

# A Simple Graphic Method for Evaluating Densities and Energy Levels of Impurities in Semiconductor from Temperature Dependence of Majority-Carrier Concentration

Hideharu MATSUURA\* and Kazuhide SONOI

Department of Electronics, Osaka Electro-Communication University, 18-8 Hatsu-cho, Neyagawa, Osaka 572, Japan

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A simple graphic method for impurity-level analysis of semiconductors is proposed. Because the concentration of majority carriers emitted from each impurity level increases monotonically with an increase of temperature ( $T$ ), the product of  $1/T$  and the total majority-carrier concentration has several peaks, and each peak results from the corresponding impurity level. Thus, from each peak value and the corresponding temperature, the density and energy level can be evaluated.

**KEYWORDS:** evaluation of impurities, graphic method, impurity density, impurity level, temperature dependence of majority-carrier concentration

## 1. Introduction

Semiconductors often include several impurities. Besides conventional dopants, impurities are sometimes intentionally doped into silicon (Si) or III-V compound semiconductors. For example, rare-earth metals are used as dopants, partially because near-infrared light can be obtained from these materials.<sup>1,2)</sup>

Since the majority-carrier concentration ( $n$  or  $p$ ) is very sensitively controlled by impurities, the dependence of  $n$  (or  $p$ ) on the inverse of temperature ( $T$ ) is used to determine the density and energy level of impurities. As pointed out by Hoffmann *et al.*,<sup>3,4)</sup> however, this analysis is very difficult in the case of several kinds of impurities with different energy levels in a semiconductor. Although Hoffmann *et al.* have proposed a differential evaluation of  $n - 1/T$  (or  $p - 1/T$ ) characteristics,<sup>3,4)</sup> the differential of experimental data results in an increase of observational errors. On the other hand, it is difficult to obtain reliable values by fitting a curve to the experimental data for  $n - 1/T$  (or  $p - 1/T$ ), because several curve-fitting parameters are required.

We propose a new simple graphic method in which the product of  $1/kT$  and  $n$  (or  $p$ ) is calculated and from each peak of this product the corresponding density and energy level are evaluated. Here,  $k$  is the Boltzmann constant.

## 2. Theoretical Consideration

To simplify arguments in the following, electrons are considered to be majority carriers. The temperature dependence of the free electron concentration  $n(T)$  in an  $n$ -type semiconductor is expressed as<sup>5)</sup>

$$n(T) = \sum_i N_{Di} \left[ 1 - \frac{1}{1 + \frac{1}{g_{Di}} \exp\left(-\frac{E_F - E_{Di}}{kT}\right)} \right], \quad (1)$$

where  $N_{Di}$  and  $E_{Di}$  are the density and energy level of the  $i$ -th impurity, respectively,  $g_{Di}$  is the degeneracy factor of the corresponding impurity, and  $E_F$  is the Fermi

level. To simplify arguments in the following, eq. (1) is rewritten as

$$n(T) = \sum_i N_{Di} F_i(T) \exp\left(-\frac{\Delta E_{Di}}{kT}\right) \quad (2)$$

with

$$F_i(T) = \frac{\exp\left(\frac{\Delta E_F}{kT}\right)}{g_{Di} + \exp\left(\frac{\Delta E_F - \Delta E_{Di}}{kT}\right)}, \quad (3)$$

$$\Delta E_{Di} = E_C - E_{Di}, \quad (4)$$

and

$$\Delta E_F = E_C - E_F, \quad (5)$$

where  $E_C$  is the energy at the bottom of the conduction band.

In order to evaluate  $\Delta E_{Di}$  and  $N_{Di}$  from the experimental data  $n(T)$ ,

$$S(T) = \frac{1}{kT} n(T) \quad (6)$$

is defined. Using eq. (2), this function is written as

$$S(T) = \sum_i N_{Di} D_i(T) \quad (7)$$

with

$$D_i(T) = \frac{1}{kT} F_i(T) \exp\left(-\frac{\Delta E_{Di}}{kT}\right) \quad (8)$$

The curve of  $S(T)$  has several peaks, because  $D_i(T)$  take a maximum at the temperature corresponding to the  $i$ -th impurity level.

## 3. Discussion

In order to demonstrate a way to evaluate  $\Delta E_{Di}$  and  $N_{Di}$  from  $n(T)$ , Si with two kinds of donors ( $\Delta E_{D1} = 0.04$  eV,  $N_{D1} = 1 \times 10^{16}$  cm<sup>-3</sup>,  $\Delta E_{D2} = 0.1$  eV, and  $N_{D2} = 1 \times 10^{16}$  cm<sup>-3</sup>) is considered. The curve of  $n(T)$  in the range  $77 \text{ K} \leq T \leq 300 \text{ K}$  is shown in Fig. 1. Here,  $g_{Di}$  is 2.

The curve of  $S(T)$  is calculated from eq. (6) using  $n(T)$  shown in Fig. 1, and is shown as the solid line of Fig. 2.

\*E-mail address : matsuura@isc.osakac.ac.jp

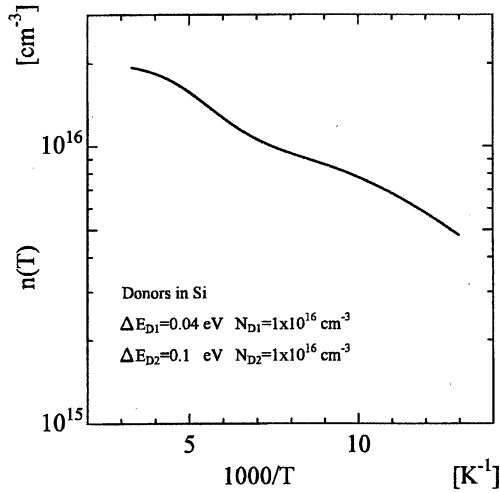


Fig. 1. Temperature dependence of majority-carrier concentration.

Because there are two discrete peaks in the figure, it is clear that two kinds of impurity levels exist in the semiconductor. From the figure,  $T_{\text{peak1}}$  and  $S(T_{\text{peak1}})$  corresponding to the first peak are 105 K and  $9.02 \times 10^{17} \text{ cm}^{-3} \cdot \text{eV}^{-1}$ , respectively.

The value of  $\Delta E_{D1}$ , which makes  $D_1(T)$  maximum at  $T_{\text{peak1}}$ , is numerically calculated. In this calculation,

$$\Delta E_F = kT \ln \left[ \frac{N_C(T)}{n(T)} \right] \quad (9)$$

and

$$N_C(T) = 5.39 \times 10^{15} T^{3/2} \quad (10)$$

are used,<sup>5)</sup> where  $N_C(T)$  is the effective density of states in the conduction band for Si. Using  $T_{\text{peak1}} = 105 \text{ K}$ ,  $\Delta E_{D1}$  is determined to be 0.0408 eV, which is close to the actual value.

The value of  $N_{D1}$  is estimated from

$$N_{D1} = \frac{S(T_{\text{peak1}}) k T_{\text{peak1}} \exp \left( \frac{\Delta E_{D1}}{k T_{\text{peak1}}} \right)}{F_1(T_{\text{peak1}})}, \quad (11)$$

since  $S(T_{\text{peak1}})$  is considered to be  $N_{D1} D_1(T_{\text{peak1}})$ . From the values obtained above,  $N_{D1}$  is estimated to be  $1.02 \times 10^{16} \text{ cm}^{-3}$ , which is close to the actual value.

In order to estimate  $\Delta E_{D2}$  and  $N_{D2}$ ,

$$S_1(T) = S(T) - N_{D1} D_1(T) \quad (12)$$

is defined, because the second peak in the solid line of Fig. 2 is affected by the shallower donors. The curve of  $S_1(T)$  is shown as the broken line of Fig. 2, using  $\Delta E_{D1} = 0.0408 \text{ eV}$  and  $N_{D1} = 1.02 \times 10^{16} \text{ cm}^{-3}$ . The peak value  $S_1(T_{\text{peak2}})$  and the corresponding temperature  $T_{\text{peak2}}$  are  $3.84 \times 10^{17} \text{ cm}^{-3} \cdot \text{eV}^{-1}$  and 245 K, respectively.

In the case of  $\Delta E_{D2} = 0.0101 \text{ eV}$ ,  $D_2(T)$  takes a maximum at  $T_{\text{peak2}} = 245 \text{ K}$ . This value of  $\Delta E_{D2}$  is close to the actual value.

The value of  $N_{D2}$  is estimated from

$$N_{D2} = \frac{S_1(T_{\text{peak2}}) k T_{\text{peak2}} \exp \left( \frac{\Delta E_{D2}}{k T_{\text{peak2}}} \right)}{F_2(T_{\text{peak2}})}, \quad (13)$$

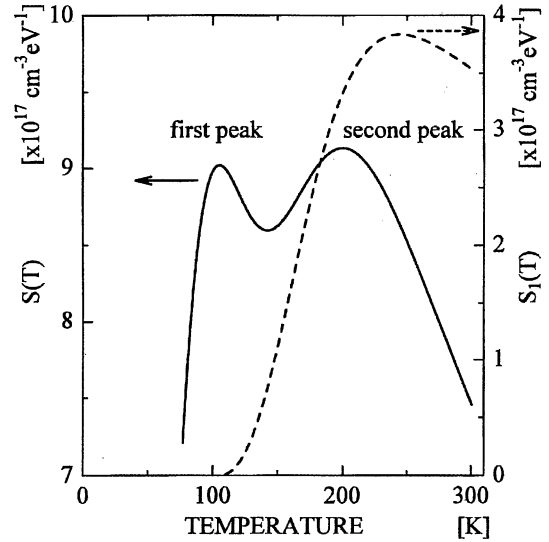


Fig. 2.  $S(T)$  and  $S_1(T)$  signals calculated from eq. (6) or (12).

since  $S_1(T_{\text{peak2}})$  is considered to correspond to  $N_{D2} D_2(T_{\text{peak2}})$ . From the obtained values,  $N_{D2}$  is estimated to be  $9.77 \times 10^{15} \text{ cm}^{-3}$ , which is close to the actual value.

As demonstrated above, several kinds of  $\Delta E_{Di}$  and  $N_{Di}$  in a semiconductor can be accurately evaluated from the temperature dependence of the majority-carrier concentration.

Next we discuss the limitations of our method. Under the conditions of  $\Delta E_{D1} = 0.04 \text{ eV}$  and  $\Delta E_{D2} = 0.1 \text{ eV}$ , the densities and energy levels of two impurities can be determined in the range  $4 \times 10^{-2} \leq N_{D1}/N_{D2} \leq 20$ . Since we aim to graphically evaluate the densities and energy levels of donors (or acceptors) which are mainly related to the majority-carrier concentration in a semiconductor, this range of  $N_{D1}/N_{D2}$  is considered to be an appropriate range. Under the conditions of  $\Delta E_{D1} = 0.04 \text{ eV}$  and  $N_{D1} = N_{D2}$ , the densities and energy levels of two impurities can be estimated when  $\Delta E_{D2}$  is larger than around 0.09 eV, that is, the energy resolution of our method is about 0.05 eV. Improvement of the energy resolution is in progress.

Next we compare our method with other methods. In the  $n - 1/T$  characteristics, the density of impurities is equal to the value of  $n(T)$  in the saturation range. The energy level is evaluated from the slope of the  $\ln n - 1/T$  curve in the freeze-out range, because  $n(T)$  in this range is approximately proportional to<sup>5)</sup>

$$\exp \left( -\frac{\Delta E_{Di}}{2kT} \right) \quad (14)$$

Since there are no saturation ranges in Fig. 1, no impurity densities can be determined. The value of  $\Delta E_{D1}$  is 0.0301 eV from the slope in the region of  $11 \text{ K}^{-1} \leq 1000/T \leq 13 \text{ K}^{-1}$ , while  $\Delta E_{D2}$  is 0.0370 eV from the slope in the region of  $4.8 \text{ K}^{-1} \leq 1000/T \leq 6.2 \text{ K}^{-1}$ . Since these values are poor approximations of the actual values, this analysis is unsuitable for evaluation of several kinds of impurities with different energy levels in a semiconductor.

Hoffmann *et al.* have proposed a differential evaluation of  $n(T)$ .<sup>3,4)</sup> For small temperature differences  $T_{j+1} - T_j$ , the derivative  $(-kT)dn/dE_F$  as a function of  $\Delta E_F$  can be approximated by

$$\frac{T_{j+1} + T_j}{2} \cdot \frac{n(T_{j+1}) - n(T_j)}{T_{j+1} \ln \left[ \frac{N_C(T_{j+1})}{n(T_{j+1})} \right] - T_j \ln \left[ \frac{N_C(T_j)}{n(T_j)} \right]} \quad (15)$$

as a function of

$$\frac{k}{2} \left\{ T_{j+1} \ln \left[ \frac{N_C(T_{j+1})}{n(T_{j+1})} \right] + T_j \ln \left[ \frac{N_C(T_j)}{n(T_j)} \right] \right\}. \quad (16)$$

The curve of  $(-kT)dn/dE_F$  takes maxima at  $\Delta E_F = \Delta E_{Di} + kT_{mi} \ln g_{Di}$ , where  $T_{mi}$  is the temperature for which  $\Delta E_F$  coincides with the abscissa of the  $i$ -th maximum. The ordinate of the  $i$ -th maximum equals  $N_{Di}/4$ . From the data in Fig. 1,  $\Delta E_{D1}$ ,  $N_{D1}$ ,  $\Delta E_{D2}$  and  $N_{D2}$  are estimated to be 0.0375 eV,  $9.07 \times 10^{15} \text{ cm}^{-3}$ , 0.0949 eV and  $9.67 \times 10^{15} \text{ cm}^{-3}$ , respectively, which implies that our method is more accurate than Hoffmann's method. Since  $T_{m1}$  is 72 K,  $n(T)$  must be measured at temperatures lower than the liquid nitrogen temperature (77 K). Under the conditions of  $\Delta E_{D1} = 0.04$  eV and  $\Delta E_{D2} = 0.1$  eV, the densities and energy levels of two impurities can be determined in the range  $N_{D1}/N_{D2} \leq 5$ . Under the conditions of  $\Delta E_{D1} = 0.04$  eV and  $N_{D1} = N_{D2}$ , the densities and energy levels of two impurities can be evaluated when  $\Delta E_{D2}$  is larger than around 0.07 eV. In simulation, judging from the accuracy and limitations of both methods, our method is considered to be comparable to Hoffmann's method.

When the derivative  $(-kT)dn/dE_F$  is calculated from

the experimental data  $n(T)$ , the calculated values are thought to be scattered, as is clear from eq. (15). In the experimental results,<sup>2,3)</sup> it is difficult to distinguish discrete peaks in the  $(-kT)dn/dE_F$  vs  $\Delta E_F$  curve. Since the experimental data  $n(T)$  are simply divided by  $kT$  in our method, it is easier to distinguish discrete peaks in the  $n(T)/kT$  vs  $T$  curve than to distinguish discrete peaks using Hoffmann's method. Therefore, the advantage of our method is apparent when the experimental data are analyzed. Application of our method to the experimental data is currently in progress.

#### 4. Summary

We have proposed a simple graphic method for evaluating densities and energy levels of impurities in a semiconductor, using the temperature dependence of the majority-carrier concentration. From the temperature dependence of the function  $n(T)/kT$ , several discrete peaks are graphically obtained. From each peak, the density and energy level of the corresponding impurity can be evaluated accurately.

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