conduction band edge, respectively, $g_{\mathrm{D}i}$ is the degeneracy factor of the i–th donor, and $\Delta E_{\mathrm{D}i+1} > \Delta E_{\mathrm{D}i}$. Thus, the function $S(T, E_{\mathrm{ref}})$ is expressed as

$$S(T, E_{\mathrm{ref}}) = \sum_i N_{\mathrm{D}i} D_i(T, E_{\mathrm{ref}}) - \frac{N_{\mathrm{A}}}{kT} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right) \tag{7}$$

with

$$D_i(T, E_{\mathrm{ref}}) = F_i(T) \cdot \frac{1}{kT} \cdot \exp\left(-\frac{\Delta E_{\mathrm{D}i} - E_{\mathrm{ref}}}{kT}\right). \tag{8}$$

Since $\exp[-(\Delta E_{\mathrm{D}i} - E_{\mathrm{ref}})/kT]/kT$ in eq. (8) has a maximum at $T = (\Delta E_{\mathrm{D}i} - E_{\mathrm{ref}})/k$, the peak temperature of $D_i(T, E_{\mathrm{ref}})$ is reduced by using a positive E_{ref}, although the peak temperature of $D_i(T, E_{\mathrm{ref}})$ is not exactly equal to $(\Delta E_{\mathrm{D}i} - E_{\mathrm{ref}})/k$ due to the factor $F_i(T)$. By changing E_{ref}, therefore, we can change each peak temperature in the $S(T, E_{\mathrm{ref}})$ curve.

2.1 *Evaluating the density and energy level of the shallowest donor and the density of all acceptors*

At low temperature, the contribution of donors with high $\Delta E_{\mathrm{D}i}$ to $n(T)$ is very small. Therefore, after reducing the lowest peak temperature (T_{peak1}) by using a positive E_{ref}, the values of N_{D1}, ΔE_{D1} and N_{A} can be determined accurately from this peak.

We define T_R as the lower temperature at which the ratio $S(T, E_{\mathrm{ref}})/S(T_{\mathrm{peak1}}, E_{\mathrm{ref}})$ has a value of R (i.e., $0 < R < 1$). In order to determine ΔE_{D1} and $N_{\mathrm{A}}/N_{\mathrm{D1}}$ using T_{peak1} and T_R, the function

$$Y_1(T, E_{\mathrm{ref}}) \equiv \frac{S(T, E_{\mathrm{ref}})}{N_{\mathrm{D1}}} \tag{9}$$

is defined. As is clear from eq. (9),

$$\frac{Y_1(T, E_{\mathrm{ref}})}{Y_1(T_{\mathrm{peak1}}, E_{\mathrm{ref}})} = \frac{S(T, E_{\mathrm{ref}})}{S(T_{\mathrm{peak1}}, E_{\mathrm{ref}})}. \tag{10}$$

When electrons emitted from the shallowest donor make a dominant contribution to $n(T)$ at T_{peak1} and T_R, the function $Y_1(T, E_{\mathrm{ref}})$ is approximately expressed as

$$Y_1(T, E_{\mathrm{ref}}) \simeq D_1(T, E_{\mathrm{ref}}) - \frac{N_{\mathrm{A}}}{N_{\mathrm{D1}}} \cdot \frac{1}{kT} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right). \tag{11}$$

We can determine ΔE_{D1} and $N_{\mathrm{A}}/N_{\mathrm{D1}}$ which maximize $Y_1(T, E_{\mathrm{ref}})$ at T_{peak1} and make $Y_1(T, E_{\mathrm{ref}})/Y_1(T_{\mathrm{peak1}}, E_{\mathrm{ref}})$ equal to R at T_R using eq. (11). As is clear from eq. (9), N_{D1} is given by

$$N_{\mathrm{D1}} = \frac{S(T_{\mathrm{peak1}}, E_{\mathrm{ref}})}{Y_1(T_{\mathrm{peak1}}, E_{\mathrm{ref}})}. \tag{12}$$

2.2 *Evaluating the densities and energy levels of deeper donors*

In order to evaluate the density and energy level of the n-th donor ($n \geq 2$), a function $S_n(T, E_{\mathrm{ref}})$ without the effects of all acceptors and donors shallower than the n-th donor level is defined as

$$S_n(T, E_{\mathrm{ref}}) \equiv S(T, E_{\mathrm{ref}}) - \sum_{i=1}^{n-1} N_{\mathrm{D}i} D_i(T, E_{\mathrm{ref}}) + \frac{N_{\mathrm{A}}}{kT} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right). \tag{13}$$

Since N_{A}, $N_{\mathrm{D}i}$ and $\Delta E_{\mathrm{D}i}$ ($i \leq n-1$) are already determined, $S_n(T, E_{\mathrm{ref}})$ can be calculated using eq. (13). In order to evaluate $\Delta E_{\mathrm{D}n}$, the following function is defined

$$Y_n(T, E_{\mathrm{ref}}) \equiv \frac{S_n(T, E_{\mathrm{ref}})}{N_{\mathrm{D}n}}. \tag{14}$$

This function is approximately expressed as

$$Y_n(T, E_{\mathrm{ref}}) \simeq D_n(T, E_{\mathrm{ref}}), \tag{15}$$

when the contribution of the $(n+1)$-th donor to $n(T)$ is small at the peak temperature ($T_{\mathrm{peak}n}$) in the $S_n(T, E_{\mathrm{ref}})$ curve. We can determine $\Delta E_{\mathrm{D}n}$ which maximizes $Y_n(T, E_{\mathrm{ref}})$ at $T_{\mathrm{peak}n}$ using eq. (15). Then, $N_{\mathrm{D}n}$ is given by

$$N_{\mathrm{D}n} = \frac{S_n(T_{\mathrm{peak}n}, E_{\mathrm{ref}})}{Y_n(T_{\mathrm{peak}n}, E_{\mathrm{ref}})}, \tag{16}$$

as is clear from eq. (14).

When $S_{n+1}(T, E_{\mathrm{ref}})$ is very small, we can conclude that n kinds of donors exist in the semiconductor. Therefore, we have determined the densities and energy levels of all donors and the total acceptor density in the semiconductor.

3. Discussion

3.1 *A semiconductor with two donors*

As a simple case, Si with two kinds of donors ($\Delta E_{\mathrm{D1}} = 0.0390\,\mathrm{eV}$, $N_{\mathrm{D1}} = 1.00 \times 10^{16}\,\mathrm{cm}^{-3}$, $\Delta E_{\mathrm{D2}} = 0.110\,\mathrm{eV}$ and $N_{\mathrm{D2}} = 1.00 \times 10^{16}\,\mathrm{cm}^{-3}$) is considered. The value $\Delta E_{\mathrm{D1}} = 0.039\,\mathrm{eV}$ corresponds to the donor level of Sb in

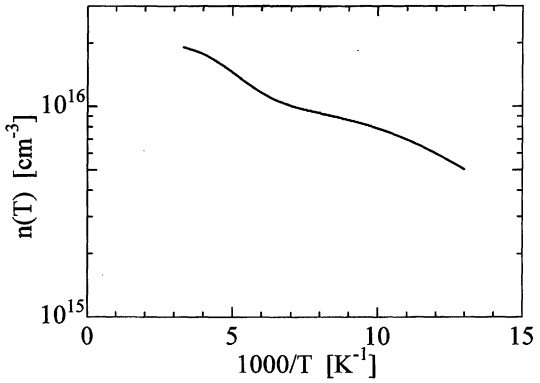

Fig. 1. Temperature dependence of majority carrier concentration calculated for Si with two kinds of donors ($\Delta E_{D1} = 0.0390\,\text{eV}$, $N_{D1} = 1.00 \times 10^{16}\,\text{cm}^{-3}$, $\Delta E_{D2} = 0.110\,\text{eV}$ and $N_{D2} = 1.00 \times 10^{16}\,\text{cm}^{-3}$).

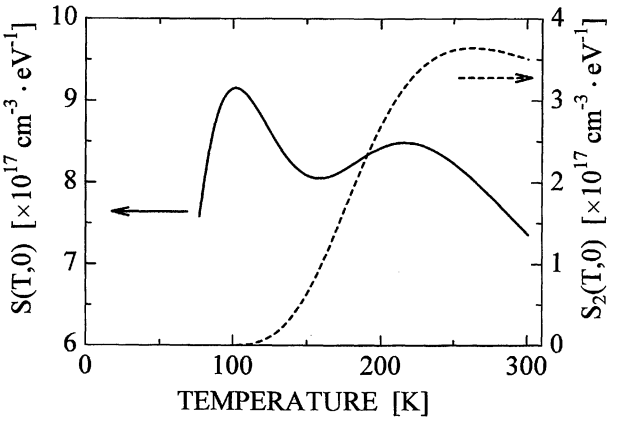

Fig. 2. $S(T,\,0)$ and $S_2(T,\,0)$ calculated using $n(T)$ in Fig. 1.

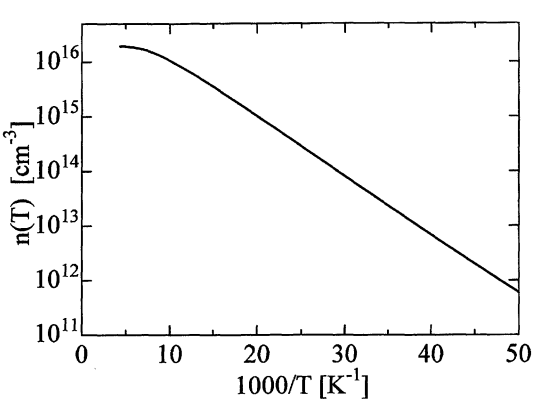

Fig. 3. Temperature dependence of majority carrier concentration calculated for Si with two kinds of donors (ΔE_{D1}=0.0390 eV, N_{D1}=1.00 $\times$ 10^{16} cm^{-3}, ΔE_{D2} = 0.0540 eV and N_{D2}=1.00 $\times$ 10^{16} cm^{-3}). The energy difference of the two donors is 0.0150 eV.

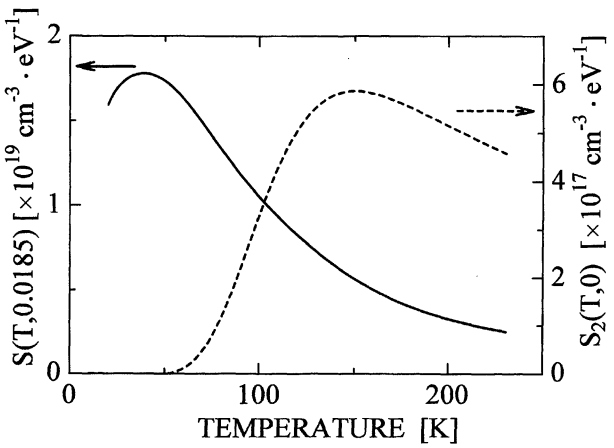

Fig. 4. $S(T, 0.0185)$ and $S_2(T, 0)$ calculated using $n(T)$ in Fig. 3.

Si.[7] The $n(T)$ curve in the range 77.0 K $\leq T \leq$ 300 K is shown in Fig. 1. In this calculation of $n(T)$, the value of g_{Di} used was 2.

The solid curve in Fig. 2 represents $S(T, 0)$ calculated using eq. (1) and $n(T)$ shown in Fig. 1. Because there are two discrete peaks in this figure, it is clear that at least two kinds of donor levels exist in the semiconductor. In this figure, T_{peak1} and $S(T_{peak1}, 0)$ are 101 K and $9.15 \times 10^{17}\,\text{cm}^{-3}\cdot\text{eV}^{-1}$, respectively, and $T_{0.85}$ is 78.5 K. The values of ΔE_{D1} and N_A/N_{D1}, which maximize $Y_1(T, 0)$ at T_{peak1} = 101 K and make $Y_1(T, 0)$ 85% of the maximum value at $T_{0.85}$ = 78.5 K, are 0.0392 eV and 0, respectively. Therefore, N_A is zero. In this calculation, the relationship

$$\Delta E_F = kT \ln \left[\frac{N_C(T)}{n(T)} \right] \tag{17}$$

is used, where $n(T)$ is that shown in Fig. 1 and $N_C(T)$ is the effective density of states in the conduction band for Si, which is given by[7]

$$N_C(T) = 5.39 \times 10^{15} T^{1.5} \quad [\text{cm}^{-3}]. \tag{18}$$

The value of $Y_1(101, 0)$ is calculated to be 90.6 eV^{-1} using eq. (11) and the obtained values (ΔE_{D1} = 0.0392 eV and $N_A/N_{D1} = 0$). Since $S(101, 0) = 9.15 \times 10^{17}\,\text{cm}^{-3}\cdot\text{eV}^{-1}$ in the solid curve of Fig. 2, N_{D1} is estimated to be $1.01 \times 10^{16}\,\text{cm}^{-3}$ using eq. (12).

The broken curve in Fig. 2 is the $S_2(T, 0)$ curve calculated using the obtained values (ΔE_{D1}, N_{D1} and N_A) and eq. (13). The values of T_{peak2} and $S_2(T_{peak2}, 0)$ in the $S_2(T, 0)$ curve are 263 K and $3.64 \times 10^{17}\,\text{cm}^{-3}\cdot\text{eV}^{-1}$, respectively. The value of ΔE_{D2}, which maximizes $Y_2(T, 0)$ at T_{peak2} = 263 K, is 0.110 eV. Using eq. (15) and ΔE_{D2} = 0.110 eV, $Y_2(263, 0)$ is calculated to be 36.6 eV^{-1}. Since $S_2(263, 0) = 3.64 \times 10^{17}\,\text{cm}^{-3}\cdot\text{eV}^{-1}$ in the broken curve of Fig. 2, N_{D2} is evaluated to be $9.95 \times 10^{15}\,\text{cm}^{-3}$. The obtained values ($\Delta E_{D1}$, N_{D1}, N_A, ΔE_{D2} and N_{D2}) are close to the actual values. Since $S_3(T, E_{ref})$ is very small over the whole temperature range, it is found that this semiconductor has two kinds of donors

3.2 A semiconductor with two donors whose energy levels are close

Si with two kinds of donors (ΔE_{D1} = 0.0390 eV, $N_{D1} = 1.00 \times 10^{16}\,\text{cm}^{-3}$, ΔE_{D2} = 0.0540 eV and $N_{D2} = 1.00 \times 10^{16}\,\text{cm}^{-3}$) is considered. The donor level of 0.054 eV corresponds to that of As in Si.[7] The $n(T)$ curve in the range 20.0 K $\leq T \leq$ 230 K is shown in Fig. 3.

The solid curve in Fig. 4 represents $S(T, 0.0185)$ calculated using $n(T)$ in Fig. 3. In order to determine the den-

sity and energy level of the shallowest donor accurately, T_{peak1} is reduced by using $E_{ref} = 0.0185\,eV$. In this figure, T_{peak1} and $S(T_{peak1}, 0.0185)$ are 38.8 K and $1.78 \times 10^{19}\,cm^{-3}\cdot eV^{-1}$, respectively, and $T_{0.9}$ is 20.3 K. The values of ΔE_{D1} and N_A/N_{D1}, which maximize $Y_1(T, 0.0185)$ at $T_{peak1} = 38.8\,K$ and make $Y_1(T, 0.0185)$ 90% of the maximum value at $T_{0.9} = 20.3\,K$, are 0.0392 eV and 0, respectively. Therefore, N_A is zero. The value of $Y_1(38.8, 0.0185)$ is calculated to be $1.68 \times 10^3\,eV^{-1}$ using eq. (11) and the obtained values (ΔE_{D1} and N_A/N_{D1}). Since $S(38.8, 0.0185) = 1.78 \times 10^{19}\,cm^{-3}\cdot eV^{-1}$ in the solid curve of Fig. 4, N_{D1} is estimated to be $1.06 \times 10^{16}\,cm^{-3}$ using eq. (12).

The broken line of Fig. 4 shows $S_2(T, 0)$ calculated using eq. (13) and the obtained values (ΔE_{D1}, N_{D1} and N_A). The values of T_{peak2} and $S_2(T_{peak2}, 0)$ are 150 K and $5.86 \times 10^{17}\,cm^{-3}\cdot eV^{-1}$, respectively. The value of ΔE_{D2}, which maximizes $Y_2(T, 0)$ at $T_{peak2} = 150\,K$, is 0.0547 eV. Using eq. (15) and $\Delta E_{D2} = 0.0547$ eV, $Y_2(150, 0)$ is calculated to be $62.3\,eV^{-1}$. Since $S_2(150, 0) = 5.86 \times 10^{17}\,cm^{-3}\cdot eV^{-1}$ in the broken curve of Fig. 4, N_{D2} is evaluated to be $9.41 \times 10^{15}\,cm^{-3}$ using eq. (16). The obtained values are close to the actual values. Since $S_3(T, E_{ref})$ is very small over the whole temperature range, it is found that this semiconductor has two kinds of donors

3.3 A semiconductor with donors and acceptors

6H-SiC with two kinds of donors ($\Delta E_{D1} = 0.110\,eV$, $N_{D1} = 1.00 \times 10^{16}\,cm^{-3}$, $\Delta E_{D2} = 0.150\,eV$ and $N_{D2} = 1.00 \times 10^{16}\,cm^{-3}$) and two kinds of acceptors ($\Delta E_{A1} = 0.200\,eV$ and $\Delta E_{A2} = 0.300\,eV$) is considered. The donor levels of 0.11 eV and 0.15 eV correspond to those of N inserted into the hexagonal site and cubic site of 6H-SiC, respectively,[1] and the acceptor levels of 0.2 eV and 0.3 eV correspond to those of Al and B in 6H-SiC, respectively.[2] In Fig. 5, the solid and broken curves represent $n(T)$ for $N_{A1} = N_{A2} = 1.00 \times 10^{15}\,cm^{-3}$ and $N_{A1} = N_{A2} = 1.00 \times 10^{13}\,cm^{-3}$, respectively, in the range $77.0\,K \le T \le 300\,K$. Using eq. (5), in other words, the solid and broken curves represent $n(T)$ for

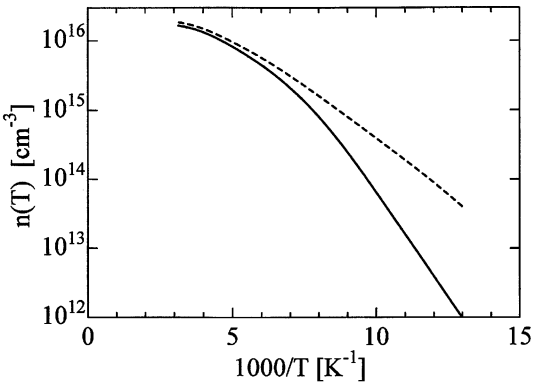

Fig. 5. Temperature dependence of majority carrier concentration calculated for 6H-SiC with two kinds of donors ($\Delta E_{D1} = 0.110\,eV$, $N_{D1} = 1.00 \times 10^{16}\,cm^{-3}$, $\Delta E_{D2} = 0.150\,eV$ and $N_{D2} = 1.00 \times 10^{16}\,cm^{-3}$) and two kinds of acceptors ($\Delta E_{A1} = 0.200\,eV$ and $\Delta E_{A2} = 0.300\,eV$). The solid curve represents the curve for $N_{A1} = N_{A2} = 1.00 \times 10^{15}\,cm^{-3}$, and the broken curve represents the curve for $N_{A1} = N_{A2} = 1.00 \times 10^{13}\,cm^{-3}$.

$N_A = 2.00 \times 10^{15}\,cm^{-3}$ and $N_A = 2.00 \times 10^{13}\,cm^{-3}$, respectively.

The solid and broken curves in Fig. 6 represent $S(T, E_{ref})$ calculated using eq. (1) and $n(T)$ expressed as the solid and broken curves in Fig. 5, respectively. From this figure, T_{peak1} and $T_{0.6}$ in the solid curve are 112 K and 77.8 K, respectively, and T_{peak1} and $T_{0.6}$ in the broken curve are 132 K and 77.4 K, respectively.

Although the values of $T_{0.6}$ in the solid and broken curves of Fig. 6 are very close, T_{peak1} in the solid curve is lower than T_{peak1} in the broken curve, indicating that N_A affects $S(T, E_{ref})$ sensitively. From the dependence of T_{peak1} and T_R on N_A in the $Y_1(T, E_{ref})$ curve which is calculated using eq. (11), ΔE_{D1} and N_A/N_{D1} can be determined using T_{peak1} and T_R.

Using the solid curve ($T_{peak1} = 112\,K$ and $T_{0.6} = 77.8\,K$) of Fig. 6, ΔE_{D1} and N_A/N_{D1} are determined to be 0.110 eV and 0.194, respectively. In this calculation, the relationship

$$N_C(T) = 1.16 \times 10^{16} T^{1.5} \quad [cm^{-3}] \tag{19}$$

is used for 6H-SiC. Since $S(112, 0.1) = 8.70 \times 10^{20}\,cm^{-3}\cdot eV^{-1}$ in the solid curve of Fig. 6, N_{D1} is estimated to be $1.10 \times 10^{16}\,cm^{-3}$ using eq. (12). Therefore, N_A is $2.13 \times 10^{15}\,cm^{-3}$.

Using the broken curve ($T_{peak1} = 132$ K and $T_{0.6} = 77.4\,K$) of Fig. 6, ΔE_{D1} and N_A/N_{D1} are evaluated to be 0.111 eV and 1.47×10^{-3}, respectively. Since $S(132, 0.046) = 1.08 \times 10^{19}\,cm^{-3}\cdot eV^{-1}$ in the broken curve of Fig. 6, N_{D1} is estimated to be $1.12 \times 10^{16}\,cm^{-3}$ using eq. (12). Then, N_A is $1.65 \times 10^{13}\,cm^{-3}$, indicating that N_A is smaller than the actual value. This is because $n(T_R)$ increases with the density of the second donor while $n(T_R)$ decreases with the densities of acceptors. Therefore, the effect of the second donor on $n(T_R)$ results in the underestimation of N_A. In order to determine the small ratio N_A/N_{D1} accurately, $n(T)$ should be measured at temperatures as low as possible, because the effect of the second donor on $n(T_R)$ decreases with decreasing temperature.

The solid and broken curves in Fig. 7 represent $S_2(T, E_{ref})$ calculated using eq. (13), the obtained values (ΔE_{D1}, N_{D1} and N_A) and $n(T)$ expressed as the solid and broken curves in Fig. 5, respectively. Using

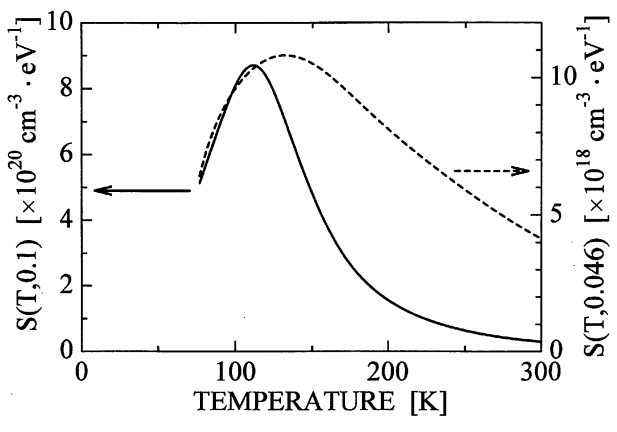

Fig. 6. $S(T, 0.1)$ (solid curve) for N_{A1}=N_{A2}=$1.00 \times 10^{15}\,cm^{-3}$ and $S(T, 0.046)$ (broken curve) for N_{A1}=N_{A2}=$1.00 \times 10^{13}\,cm^{-3}$.

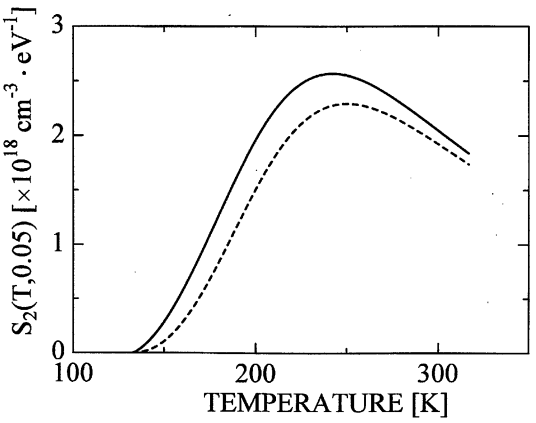

Fig. 7. $S_2(T, 0.05)$ (solid curve) for $N_{A1}=N_{A2}=1.00\times10^{15}$ cm^{-3} and $S_2(T, 0.05)$ (broken curve) for $N_{A1}=N_{A2}=1.00\times10^{13}$ cm^{-3}.

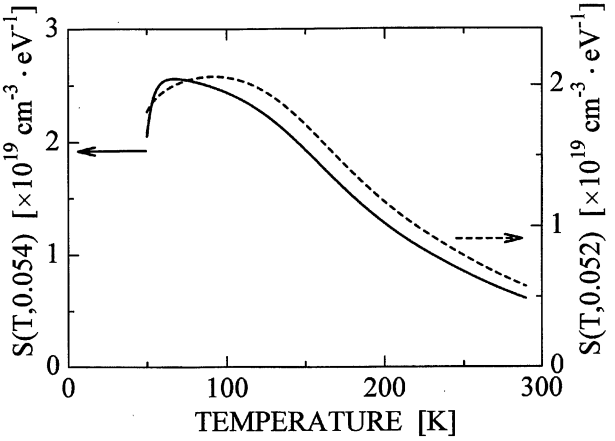

Fig. 8. $S(T, 0.054)$ (solid curve) for $N_{A1}=N_{A2}=1.00\times10^{11}$ cm^{-3} and $S(T, 0.052)$ (broken curve) for $N_{A1}=N_{A2}=1.00\times10^{10}$ cm^{-3}.

the solid curve of Fig. 7, the value of ΔE_{D2}, which maximizes $Y_2(T, 0.05)$ at $T_{peak2} = 242$ K, is 0.154 eV. Since $S_2(T, 0.05) = 2.57 \times 10^{18}$ cm$^{-3}\cdot$eV^{-1} in the solid curve of Fig. 7, N_{D2} is evaluated to be 9.32×10^{15} cm^{-3} using eq. (16). The obtained values are close to the actual values. Since $S_3(T, E_{ref})$ is very small over the whole temperature range, it is found that this semiconductor has two kinds of donors.

Using the broken curve of Fig. 7, the value of ΔE_{D2}, which maximizes $Y_2(T, 0.05)$ at $T_{peak2} = 250$ K, is 0.155 eV. Since $S_2(T, 0.05) = 2.29 \times 10^{18}$ cm$^{-3}\cdot$eV^{-1} in the broken curve of Fig. 7, N_{D2} is evaluated to be 8.99×10^{15} cm$^{-3}\cdot$eV^{-1} using eq. (16). The values of ΔE_{D2} and N_{D2} are close to the actual values, although N_A is underestimated as mentioned above. Since $S_3(T, E_{ref})$ is very small over the whole temperature range, it is found that this semiconductor has two kinds of donors.

In order to investigate the limitation for N_A/N_{D1}, we consider 6H–SiC with two sets of acceptors; ($N_{A1} = N_{A2} = 1.00 \times 10^{11}$ cm^{-3}) and ($N_{A1} = N_{A2} = 1.00 \times 10^{10}$ cm^{-3}). The values (ΔE_{D1}, N_{D1}, ΔE_{D2}, N_{D2}, ΔE_{A1} and ΔE_{A2}) are the same as those mentioned above. The temperature range is between 50.0 K and 290 K. Figure 8 shows $S(T, 0.054)$ for $N_A = 2.00 \times 10^{11}$ cm^{-3} (the solid curve) and $S(T, 0.052)$ for $N_A = 2.00 \times 10^{10}$ cm^{-3} (the broken curve).

Using the solid curve ($T_{peak1} = 67.6$ K and $T_{0.8} = 50.0$ K), ΔE_{D1} and N_A/N_{D1} are evaluated to be 0.110 eV and 1.96×10^{-5}, respectively, using eq. (11). Since $S(67.6, 0.054) = 2.55\times10^{19}$ cm$^{-3}\cdot$eV^{-1} in the solid curve of Fig. 8, N_{D1} is estimated to be 1.01×10^{16} cm^{-3} using eq. (12). Therefore, N_A is 1.98×10^{11} cm^{-3}. A value of N_A close to the actual value is obtained, although the ratio N_A/N_{D1} is very small (i.e., 2×10^{-5}).

Using the broken curve ($T_{peak1} = 91.8$ K and $T_{0.9} = 52.4$ K), ΔE_{D1} and N_A/N_{D1} are evaluated to be 0.110 eV and 8.88×10^{-7}, respectively, using eq. (11). Since $S(91.8, 0.052) = 2.06 \times 10^{19}$ cm$^{-3}\cdot$eV^{-1} in the broken curve of Fig. 8, N_{D1} is estimated to be 1.03×10^{16} cm^{-3} using eq. (12). Therefore, N_A is 9.15×10^{9} cm^{-3}, and N_A is smaller than the actual value, suggesting that $n(T)$ should be measured at temperatures as low as possible in order to evaluate a small ratio N_A/N_{D1}.

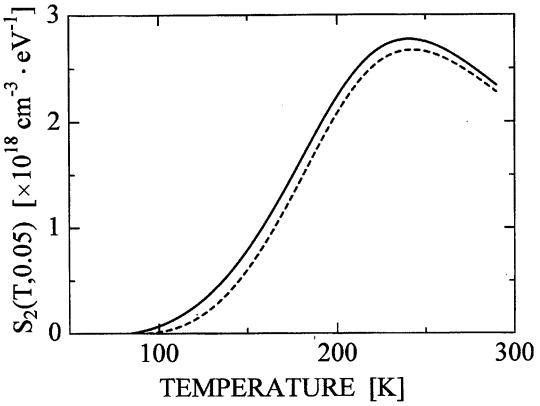

Fig. 9. $S_2(T, 0.05)$ (solid curve) for $N_{A1}=N_{A2}=1.00\times10^{11}$ cm^{-3} and $S_2(T, 0.05)$ (broken curve) for $N_{A1}=N_{A2}=1.00\times10^{10}$ cm^{-3}.

The solid and broken curves in Fig. 9 represent $S_2(T, E_{ref})$ calculated using eq. (13), the obtained values (ΔE_{D1}, N_{D1} and N_A) and $n(T)$ for $N_A = 2.00 \times 10^{11}$ cm^{-3} and $N_A = 2.00 \times 10^{10}$ cm^{-3}, respectively. Using the solid curve [$T_{peak2} = 241$ K and $S_2(T_{peak2}, 0.05) = 2.77 \times 10^{18}$ cm$^{-3}\cdot$eV^{-1}], ΔE_{D2} and N_{D2} are evaluated to be 0.151 eV and 9.93×10^{15} cm^{-3}, respectively, using eqs. (15) and (16). Using the broken curve [$T_{peak2} = 243$ K and $S_2(T_{peak2}, 0.05) = 2.67 \times 10^{18}$ cm$^{-3}\cdot$eV^{-1}], ΔE_{D2} and N_{D2} are evaluated to be 0.151 eV and 9.76×10^{15} cm^{-3}, respectively, using eqs. (15) and (16). Using the broken curve, although N_A is underestimated as mentioned above, the values of ΔE_{D2} and N_{D2} are close to the actual values. In both cases, it is found that this semiconductor has two kinds of donors, since $S_3(T, E_{ref})$ is very small over the whole temperature range.

As discussed above, the densities and energy levels of donors can be determined accurately, while N_A is apt to be underestimated. In order to determine N_A accurately, $n(T)$ should be measured at temperatures as low as possible.

3.4 Limitations of this method

Let us discuss the limitations of this method. For Si with $\Delta E_{D1} = 0.039$ eV and $\Delta E_{D2} = 0.054$ eV, the den-

sities and energy levels of the two donors can be determined in the range $4 \times 10^{-2} \leq N_{D1}/N_{D2} \leq 20$. Since the purpose of this study is to graphically determine the densities and energy levels of impurities which are mainly related to the majority carrier concentration in a semiconductor, this range N_{D1}/N_{D2} is considered to be appropriate. Under the conditions that $\Delta E_{D1} = 0.039$ eV and $N_{D1} = N_{D2}$, the densities and energy levels of the two donors can be determined when ΔE_{D2} is larger than around 0.045 eV, that is, the energy resolution of this method is about 0.006 eV.

In the case of n-type semiconductors with donors and acceptors, this method is in principle available for $N_A/N_{D1} < 1$. The densities and energy levels of donors can be evaluated accurately, while N_A is apt to be underestimated. In order to avoid this underestimation of N_A, $n(T)$ should be measured at temperatures as low as possible. In §3.3, N_A can be determined for $N_A/N_{D1} \geq 2 \times 10^{-5}$ accurately. This range N_A/N_{D1} is considered to be appropriate.

3.5 Comparison with other methods

In the $n(T) - 1/T$ characteristics, the donor density is equal to $n(T)$ in the saturation region.[7] 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[7]

$$\exp\left(-\frac{\Delta E_{Di}}{2kT}\right). \tag{20}$$

Since there are no saturation regions in Fig. 1, no donor densities can be determined. The value of ΔE_{D1} is 0.0284 eV from the slope in the range $11\,K^{-1} \leq 1000/T \leq 13\,K^{-1}$, and ΔE_{D2} is 0.0386 eV from the slope in the range $4.8\,K^{-1} \leq 1000/T \leq 6.2\,K^{-1}$. As is clear from Fig. 3, it is considered that only one kind of donor exists, and ΔE_{D1} determined in the range $15\ K^{-1} \leq 1000/T \leq 50\,K^{-1}$ and N_{D1} determined at $1000/T = 4.35\,K^{-1}$ are 0.0431 eV and $1.95 \times 10^{16}\,cm^{-3}$, respectively. In Fig. 5, ΔE_{D1} and N_{D1} are determined in the range $8\ K^{-1} \leq 1000/T \leq 13\,K^{-1}$ and at $1000/T = 3.33\,K^{-1}$, respectively. Using the solid curve, ΔE_{D1} and N_{D1} are evaluated to be 0.234 eV and $1.66 \times 10^{16}\,cm^{-3}$, respectively, and using the broken curve ΔE_{D1} and N_{D1} are determined to be 0.126 eV and $1.86 \times 10^{16}\,cm^{-3}$, respectively. Since the obtained values are poor approximations of the actual values, this analysis is unsuitable for the evaluation of several kinds of impurities with different energy levels in a semiconductor.

When we determine ΔE_{Di}, N_{Di} and N_A by fitting a curve to experimental data for $n(T)-1/T$ characteristics, it is necessary to determine how many kinds of donors exist in the semiconductor before the curve-fitting procedure is carried out. Therefore, it is difficult to apply this method when we do not know how many kinds of donors exist in the semiconductor. Moreover, because so many curve-fitting parameters are required to fit a curve to experimental data, it is difficult to evaluate the densities and energy levels accurately.

Hoffmann proposed a differential evaluation of $n(T)$.[6] For small temperature differences $T_{j+1} - T_j$, the derivative $(-kT) \cdot dn/dE_F$ as a function of ΔE_F can be approximated by[6,10]

$$\frac{T_{j+1}+T_j}{2} \cdot \frac{n(T_{j+1}) - n(T_j)}{T_{j+1} \ln\left[\frac{N_C(T_{j+1})}{n(T_{j+1})}\right] - T_j \ln\left[\frac{N_C(T_j)}{n(T_j)}\right]} \tag{21}$$

as a function of

$$\frac{k}{2}\left\{T_{j+1} \ln\left[\frac{N_C(T_{j+1})}{n(T_{j+1})}\right] + T_j \ln\left[\frac{N_C(T_j)}{n(T_j)}\right]\right\}. \tag{22}$$

The $(-kT)\cdot dn/dE_F$ curve has maxima at $\Delta E_F = \Delta E_{Di} + kT_{mi} \ln g_{Di}$, where T_{mi} is the temperature corresponding to the i-th maximum. The ordinate of the i-th maximum equals $N_{Di}/4$.

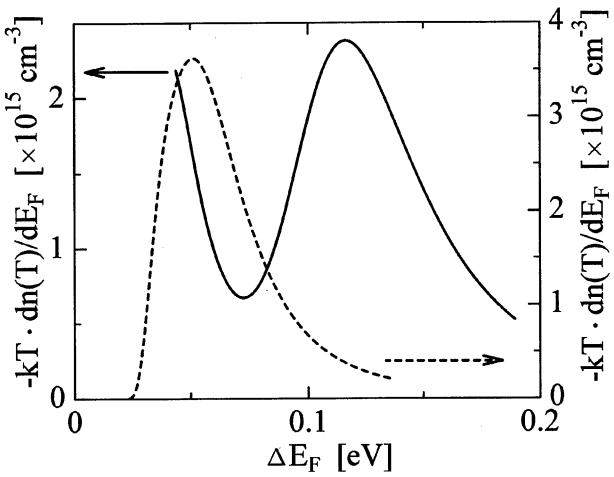

Fig. 10. The dependence of $(-kT) \cdot dn(T)/dE_F$ on ΔE_F. The solid and broken curves are calculated using $n(T)$ in Figs. 1 and 3, respectively.

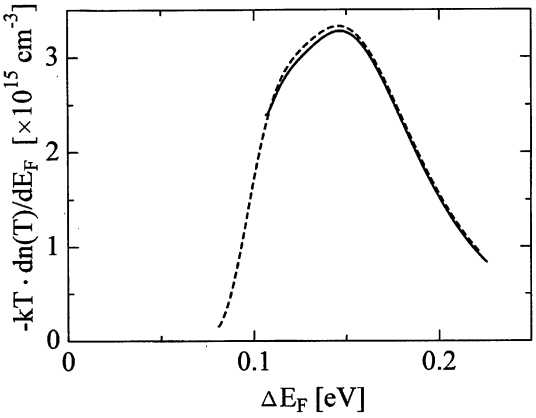

Fig. 11. The dependence of $(-kT) \cdot dn(T)/dE_F$ on ΔE_F. The solid and broken curves are calculated using $n(T)$ expressed as the solid and broken curves in Fig. 5, respectively.

Figure 10 shows the relationship between $(-kT) \cdot dn(T)/dE_F$ and ΔE_F, and the solid and broken curves represent the data calculated using $n(T)$ in Figs. 1 and 3, respectively. Using the solid curve, ΔE_{D2} and N_{D2} are evaluated to be 0.105 eV and $9.52 \times 10^{15}\,cm^{-3}$, respectively, while ΔE_{D1} and N_{D1} cannot be evaluated because the measurement temperatures are not low enough to evaluate these values. In our method, however, ΔE_{D1} and N_{D1} can be evaluated at these measurement temperatures.

From the broken curve, it is considered that there is only one kind of donor, and ΔE_{D1} and N_{D1} are evaluated to be 0.0454 eV and $1.45 \times 10^{16}\,\mathrm{cm}^{-3}$, respectively. In our method, the densities and energy levels of the two kinds of donors can be evaluated accurately.

Figure 11 shows the relationship between $(-kT) \cdot \mathrm{d}n(T)/\mathrm{d}E_F$ and ΔE_F, and the solid and broken curves represent the data calculated using $n(T)$ expressed as the solid and broken curves in Fig. 5, respectively. As is clear from this figure, it is considered that only one kind of donor exists, although there are actually two kinds of donors and two kinds of acceptors in the semiconductor. The values of ΔE_{D1} and N_{D1} are evaluated to be 0.133 eV and $1.33 \times 10^{16}\,\mathrm{cm}^{-3}$, respectively, using the broken curve, and 0.134 eV and $1.31 \times 10^{16}\,\mathrm{cm}^{-3}$, respectively, using the solid curve. Since the values obtained using the Hoffmann's method are poor approximations of the actual values and since it is impossible in principle to determine N_A using Hoffmann's method, the method proposed here is more suitable than Hoffmann's method.

4. Conclusion

We propose a simple graphical method for accurately determining the densities and energy levels of impurities in a semiconductor from the temperature dependence of the majority carrier concentration. The function $S(T, E_{ref})$, which is defined as $n(T)\exp(E_{ref}/kT)/kT$, has peaks corresponding to impurity levels. From each peak, the density and energy level of the corresponding impurity can be evaluated accurately. Using this method, the densities and energy levels of impurities which produce majority carriers can be evaluated, and the density of all impurities which produce minority carriers can be estimated. The energy resolution of this method is about 0.006 eV. This method can be used under the condition that the ratio of the density of all impurities for minority carriers to the density of the shallowest impurity for majority carriers is smaller than 1. This method is suitable for accurately evaluating the densities and energy levels of impurities in a semiconductor with several kinds of donors and acceptors, and it can be used to investigate how many kinds of impurities, which produce majority carriers, exist in a semiconductor.

Acknowledgement

The author wishes to extend his gratitude to Mr. K. Sonoi for fruitful discussions.

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