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A Method for Evaluating the Densities and Energy Levels of Impurities in Semiconductors from the Temperature Dependence of Majority-Carrier Concentration

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SUMMARY

The characteristics of impurities in semiconductors strongly influence the electronic properties of the semiconductor. Therefore, impurity densities and energy levels must be precisely evaluated. This paper describes a way to graphically evaluate the characteristics of impurities in a semiconductor with donors and acceptors by using the temperature dependence of the majority carrier concentration $n(T)$. The function to be evaluated is defined by $n(T)n(T)\exp(E_{\mathrm{ref}}/kT)/kT/N_C(T)$, where k is the Boltzmann constant, T is the temperature, $N_C(T)$ is the effective density of states, and E_{ref} is a parameter. Since this function has a peak at a temperature corresponding to each impurity level, the impurity density and energy level can be obtained by using the peak value and temperature. © 1998 Scripta Technica. Electron Comm Jpn Pt 2, 80(10): 37–42, 1997

Key words: Impurity evaluation; graphic approach; donor density; donor level; acceptor density; acceptor level; temperature dependence of majority carrier concentration.

1. Introduction

Semiconductors often contain a variety of impurities and these impurities greatly influence semiconductor characteristics. For example, in 6H-SiC and 4H-SiC, nitrogen has two energy levels and behaves as a donor [1], while Al and B play the role of acceptor [1, 2]. Frequently, both donors and acceptors are contained in the semiconductor [3, 4]. In order to emit infrared light, rare-earth elements are added to the semiconductor [5], besides conventional dopants.

This paper proposes a method to graphically evaluate the densities and energy levels of multiple impurities (donors and acceptors) that influence the majority carrier concentration. In general, the impurity density and energy level are obtained as follows [6]. First, the temperature dependence of the majority carrier concentration $n(T)$ is graphically expressed by using the relationship between ln $n(T)$ and $1/T$. This slope provides the impurity level and the saturated value provides the impurity density. However, when more than two kinds of impurities are involved, the above method is not effective [7].

In order to evaluate the contributions from multiple impurities that generate majority carriers, Hoffmann proposed a method in which the temperature dependence of the majority carrier concentration is differentiated by Fermi levels [7]; the analytical results based on this method have been reported [5, 7, 8]. When multiple impurity levels are present, peaks corresponding to these energy levels appear in the graph. The peak value and the Fermi level for a peak provide the impurity density and energy level, respectively. However, in this method, the majority carrier concentrations at various temperatures must be differentiated by Fermi level. As a result, measurement error is amplified and the peaks are often unobserved. In this method, the limit of energy level separation is about 0.03 eV. In addition, impu-

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rities that generate minority carriers cannot be evaluated by this method.

The authors have been developing a method for evaluating the impurity density and energy level without differentiation [9]. However, this method can be used only when either donor or acceptor, but not both, was present. In addition, the resolution of the energy levels by this method was about 0.05 eV.

The purpose of this paper is to discuss a method that can be used to evaluate impurities that generate minority carriers (Hoffmann's method [7] and our previous method [9] could not evaluate these impurities), other than the impurities that generate the majority carriers, with an energy resolution of 0.005 eV.

In this paper, semiconductors with both donors and acceptors will be discussed. If T is a variable and DE_{Di}, N_{Di}, E_{ref}, and k are parameters, Eq. (1) provides the maximum value of $N_{Di}\exp(-1)/(DE_{Di} - E_{ref})$ when $T = (DE_{Di} - E_{ref})/k$:

$$\frac{N_{Di}}{kT}\exp\left(-\frac{\Delta E_{Di} - E_{ref}}{kT}\right) \tag{1}$$

Using the majority carrier concentration $n(T)$, a function similar to Eq. (1) is derived. The peak value and the temperature for the peak then provide the impurity density and energy level, respectively. In order to increase the energy level resolution, the peak temperature is shifted in the direction of lower temperatures using the parameter E_{ref}.

2. Evaluation Method

In order to simplify the discussion, n-type semiconductors will be discussed, since p-type semiconductors can be discussed in the same manner. In order to obtain a function similar to Eq. (1), a function $F(T, E_{ref})$ is defined by Eq. (2), using the temperature dependence of the free electron concentration measured by the Hall effect:

$$F(T, E_{ref}) \equiv \frac{1}{N_C(T)} \cdot \frac{1}{kT} n(T) n(T) \exp\left(\frac{E_{ref}}{kT}\right) \tag{2}$$

where $N_C(T)$ is the effective density of states and k is the Boltzmann constant.

Let us theoretically discuss whether the definition in Eq. (2) can provide an equation similar to Eq. (1). The electron concentration $n(T)$ obtained from the electrical neutrality condition is given by Eq. (3) [6]:

$$n(T) = \sum_i N_{Di} \cdot \frac{\exp\left(-\frac{E_F - E_{Di}}{kT}\right)}{g_{Di} + \exp\left(-\frac{E_F - E_{Di}}{kT}\right)} - N_A \tag{3}$$

where N_{Di} and E_{Di} are the i-th donor density and energy level, respectively; g_{Di} is the i-th degeneracy factor, N_A is the acceptor density, and E_F is the Fermi level.

The electron concentration $n(T)$ obtained from $N_C(T)$ and E_F is given by

$$n(T) = N_C(T)\exp\left(-\frac{E_C - E_F}{kT}\right) \tag{4}$$

where E_C is the energy at the bottom of the conduction band [6].

Substituting Eq. (3) for one of the $n(T)$ in Eq. (2) and substituting Eq. (4) for the other $n(T)$ in Eq. (2) gives

$$F(T, E_{ref}) = \sum_i F_i(T, E_{ref}) - \frac{N_A}{kT}\exp\left(-\frac{\Delta E_F - E_{ref}}{kT}\right) \tag{5}$$

where

$$F_i(T, E_{ref}) = \frac{1}{g_{Di} + \exp\left(-\frac{\Delta E_{Di} - \Delta E_F}{kT}\right)} \times \frac{N_{Di}}{kT}\exp\left(-\frac{\Delta E_{Di} - E_{ref}}{kT}\right) \tag{6}$$

$$\Delta E_{Di} = E_C - E_{Di}, \tag{7}$$

$$\Delta E_F = E_C - E_F, \tag{8}$$

$$\Delta E_{Di+1} > \Delta E_{Di} \tag{9}$$

Now, the function $F(T, E_{ref})$ contains an expression similar to Eq. (1). In addition, by squaring the majority carrier concentration in Eq. (2), the temperature dependence of the function in $F_i(T, E_{ref})$ other than Eq. (1) was reduced, compared with the temperature dependence of the function previously reported [9]. However, because of the temperature dependence of the function other than Eq. (1), the temperature at which each $F_i(T, E_{ref})$ shows a peak is slightly lower than $(DE_{Di} - E_{ref})/k$. As described, $F_i(T, E_{ref})$ for each donor has a peak a different temperature. Using this characteristic, the impurity density and energy level can be evaluated.

3. Discussion

In this study, n-type 4H-SiC (bandgap $E_g = 3.26$ eV) with a shallow donor ($DE_{D1} = 0.06$ eV, $N_{D1} = 7.5 \times 10^{15}$ cm^{-3}), deep donor ($DE_{D2} = 0.156$ eV, $N_{D2} = 9.4 \times 10^{15}$ cm^{-3}) and acceptor ($N_A = 1.6 \times 10^{14}$ cm^{-3}) will be evaluated. The value of $n(T)$ in this 4H-SiC is calculated using Eqs. (3) and (4), as shown in Fig. 1, where $g_{Di} = 2$ and $N_C(T)$ of 4H-SiC is given by Eq. (10) [4]:

$$N_C(T) = 2.71 \times 10^{15} T^{\frac{3}{2}} \tag{10}$$

Using $n(T)$ shown in Fig. 1, the effectiveness of this method will be discussed.

The term exp (DE_F/kT) is given by Eq. (11)

$$\exp\left(\frac{\Delta E_F}{kT}\right) = \frac{N_C(T)}{n(T)} \tag{11}$$

where $n(T)$ is given in Fig. 1 and $N_C(T)$ is given by Eq. (10).

3.1. Evaluation of shallow donor and acceptor

Figure 2 shows the temperature dependence of $F(T, E_{ref})$ for $E_{ref} = 0$ and 0.05 eV. When $E_{ref} = 0$ eV (dotted line), two peaks are observed, indicating that two types of donors are present. If $E_{ref} = 0.05$ eV, the first peak in the dotted line moves to the left (lower temperature). In the $F(T, 0.05)$ curve, the peak occurs at 84 K (T_{peak1}) and the peak value is 9.40×10^{16} cm^{-3} eV^{-1}. By shifting T_{peak1} to a lower temperature, the influences of the shallow donor and acceptor on $n(T_{peak1})$ are enhanced.

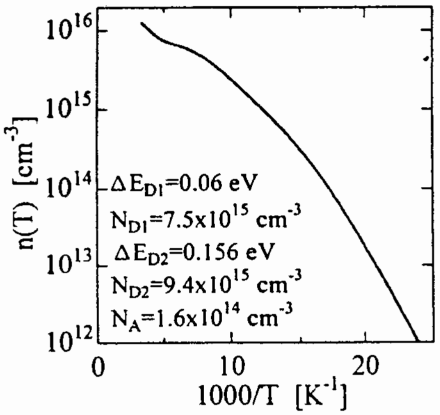

Fig. 1. Temperature dependence of free electron concentration.

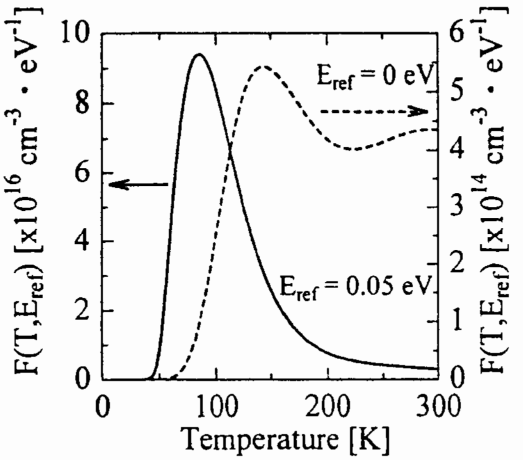

Fig. 2. $F(T, E_{ref})$ calculated from $n(T)$ in Fig. 1.

The influence of the acceptor density on $F(T, 0.05)$ will now be discussed. Using $n(T)$ for $N_A = 0$ cm^{-3} (dashed line), $N_A = 1 \times 10^{14}$ cm^{-3} (solid line) and $N_A = 1 \times 10^{15}$ cm^{-3} (dashed-dotted line), $F(T, 0.05)$ is from the definition in Eq. (2) as shown in Fig. 3. We find that $T_{peak1} = 75$ K, 82 K, and 98 K when $N_A = 0$, 1×10^{14} and 1×10^{15} cm^{-3}, respectively. The dependence of T_{peak1} on the acceptor density is used to find the acceptor density.

The deep donor is hardly ionized at low temperature and the shallow donor and acceptor are the major contributors influencing $F(T, E_{ref})$. Therefore, Eq. (5) can be approximated by

$$F(T, E_{ref}) \simeq F_1(T, E_{ref}) - \frac{N_A}{kT} \exp\left(-\frac{\Delta E_F - E_{ref}}{kT}\right) \tag{12}$$

In order to reduce the number of unknowns to two, that is, DE_{D1} and N_A/N_{D1}, the following function is introduced:

$$f_1(T, E_{ref}) \equiv \frac{F(T, E_{ref})}{N_{D1}} \simeq \frac{F_1(T, E_{ref})}{N_{D1}} - \frac{1}{kT} \cdot \frac{N_A}{N_{D1}} \exp\left(-\frac{\Delta E_F - E_{ref}}{kT}\right) \tag{13}$$

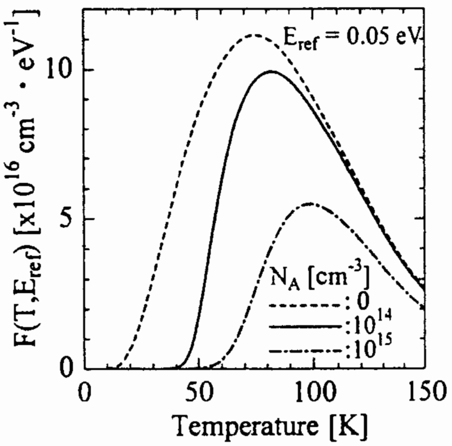

Fig. 3. $F(T, E_{ref})$ corresponding to various N_A.

$$
\begin{aligned}
&= \frac{1}{g_{D1} + \exp\left(-\dfrac{\Delta E_{D1} - \Delta E_F}{kT}\right)} \\
&\quad \times \frac{1}{kT} \exp\left(-\frac{\Delta E_{D1} - E_{ref}}{kT}\right) \\
&\quad - \frac{1}{kT} \cdot \frac{N_A}{N_{D1}} \exp\left(-\frac{\Delta E_F - E_{ref}}{kT}\right)
\end{aligned}
\tag{14}
$$

T_{peak1} of the graph for $E_{ref} = 0.05$ eV (solid line) shown in Fig. 2 is 84 K. The relationship between $DE_{\Delta 1}$ and N_A/N_{D1} that maximize $f_1(T, 0.05)$ in Eq. (14) at 84 K is shown by a solid line in Fig. 4. $F(T, 0.04)$ has a peak at $T = 98$ K. The relationship between $DE_{\Delta 1}$ and $N_A/N_{\Delta 1}$ that maximizes $f_1(T, 0.04)$ (see Eq. (14)) is shown by the dotted line in Fig. 4. The solution is given by $E_{\Delta 1}$ and $N_A/N_{\Delta 1}$ that satisfy the above two relationships. Therefore, the solution is given by the intersection of the two curves. Now, $DE_{\Delta 1} = 0.0599$ eV and $N_A/N_{\Delta 1} = 0.0203$. Although the intersection was obtained using curves for $E_{ref} = 0.04$ and 0.05 eV, the DE_{D1} - N_A/N_{D1} curve always passes through this point regardless of E_{ref}.

As shown in Eq. (13), N_{D1} is given by

$$
N_{D1} = \frac{F(T_{peak1}, E_{ref})}{f_1(T_{peak1}, E_{ref})} \tag{15}
$$

Substituting the solution ($DE_{D1} = 0.0599$ eV, $N_A/N_{D1} = 0.0203$) and the peak value 9.40×10^{16}cm^{-3}eV^{-1} of $F(T, 0.05)$ into Eq. (15), we obtain $N_{D1} = 7.59 \times 10^{15}$cm^{-3}. Therefore, $N_A = 1.54 \times 10^{14}$cm^{-3}. The same result is obtained for $F(T, 0.04)$.

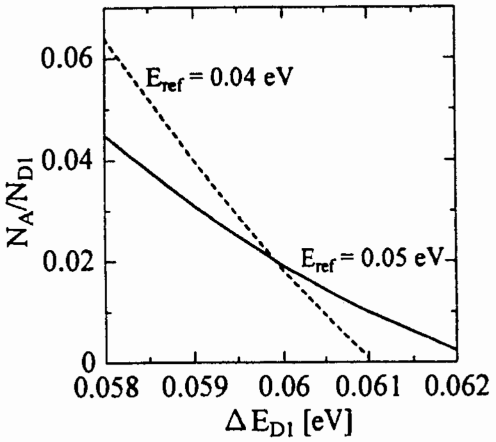

Fig. 4. Relationship between DE_{D1} and N_A/N_{D1} when $f_1(T, E_{ref})$ has a maximum at T_{peak1}.

As described, the shallow donor density and energy level and acceptor density can be obtained.

3.2. Deep donor

In order to evaluate the deep donor, a function that is not influenced by the shallow donor and acceptor will be introduced as shown below:

$$
\begin{aligned}
FF(T, E_{ref}) \equiv\ & F(T, E_{ref}) \\
& - \frac{1}{g_{D1} + \exp\left(-\dfrac{\Delta E_{D1} - \Delta E_F}{kT}\right)} \\
& \times \frac{N_{D1}}{kT} \exp\left(-\frac{\Delta E_{D1} - E_{ref}}{kT}\right) \\
& + \frac{N_A}{kT} \exp\left(-\frac{\Delta E_F - E_{ref}}{kT}\right)
\end{aligned}
\tag{16}
$$

Using $n(T)$ shown in Fig. 1, $F(T, E_{ref})$ shown in Eq. (2) and the values of DE_{D1}, N_{D1}, and N_A obtained in the previous section, $FF(T, E_{ref})$ was calculated as shown in Fig. 5. When $E_{ref} = 0$ eV (dotted line), the peak is considered to appear at temperatures above 300 K. Using the curve for $E_{ref} = 0.1$ eV (solid line), the peak of $FF(T, 0.1)$ is made to appear within the measurement temperature ($T_{peak2} = 240$ K). The peak value is 1.18×10^{16}cm^{-3}eV^{-1}.

Since $FF(T, E_{ref})$ is uninfluenced by the shallow donor and acceptor, it is equivalent to $F_2(T, E_{ref})$ in Eq. (6). In order to evaluate DE_{D2}, the function shown in Eqs. (17) and (18) is introduced.

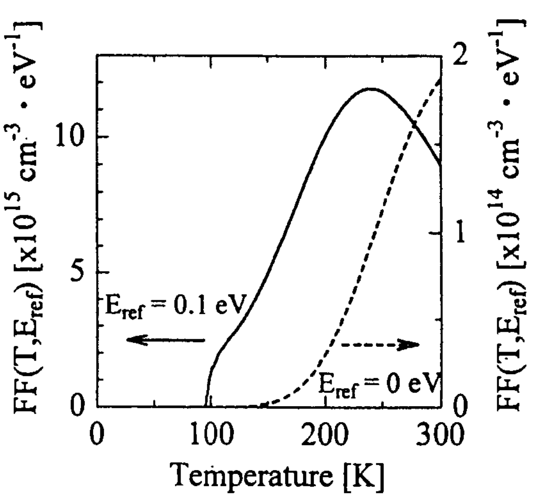

Fig. 5. $FF(T, E_{ref})$ corresponding to two kinds of E_{ref}.

$$
\begin{aligned}
f_2(T, E_{ref}) &\equiv \frac{FF(T, E_{ref})}{N_{D2}} \qquad (17)\\
&\simeq \frac{F_2(T, E_{ref})}{N_{D2}}\\
&= \frac{1}{g_{D2} + \exp\left(-\dfrac{\Delta E_{D2} - \Delta E_F}{kT}\right)}\\
&\quad \times \frac{1}{kT}\exp\left(-\frac{\Delta E_{D2} - E_{ref}}{kT}\right) \qquad (18)
\end{aligned}
$$

When $E_{ref} = 0.1$ eV, $T_{peak2} = 240$ K. Then, the value of DE_{D2} that provides a maximum of $f_2(T, E_{ref})$ in Eq. (18) is 0.156 eV. For E_{ref} that causes the peak of $FF(T, E_{ref})$ to appear within the measurement temperature (<300 K), a similar result is obtained.

From Eq. (17), N_{D2} is given by

$$
N_{D2} = \frac{FF(T_{peak2},\ 0.1)}{f_2(T_{peak2},\ 0.1)} \qquad (19)
$$

From the curve shown in Fig. 5, $FF(T_{peak2}, 0.1)$ is 1.18×10^{16}cm^{-3}eV^{-1}. Substituting $DE_{D2} = 0.1$ eV, $T_{peak2} = 240$ K, and $E_{ref} = 0.1$ eV into Eq. (18), $f_2(T_{peak2}, 0.1)$ is obtained. When these numbers are substituted into Eq. (19), we obtain $N_{D2} = 1.04 \times 10^{16}$cm^{-3}.

As described above, the method proposed in this paper provides the densities and energy levels of multiple donors and acceptors in semiconductors.

3.3. Comparison and discussion

It was found that the proposed method is effective in accurately finding N_A if $N_A/N_{D1} > 10^{-5}$. In addition, when $N_{D1} = N_{D2}$, the resolution of neighboring donor levels is 0.005 eV.

When the graphical method using the ln $n(T)$ – $1/T$ relationship is employed, $n(T)$ in the saturated region is N_{Di} and the slope of the curve provides DE_{Di} [6]. However, as shown in Fig. 1, the saturated region cannot be clearly defined and the slope is unclear. Therefore, the result is not reliable.

On the other hand, when $n(T)$ is evaluated by the Hoffmann method [7], the shallow donor ($DE_{D1} = 0.0629$ eV, $N_{D1} = 4.29 \times 10^{15}$cm^{-3}) and the deep donor ($DE_{D2} = 0.164$ eV, $N_{D2} = 8.93 \times 10^{15}$ cm^{-3}) are found. However, neither the shallow donor nor deep donor can be evaluated accurately by the Hoffmann method. In addition, the acceptor level cannot be found by this method. When $N_{D1} = N_{D2}$ and the energy level difference between the two donors is less than 0.03 eV, only one peak appears, indicating that there is only one kind of donor instead of two. When this type of error occurs, the donor density is twice as high as the correct value.

As described above, our new method is superior to the methods previously reported.

4. Conclusions

Using the data on the temperature dependence of the majority carrier concentration obtained by Hall effect measurements, the peak value and peak temperature of the function $n(T)n(T)\exp(E_{ref}/kT)/N_C/kT$ are obtained. Using these values, the characteristics of multiple impurities in a semiconductor can be evaluated. The above function shows a peak at the temperature corresponding to each donor level. Using this property, multiple donors were evaluated. In this study, only the n-type semiconductor was discussed. However, p-type semiconductors can be evaluated in a similar manner. When deep impurity levels are present, the temperature dependence of the majority carrier concentration at high temperature must be measured. Our proposed method is still effective even when the temperature range is arbitrarily limited.

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