Jpn. J. Appl. Phys. Vol. 41 (2002) pp. 496–500
Part 1, No. 2A, February 2002

Acceptor Densities and Acceptor Levels in Undoped GaSb Determined by Free Carrier Concentration Spectroscopy

Hideharu MATSUURA*, Kouhei MORITA, Kazuhiro NISHIKAWA, Takeo MIZUKOSHI,
Masaharu SEGAWA and Wataru SUSAKI

Department of Electronic Engineering and Computer Science, Osaka Electro-Communication University,
18-8 Hatsu-cho, Neyagawa, Osaka 572-8530, Japan

(Received June 19, 2001; accepted for publication November 1, 2001)

Without any assumptions regarding residual impurity species in an undoped semiconductor, it is experimentally demonstrated that the densities and energy levels of impurities can be precisely determined by the graphical peak analysis method based on Hall-effect measurements, referred to as free carrier concentration spectroscopy (FCCS). Using p-type undoped GaSb epilayers grown by molecular beam epitaxy (MBE), the densities and energy levels of several acceptor species are accurately determined. Five acceptor species are detected in the undoped GaSb epilayers grown by MBE, while two are also found in p-type undoped GaSb wafers. A 21–41 meV acceptor and a 75–99 meV acceptor exist both in the epilayers and in the wafer. On the other hand, a 164–181 meV acceptor is detected in epilayers grown at an Sb_4/Ga flux beam equivalent pressure ratio of 8 or 10, while a 259 meV acceptor is found in the epilayer grown at $Sb_4/Ga = 6$. In addition, a very shallow acceptor, which is completely ionized at 80 K, is found in the epilayers. The densities of the very shallow acceptor and the 21–41 meV acceptor are minimum at $Sb_4/Ga = 8$, which makes the hole concentration lowest in the temperature range of the measurement. [DOI: 10.1143/JJAP.41.496]

KEYWORDS: GaSb, undoped GaSb, acceptor level, acceptor density, determination of acceptor density and acceptor level, graphical peak analysis method

1. Introduction

GaSb-based semiconductors have been regarded as promising for the fabrication of near- and mid-infrared laser diodes and photodiodes, which can be used for monitoring the concentrations of CO_2, CO, NO_x and SO_x in the atmosphere.[1] In order to fabricate device-quality n-type or p-type GaSb, it is necessary to lower the densities of electrically active residual impurities and defects in undoped GaSb before a dopant (donor or acceptor) is added to GaSb. Next, a dopant with low ionization energy is required to be researched. Therefore, an accurate determination of the densities and energy levels of acceptors or donors in undoped and doped GaSb is essential.

Using the temperature dependence of the hole concentration, $p(T)$, obtained by Hall-effect measurements, the densities and energy levels of residual acceptor species in undoped GaSb, which exhibited p-type conduction, were determined.[2–9] Although the acceptor density and acceptor level are usually determined using the $p(T)$–$1/T$ curve, such analysis cannot be applied in the case of semiconductors with more than one acceptor species or in the case of compensated semiconductors. Moreover, it is difficult to obtain reliable values by fitting a curve to the experimental data of $p(T)$, because too many curve-fitting parameters must be simultaneously determined. In order to reduce the number of curve-fitting parameters, the following assumptions were adopted in the case of undoped GaSb. According to the double acceptor model where the acceptor can be ionized singly as well as doubly,[2,3,5,6] it was assumed that the two acceptor species had the same densities, but different energy levels. In the other cases, it was assumed that there was a very shallow acceptor as well as two acceptor species with acceptor levels of 40 meV and 80 meV,[7] or that there were two acceptor species with acceptor levels of 31.2 meV and 102 meV.[8]

Without any assumptions regarding acceptor species, graphical peak analysis methods can determine the densities and energy levels of acceptors. Although Hoffmann[10] proposed a differential evaluation of $p(T)$, the differential of the experimental data results in an increase in observed errors. One of the authors has proposed and tested a precise determination without the differential evaluation of $p(T)$, referred to as free carrier concentration spectroscopy (FCCS),[11] and has applied FCCS to p-type Si irradiated with high-energy protons or electrons,[12,13] and n-type SiC.[14,15] Since each peak in the FCCS signal corresponds one-to-one to an impurity or a defect, the density and energy level can be accurately determined.

In this study, we determine the densities and energy levels of several acceptors in p-type undoped GaSb epilayers grown by molecular beam epitaxy (MBE) using FCCS without any assumptions regarding acceptor species, and investigate the dependence of each acceptor density on an Sb_4/Ga flux beam equivalent pressure ratio (Sb_4/Ga BEP ratio) during the growth.

2. Free Carrier Concentration Spectroscopy

2.1 Basic concept

Deep level transient spectroscopy (DLTS)[16] or isothermal capacitance transient spectroscopy (ICTS)[17] can uniquely determine the densities and energy levels of traps in semiconductors, because each peak in the signal corresponds one-to-one to a trap. For example, the ICTS signal is defined as $S(t) \equiv t\mathrm{d}C(t)^2/\mathrm{d}t$, where $C(t)$ is the transient capacitance after a reverse bias is applied. Since $S(t)$ is theoretically described as the sum of $N_i e_i t \exp(-e_i t)$, it has a peak value of $N_i \exp(-1)$ at a peak time of $t_{\mathrm{peak}i} = 1/e_i$. Here, N_i and e_i are the density and emission rate of the i-th trap, respectively. Therefore, the function $N_i e_i t \exp(-e_i t)$ plays an important role in ICTS analysis.

In order to analyze $p(T)$, we have introduced the function theoretically described as the sum of

---

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

$N_i \exp(-\Delta E_i/kT)/kT$,[18,19] where N_i and ΔE_i are the density and energy level of the i-th impurity, respectively, T is the measurement temperature and k is the Boltzmann constant. The function $N_i \exp(-\Delta E_i/kT)/kT$ has a peak at $T_{\mathrm{peak}i} = \Delta E_i/kT$, which does not apply to all impurities in the temperature range of the measurement. If we can introduce a function in which the peak appears at $T_{\mathrm{peak}i} = (\Delta E_i - E_{\mathrm{ref}})/k$, we can shift the peak temperature to the measurement temperature range by changing the parameter E_{ref}. This indicates that we can determine N_i and ΔE_i in a wide impurity-energy-level range. Therefore, the function to be evaluated should be approximately described as the sum of $N_i \exp[-(\Delta E_i - E_{\mathrm{ref}})/kT]/kT$. It should be noted that N_i and ΔE_i determined by this method are independent of E_{ref}. In addition, we have avoided introducing a differential evaluation of $p(T)$.

2.2 *Theoretical consideration*

For the following theoretical consideration, we assume a p-type semiconductor with one very shallow acceptor (density N_{A1}), n different acceptor species (density $N_{\mathrm{A}i}$ and energy level $\Delta E_{\mathrm{A}i}$ of the i-th acceptor for $2 \le i \le n+1$), and one donor (density N_{D}). Here, the very shallow acceptor is the acceptor completely ionized below the measurement temperature. The acceptor levels ($\Delta E_{\mathrm{A}i}$) are measured from the top of the valence band (E_{V}). From the charge neutrality condition, $p(T)$ can be described as

$$p(T) = \sum_{i=2}^{n+1} N_{\mathrm{A}i} f(\Delta E_{\mathrm{A}i}) - (N_{\mathrm{D}} - N_{\mathrm{A1}}), \tag{1}$$

where $f(\Delta E_{\mathrm{A}i})$ is the Fermi–Dirac distribution function given by

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

ΔE_{F} is the Fermi level measured from E_{V}, and g_{A} is the degeneracy factor of acceptors. On the other hand, using the effective density of states (N_{V}) in the valence band, $p(T)$ is described as

$$p(T) = N_{\mathrm{V}}(T) \exp\left(-\frac{\Delta E_{\mathrm{F}}}{kT}\right), \tag{3}$$

where

$$N_{\mathrm{V}}(T) = N_{\mathrm{V0}} k^{3/2} T^{3/2}, \tag{4}$$

$$N_{\mathrm{V0}} = 2\left(\frac{2\pi m^*}{h^2}\right)^{3/2}, \tag{5}$$

m^* is the hole effective mass, and h is Planck's constant. From eqs. (1) and (3), a favorable function to determine $N_{\mathrm{A}i}$ and $\Delta E_{\mathrm{A}i}$ can be introduced as follows. The function to be evaluated is defined as

$$H1(T, E_{\mathrm{ref}}) \equiv \frac{p(T)^2}{(kT)^{5/2}} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right). \tag{6}$$

Substituting eq. (1) for one of the $p(T)$ in eq. (6) and substituting eq. (3) for the other $p(T)$ in eq. (6) yield

$$H1(T, E_{\mathrm{ref}}) = \sum_{i=2}^{n+1} \frac{N_{\mathrm{A}i}}{kT} \exp\left(-\frac{\Delta E_{\mathrm{A}i} - E_{\mathrm{ref}}}{kT}\right) I(\Delta E_{\mathrm{A}i}) - \frac{(N_{\mathrm{D}} - N_{\mathrm{A1}}) N_{\mathrm{V0}}}{kT} \exp\left(\frac{E_{\mathrm{ref}} - \Delta E_{\mathrm{F}}}{kT}\right), \tag{7}$$

where

$$I(\Delta E_{\mathrm{A}i}) = \frac{N_{\mathrm{V0}}}{g_{\mathrm{A}} + \exp\left(\dfrac{\Delta E_{\mathrm{F}} - \Delta E_i}{kT}\right)}. \tag{8}$$

Finally, using a personal computer,[11] we can easily determine $N_{\mathrm{A}i}$ and $\Delta E_{\mathrm{A}i}$ for each peak, taking the temperature dependence of $I(\Delta E_{\mathrm{A}i})$ into account.

3. Experimental

2-μm-thick undoped GaSb epilayers were grown on semi-insulating (100) GaAs[20] at 470°C by water-cooled MBE with three different $\mathrm{Sb_4}$/Ga BEP ratios of 6, 8 and 10. The growth rate was about 0.5 μm/h.

After each undoped GaSb epilayer was cut into pieces of $7 \times 7\,\mathrm{mm}^2$ size, $p(T)$ was measured by the van der Pauw method at temperatures between 80 K and 390 K, in a magnetic field of 1.4 T and at a current of 0.1 mA. In addition, after a 500-μm-thick undoped GaSb wafer was cut to a $10 \times 10\,\mathrm{mm}^2$ size, $p(T)$ was measured. In the FCCS analysis, g_{A} of 4 and m^*/m_0 of 0.5 were used, where m_0 is the free-space electron mass.

4. Results

Figure 1 shows a set of three $p(T)$ in undoped GaSb epilayers for $\mathrm{Sb_4}$/Ga BEP ratios of 6, 8 and 10. In the figure, $p(T)$ for $\mathrm{Sb_4}/\mathrm{Ga} = 8$ is the lowest in the temperature range of the measurement, while $p(T)$ for $\mathrm{Sb_4}/\mathrm{Ga} = 6$ is the highest.

Figure 2 shows the $H1(T, E_{\mathrm{ref}})$ of the undoped GaSb epilayer grown at $\mathrm{Sb_4}/\mathrm{Ga} = 10$. Using eq. (6), the

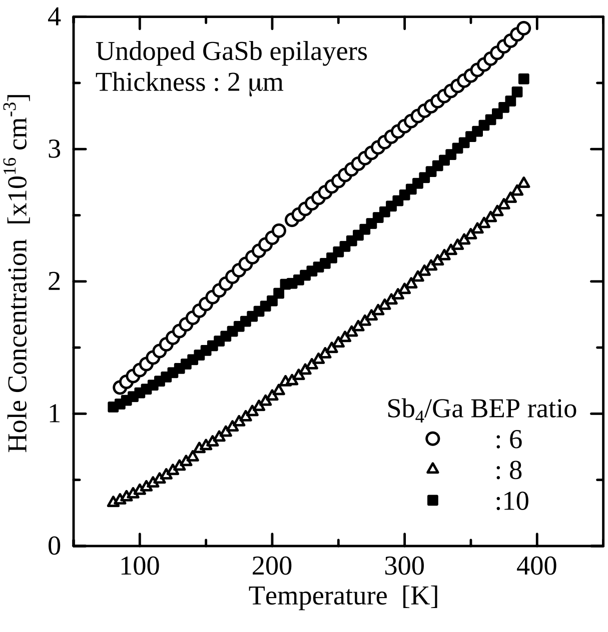

Fig. 1. Temperature dependence of hole concentration in undoped GaSb epilayer grown at different $\mathrm{Sb_4}$/Ga BEP ratios.

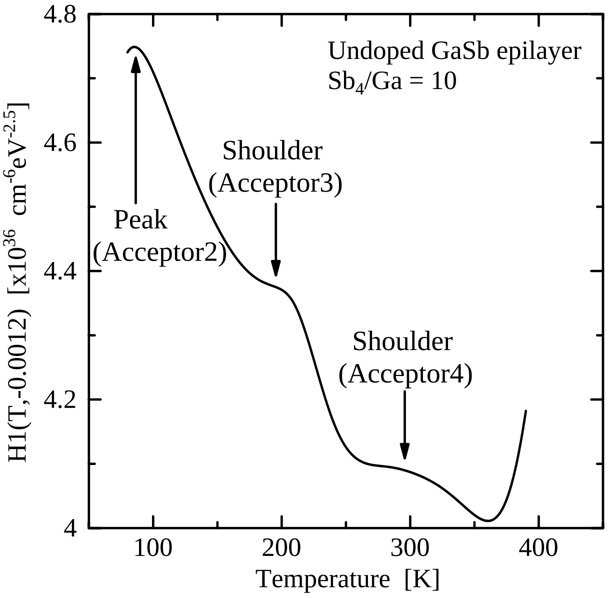

Fig. 2. $H1(T, E_{\rm ref})$ with $E_{\rm ref} = -0.0012\,{\rm eV}$.

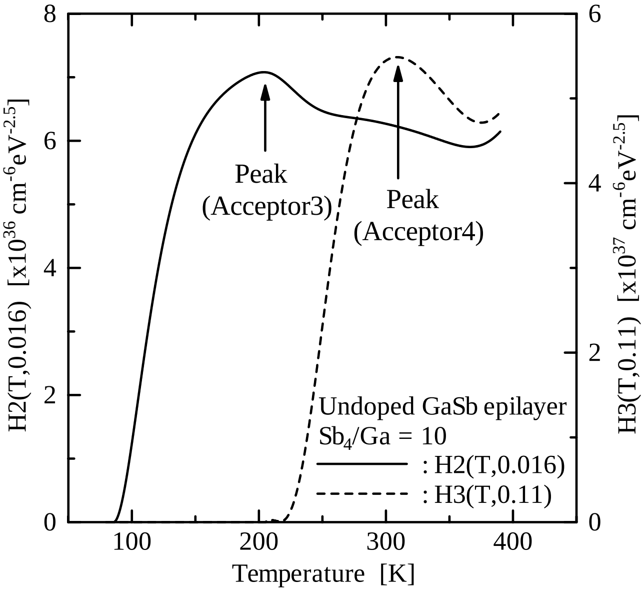

Fig. 3. $H2(T, E_{\rm ref})$ with $E_{\rm ref} = 0.016\,{\rm eV}$ and $H3(T, E_{\rm ref})$ with $E_{\rm ref} = 0.11\,{\rm eV}$.

$H1(T, E_{\rm ref})$ with $E_{\rm ref} = -0.0012\,{\rm eV}$ is calculated by interpolating $p(T)$ with a cubic smoothing natural spline function. Since one peak and two shoulders appear in the figure, it is determined that at least three acceptor species are included in this undoped GaSb epilayer. Here, the acceptor corresponding to the peak is called Acceptor2. From the peak, the density ($N_{\rm A2}$) and energy level ($\Delta E_{\rm A2}$) of Acceptor2 are determined to be $3.8 \times 10^{15}\,{\rm cm}^{-3}$ and 28 meV, respectively, and also, the value of $(N_{\rm A1} - N_{\rm D})$ is evaluated to be $9.2 \times 10^{15}\,{\rm cm}^{-3}$. Since the value of $(N_{\rm A1} - N_{\rm D})$ is positive, it is determined that the very shallow acceptor (Acceptor1) is included in the epilayer.

As is clear from eqs. (6) and (7), the function, which is not influenced by Acceptor1, Acceptor2 or the donor, is introduced as

$$\begin{aligned} H2(T, E_{\rm ref}) \equiv{}& \frac{p(T)^2}{(kT)^{5/2}} \exp\left(\frac{E_{\rm ref}}{kT}\right) \\ &- \frac{N_{\rm A2}}{kT} \exp\left(-\frac{\Delta E_{\rm A2} - E_{\rm ref}}{kT}\right) I(\Delta E_{\rm A2}) \\ &- \frac{(N_{\rm A1} - N_{\rm D}) N_{\rm V0}}{kT} \exp\left(\frac{E_{\rm ref} - \Delta E_{\rm F}}{kT}\right). \end{aligned} \tag{9}$$

The solid line in Fig. 3 represents the $H2(T, E_{\rm ref})$ with $E_{\rm ref} = 0.016\,{\rm eV}$. From the peak, $N_{\rm A3}$ and $\Delta E_{\rm A3}$ of Acceptor3 are determined to be $1.2 \times 10^{16}\,{\rm cm}^{-3}$ and 75 meV, respectively.

The function, which is not influenced by Acceptor1, Acceptor2, Acceptor3 or the donor, is introduced as

$$\begin{aligned} H3(T, E_{\rm ref}) \equiv{}& \frac{p(T)^2}{(kT)^{5/2}} \exp\left(\frac{E_{\rm ref}}{kT}\right) \\ &- \sum_{i=2}^{3} \frac{N_{{\rm A}i}}{kT} \exp\left(-\frac{\Delta E_{{\rm A}i} - E_{\rm ref}}{kT}\right) I(\Delta E_{{\rm A}i}) \\ &- \frac{(N_{\rm A1} - N_{\rm D}) N_{\rm V0}}{kT} \exp\left(\frac{E_{\rm ref} - \Delta E_{\rm F}}{kT}\right). \end{aligned} \tag{10}$$

The broken line in Fig. 3 represents the $H3(T, E_{\rm ref})$ with $E_{\rm ref} = 0.11\,{\rm eV}$. From the peak, $N_{\rm A4}$ and $\Delta E_{\rm A4}$ of Acceptor4 are determined to be $2.4 \times 10^{16}\,{\rm cm}^{-3}$ and 164 meV, respectively.

The solid line in Fig. 4 shows simulated $p(T)$ using the values determined by FCCS. The open circles represent experimental $p(T)$. The simulated $p(T)$ is quantitatively in good agreement with the experimental $p(T)$, indicating that the values determined by FCCS are reliable.

Similarly to those for the undoped GaSb epilayer grown at $\rm Sb_4/Ga = 10$, the densities and energy levels of accepters in the undoped GaSb epilayers grown at $\rm Sb_4/Ga$ BEP ratios of 6 and 8 and also in the 500-μm-thick undoped GaSb wafer are determined, and are listed in Table I.[21] Since the value

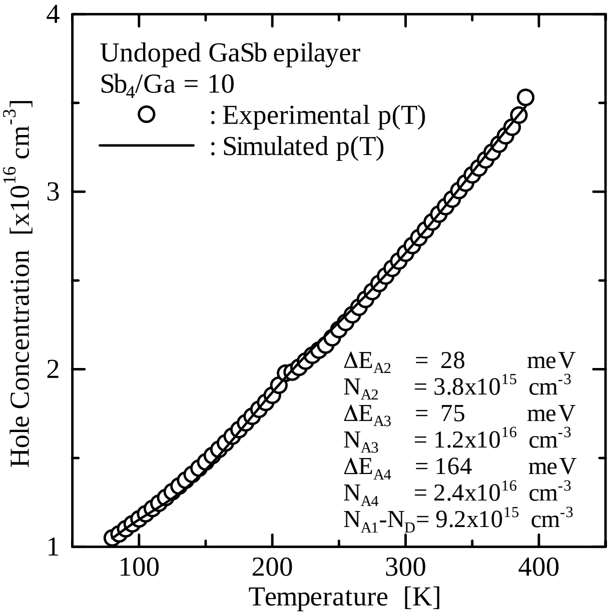

Fig. 4. Comparison of simulated $p(T)$ with experimental $p(T)$.

Table I. Results obtained by FCCS.

		Sb$_4$/Ga BEP ratios			Wafer
		6	8	10	
$N_{A1} - N_D$	Density (cm^{-3})	1.1×10^{16}	7.2×10^{15}	9.2×10^{15}	—
Acceptor2	Energy level (meV)	41	—	28	21
	Density (cm^{-3})	1.1×10^{16}	—	3.8×10^{15}	2.5×10^{17}
Acceptor3	Energy level (meV)	99	94	75	83
	Density (cm^{-3})	1.8×10^{16}	1.3×10^{16}	1.2×10^{16}	7.2×10^{16}
Acceptor4	Energy level (meV)	—	181	164	—
	Density (cm^{-3})	—	2.4×10^{16}	2.4×10^{16}	—
Acceptor5	Energy level (meV)	259	—	—	—
	Density (cm^{-3})	9.2×10^{16}	—	—	—
$N_D - N_{A1}$	Density (cm^{-3})	—	—	—	1.8×10^{16}

of ($N_{A1} - N_D$) is negative in the case of the wafer, the donor density is higher than the very shallow acceptor density, or the very shallow acceptor does not exist in the wafer. In the case of Sb$_4$/Ga = 6, another acceptor (Acceptor5) is found in the epilayer, while Acceptor4 is not detected. The values of ($N_{A1} - N_D$) and N_{A2} are minimum at Sb$_4$/Ga = 8, while N_{A3} is almost independent of the Sb$_4$/Ga BEP ratio. Therefore, in order to lower $p(T)$ in undoped GaSb epilayers, it is necessary to lower the densities of Acceptor1 and Acceptor2, and then the optimum Sb$_4$/Ga BEP ratio becomes 8.

5. Discussion

During the growth of GaSb epilayers at 470°C by MBE, Sb is more apt to be evaporated from the epilayer than Ga, because the vapor pressure of Sb is much higher than that of Ga. This results in the formation (V_{Sb}) of a vacancy at an Sb site or the substitution (Ga_{Sb}) of Ga for Sb. Moreover, complex defects such as $V_{Ga}Ga_{Sb}$ and $V_{Ga}Ga_{Sb}V_{Ga}$ have been discussed.[4,8)]

In order to fit a curve to the experimental $p(T)$, the double acceptor model was assumed.[6)] According to the double acceptor model,[2,3,5)] the acceptor behaves as a singly ionized acceptor (20–40 meV) or a doubly ionized acceptor (60–100 meV). In this case, the density of the 20–40 meV acceptor should be equal to that of the 60–100 meV acceptor. The 20–40 meV acceptor and the 60–100 meV acceptor are considered to correspond to Acceptor2 and Acceptor3 in our results obtained by FCCS, respectively. However, since the density of Acceptor2 is different from that of Acceptor3, the double acceptor model is not considered to be appropriate.

In order to fit a curve to the experimental $p(T)$, Eltoukhy and Greene[7)] assumed three acceptor species; one very shallow acceptor and the other two acceptors with acceptor levels of 40 meV and 80 meV, indicating that the fitting parameters were only the three acceptor densities. The very shallow acceptor was reported to be related to both V_{Sb} and donor impurities, the most likely being oxygen. The density of the 40 meV acceptor was considered to be directly related to V_{Sb} or equivalent point-defect complexes, since this changed with the Sb$_4$/Ga BEP ratio. On the other hand, the 80 meV acceptor was determined to be associated with electrically active sites on dislocations originating at the GaSb/GaAs interface. If Acceptor3 in our results obtained by FCCS, which corresponds to the 80 meV acceptor, is related to the interface or the surface, the density of Acceptor3 in the 500-μm-thick wafer should be lower by about 250 than that in the 2-μm-thick epilayer, because the density was calculated by dividing the experimental sheet carrier density by the thickness. However, since the density of Acceptor3 in the thick GaSb wafer is higher than those in the thin epilayers, Acceptor3 must be related to the impurities or defects in the bulk, neither those at the GaSb/GaAs interface nor those at the GaSb surface. From the above discussion, it is considered that Acceptor1, Acceptor2 and Acceptor3 are included in the bulk.

The decrease in the density of Acceptor2 made $p(T)$ minimum at Sb$_4$/Ga = 8. Since the density of Acceptor2 strongly depends on the Sb$_4$/Ga BEP ratio, the origin of Acceptor2 is considered to be related to V_{Sb} or Ga_{Sb} or equivalent point-defect complexes. If the origin of Acceptor2 for all the Sb$_4$/Ga BEP ratios is the same, the density of Acceptor2 should decrease with the Sb$_4$/Ga BEP ratio. Therefore, the origin of Acceptor2 for Sb$_4$/Ga = 6 is expected to be different from that for Sb$_4$/Ga = 10. For example, Acceptor2 for Sb$_4$/Ga = 6 might result from Ga_{Sb} due to the Ga-rich condition, while Acceptor2 for Sb$_4$/Ga = 10 might arise from V_{Sb} due to the Ga-poor condition. Thus, there is a possibility that the sum of the densities of Ga_{Sb} and V_{Sb} will be minimum at Sb$_4$/Ga = 8. A detailed investigation is under way.

6. Conclusion

Even if the number of impurity species included in a semiconductor is unknown, it has been illustrated that FCCS can determine the density and energy level of each impurity accurately. In undoped GaSb epilayers grown by MBE, one very shallow acceptor as well as four acceptors with acceptor levels of 28–41 meV, 75–99 meV, 164–181 meV and 259 meV have been detected. On the other hand, in a thick undoped GaSb wafer, two acceptor species with acceptor levels of 21 meV and 83 meV have been detected.

Acknowledgement

This work was partially supported by the Academic Frontier Promotion Projects of the Ministry of Education, Culture, Sports, Science and Technology.

1) G. W. Turner, H. K. Choi and M. J. Manfra: Appl. Phys. Lett. **72** (1998) 876.

2) R. D. Baxter, R. T. Bate and F. J. Reid: J. Phys. Chem. Solids **26** (1965) 41.

3) R. D. Baxter, F. J. Reid and A. C. Beer: Phys. Rev. **162** (1967) 718.

4) M. D. Campos, A. Gouskov, L. Gouskov and J. C.Pons: J. Appl. Phys. **44** (1973) 2642.

5) R. A. Noack, W. Rühle and T. N. Morgan: Phys. Rev. B **18** (1978) 6944.

6) K. Nakashima: Jpn. J. Appl. Phys. **20** (1981) 1085.

7) A. H. Eltoukhy and J. E. Greene: J. Appl. Phys. **50** (1979) 6396.

8) P. S. Dutta, V. Prasad, H. L. Bhat and V. Kumar: J. Appl. Phys. **80** (1996) 2847.

9) G. Y. Zhao, H. Ebisu, T. Soga, T. Egawa, T. Jimbo and M. Umeno: Jpn. J. Appl. Phys. **37** (1998) 1704.

10) H. J. Hoffmann: Appl. Phys. **19** (1979) 307.

11) The Windows application software for FCCS can be freely downloaded from our web site (http://www.osakac.ac.jp/labs/matsuura/).

12) H. Matsuura, Y. Uchida, T. Hisamatsu and S. Matsuda: Jpn. J. Appl. Phys. **37** (1998) 6034.

13) H. Matsuura, Y. Uchida, N. Nagai, T. Hisamatsu, T. Aburaya and S. Matsuda: Appl. Phys. Lett. **76** (2000) 2092.

14) H. Matsuura, T. Kimoto and H. Matsunami: Jpn. J. Appl. Phys. **38** (1999) 4013.

15) H. Matsuura Y. Masuda, Y. Chen and S. Nishino: Jpn. J. Appl. Phys. **39** (2000) 5069.

16) D. V. Lang: J. Appl. Phys. **45** (1974) 3023.

17) H. Okushi: Philos. Mag. B **52** (1985) 33.

18) H. Matsuura and K. Sonoi: Jpn. J. Appl. Phys. **35** (1996) L555.

19) H. Matsuura: Jpn. J. Appl. Phys. **36** (1997) 3541.

20) Since the semi-insulating GaAs substrate used here slightly exhibited n-type conduction, the depletion region was formed in the vicinity of the p-type GaSb/GaAs interface, resulting in less information on defects in this vicinity being obtained from the Hall-effect measurement. Moreover, since the acceptor densities in the GaSb epilayer were found to be much higher than the donor density in the GaAs substrate, the depletion layer in the GaSb epilayer is expected to be thin, suggesting that the GaSb thickness used in the estimation of $p(T)$ is similar to the epilayer thickness.

21) The acceptor species were classified according to the literature. However, for example, the origin of the 41 meV acceptor might be different from those of the 28 meV acceptor in the epilayer and the 21 meV acceptor in the wafer.