Boron and Nitrogen in GaAs and InP Melts Equilibrated with B₂O₃ Flux

Tsuyoshi Yamada¹, Taku Kudo^{*1}, Kazuki Tajima^{*2}, Akira Otsuka²,
Takayuki Narushima³, Chiaki Ouchi³ and Yasutaka Iguchi³

¹Compound Semiconductor Wafer Dept., Dowa Semiconductor Co., Ltd, Akita 011-0911, Japan

²Semiconductor Business Unit, Dowa Mining Co., Ltd., Tokyo 100-8282, Japan

³Department of Metallurgy, Tohoku University, Sendai 980-8579, Japan

The boron and nitrogen contents of GaAs and InP melts equilibrated with B₂O₃ flux were examined at 1523 and 1373 K, respectively, using a chemical equilibrium technique. GaAs or InP was melted with B₂O₃ flux in a silica ampoule with and without a BN crucible. The boron content decreased with increasing nitrogen content in both of the melts equilibrated with B₂O₃ flux and BN. The solubility product of BN in the melts was expressed as a function of nitrogen content. The relationship between the boron and nitrogen contents of a GaAs melt coexisted with BN agreed well with that in the residue after LEC crystal growth of GaAs. The boron content of the GaAs melt coexisted with silica was much larger than that of the GaAs melt with BN. It was suggested that the reduction of B₂O₃ by silicon introduced into the melt from silica led the increase of boron content.

(Received December 17, 2003; Accepted February 17, 2004)

Keywords: liquid-encapsulated Czochralski method, GaAs, InP, B₂O₃, nitrogen, boron

1. Introduction

III-V compound semiconductors such as GaAs and InP are used to high-speed and high-frequency devices and optical devices because of their excellent electrical and optical properties. Large-diameter single crystals of GaAs and InP are mainly produced by the liquid-encapsulated Czochralski (LEC) and the vertical gradient freeze (VGF) methods.¹⁾ In both of the processes, the melt of GaAs or InP coexists with B₂O₃ flux as a liquid encapsulant and is in contact with a crucible made of BN or silica at high temperature and high pressure. Impurities such as boron, carbon, nitrogen or oxygen can be introduced from the B₂O₃ flux and the crucible into the III-V melt, and incorporated into the single crystal during the growth process.²⁻⁴⁾ Therefore, the reactions between a III-V melt and B₂O₃ flux or crucible are important factors governing the content and distribution of impurities in III-V single crystals. Boron and carbon are important residual impurities in undoped GaAs single crystals grown by the LEC and VGF methods.⁵⁾ Carbon has been shown to be the dominant residual acceptor impurity which affects the characteristics of undoped semi-insulating crystals.^{2,6)} Effects of boron on electrical properties have also been reported.⁷⁾ It is known that boron and carbon contents can be decreased by decreasing the water content of the B₂O₃ flux^{3,8,9)} or increasing the strength of the magnetic field.¹⁰⁾ These methods, however, cannot control the carbon and boron contents independently.

Recent reports have noted that adjustment of ambient gas partial pressures in a crystal growth chamber can independently control the contents of boron and carbon in III-V crystals.¹¹⁻¹⁵⁾ Increasing the ambient N₂ gas pressure in the crystal growth chamber increases the nitrogen content in a III-V melt according to eq. (1).

$$\frac{1}{2} \text{N}_2(\text{g}) = \underline{\text{N}}(\text{in III-V melt}) \quad (1)$$

When BN is used as a crucible material, eq. (2) suggests that the boron content of a III-V melt decreases with increasing pressure of ambient N₂ gas.

$$\underline{\text{B}}(\text{in III-V melt}) + \frac{1}{2} \text{N}_2(\text{g}) = \text{BN}(\text{s}) \quad (2)$$

Therefore, thermodynamic study of boron and nitrogen in III-V melts is needed in order to control the transport of impurities during the crystal growth. Although Korb *et al.* calculated the contents of boron and nitrogen in a GaAs melt,¹⁴⁾ there are no experimental reports on the relationship between the boron and nitrogen contents of III-V melts.

In the present work, the boron and nitrogen contents of GaAs and InP melts equilibrated with B₂O₃ flux in a BN crucible were measured at 1523 and 1373 K, respectively, and are discussed from a thermodynamic standpoint. The boron and nitrogen contents of the GaAs melt are compared with those in the residue after the industrial LEC crystal growth process.

2. Experimental

A silica ampoule (17^{OD} × 13^{ID} × 100^H) made of highly pure quartz glass tube (T2030, Toshiba Ceramics Co., Ltd.) was employed for the melting of GaAs (99.999%) or InP (99.999%) and B₂O₃ flux in a BN crucible (12^{OD} × 10^{ID} × 30^H, N-1, Denka) as shown in Fig. 1(a). Figure 1(b) shows the schematic cross section of the Ga-As alloy and B₂O₃ flux, which were directly melted in a silica ampoule.¹⁶⁾ The As content of the Ga-As alloy varied from 0 to 50 at%. Before the equilibrium experiment in a silica ampoule, B₂O₃ flux was prepared by melting B₂O₃ with an H₂O content of less than 103 mass ppm and Ga₂O₃ or In₂O₃ in a platinum crucible. B₂O₃ fluxes saturated with Ga₂O₃ and In₂O₃ were used in the melting of GaAs and InP, respectively. The solubility of Ga₂O₃ or In₂O₃ in B₂O₃ flux and the solid phase

^{*1}Graduate Student, Tohoku University.

^{*2}Graduate Student, Tohoku University, Present address: Synergy Materials Research Center, AIST, Nagoya 463-8560, Japan.

Fig. 1 Schematic cross sections of (a) stoichiometric GaAs or InP melt equilibrated with B₂O₃ flux and BN and (b) Ga-As melt (As: 0-50 at.%) equilibrated with B₂O₃ flux and SiO₂.

equilibrated with B₂O₃ flux have been reported elsewhere by the present authors.¹⁷⁾ It was confirmed that the content of Ga₂O₃ or In₂O₃ in the flux was at the solubility limit at each equilibrium temperature.

A silica ampoule with GaAs or InP (small pieces, 3 g) and B₂O₃ flux (small pieces, 0.5 g), which was evacuated to vacuum (<1 Pa) and sealed at room temperature, was heated in an alumina reaction tube using an electrical resistance furnace and held at 1523 or 1373 K. The holding time was 86.4 ks, which was sufficient time for boron and nitrogen to attain equilibrium in the III-V melt coexisted with the B₂O₃ flux and BN or silica. After establishing equilibrium, the III-V melt and B₂O₃ flux in a silica ampoule was quenched with liquid nitrogen, followed by chemical analysis.

The boron, nitrogen and silicon contents of the quenched III-V specimen were analyzed quantitatively. The boron and silicon contents were determined by inductively coupled plasma (ICP) atomic emission spectroscopy (ICPS8100, Shimadzu). The glow discharge plasma mass spectroscopy (GDMS) method (VG9000, VG)¹⁸⁾ was employed for nitrogen analysis, because the nitrogen content of the III-V melt was less than 10 mass ppm. The GDMS merits attention as an analysis method for a trace element in a solid sample. The system is used for the quantitative analysis of high-purity materials including the determination of dopants and impurities at ultratrace levels in semiconductors. The stable and low electrical power discharge minimizes matrix effects and generates fewer multivalent ions than SSMS (spark source mass spectrometry) in the sputtering and ionization process. A double focus mass spectrometer, which provides a means of performing trace determinations at very low levels, was used for mass spectrometry. The relative sensitivity factor (RSF) is needed to quantify the nitrogen content from the ion intensity. The value of the RSF of nitrogen in GaAs has not been reported. It is known that the value of the RSF is related to the first ionization potential.^{19,20)} The value of the RSF of oxygen in GaAs has been reported to be 13.²¹⁾ Since the first ionization potential of nitrogen is comparable to that of oxygen, 10 was used for the RSF of nitrogen in the present work. The in-depth profile of nitrogen in a GaAs single crystal was measured to examine the influence of nitrogen adsorbed on the surface of specimens physically and chemically. A constant value was obtained for the nitrogen content

Fig. 2 Depth profile of nitrogen concentration in single crystal GaAs measured by GDMS.

Fig. 3 Relationship between boron and nitrogen contents of a GaAs melt equilibrated with B₂O₃ flux and BN crucible at 1523 K.

after sputtering 60 μm from the surface of GaAs as shown in Fig. 2. Therefore, the ion intensity at a depth of 60 μm was used to calculate the nitrogen content of GaAs.

3. Results and Discussion

3.1 Boron and nitrogen contents of a III-V melt

Figures 3 and 4 show the relationship between the boron and nitrogen contents of GaAs and InP melts equilibrated with B₂O₃ flux at 1523 and 1373 K, respectively. The melt was coexisted with BN. The boron content increased with decreasing nitrogen content in both the GaAs and InP melts. The equilibrium reaction between boron and nitrogen in a III-V melt coexisted with BN can be expressed by eq. (3).

Fig. 4 Relationship between boron and nitrogen contents of an InP melt equilibrated with B_2O_3 flux and BN at 1373 K.

Since the purity of the BN crucible used in the present work was greater than 99%, the activity of BN can be set to unity referred to pure solid BN. Then, the equilibrium constant of eq. (3) can be written as eq. (4).

$$K_{(3)} = \frac{1}{a_B \cdot a_N} = \frac{1}{f_B [C_B / \text{mass}\%] \cdot f_N [C_N / \text{mass}\%]} \quad (4)$$

where a_i is the Henrian activity of species i (= boron or nitrogen) and its standard state in a III-V melt is taken as 1 mass%, and f_i is the Henrian activity coefficient of species i in III-V melt. Equation (4) gives eq. (5).

$$\log[C_B / \text{mass}\%] = -\log[C_N / \text{mass}\%] - \{\log K_{(3)} + \log(f_B \cdot f_N)\} \quad (5)$$

Figure 5 shows the relationship between the boron and nitrogen contents of GaAs and InP melts coexisted with BN. If there is no interaction between solutes in the III-N melt, *i.e.*, $\log f_B \approx 0$ and $\log f_N \approx 0$, the slope of the line shown in Fig. 5 is expected to be -1 from eq. (5). Since the slopes of the lines in Fig. 5 are -0.14 and -0.07 for GaAs and InP melts, respectively, the interaction between solutes in the III-V melt appears to be strong.

Figure 6 shows the solubility product of BN in a III-V melt ($K'_{(3)} = [C_B / \text{mass}\%] \cdot [C_N / \text{mass}\%]$) as a function of nitrogen content (C_N). Equations (6) and (7) can be obtained by assuming a linear relationship between $\log K'_{(3)}$ and $\log[C_N / \text{mass}\%]$.

$$\log K'_{(3)} \text{ in GaAs} = 0.863 \log[C_N / \text{mass}\%] - 3.21 \quad (1523 \text{ K}, \log[C_N / \text{mass}\%]: -5.3 \sim -3.5) \quad (6)$$

$$\log K'_{(3)} \text{ in InP} = 0.927 \log[C_N / \text{mass}\%] - 3.50 \quad (1373 \text{ K}, \log[C_N / \text{mass}\%]: -5.0 \sim -3.6) \quad (7)$$

The boron content of the melt of Ga-As binary alloy with a range of As content up to 50 at% equilibrated with B_2O_3 flux

Fig. 5 Log-log plots of the relationship between boron and nitrogen content of GaAs and InP melts equilibrated with B_2O_3 flux and BN at 1523 K and 1373 K, respectively.

Fig. 6 Solubility products of boron and nitrogen in GaAs and InP melts equilibrated with B_2O_3 flux and BN at 1523 K and 1373 K, respectively.

and silica is shown in Fig. 7. The boron content ranged between 300 and 500 mass ppm, which is much higher than that in the GaAs melt coexisted with BN (see Fig. 3). As mentioned in section 3.2, the amount of silicon introduced into the melt of Ga-As alloy from silica is related to the increase of the boron content.

3.2 Comparison with reported values of boron and nitrogen contents of III-V melts

Although the boron and nitrogen contents of a III-V melt have not been measured experimentally, there are many experimental reports of the boron contents of single crystal GaAs, which is of commercial significance.^{3,7,8,10,12,22-30} The maximum content of boron in undoped GaAs single crystal grown by the LEC or VGF method ranged from $1 \times 10^{17} \text{ cm}^{-3}$ (0.34 mass ppm) to $1 \times 10^{18} \text{ cm}^{-3}$ (3.4 mass ppm).^{3,8,10,12,22} It has been reported that the addition of

Fig. 7 Boron content of the melt of Ga-As alloy equilibrated with SiO₂ and B₂O₃ flux at 1523 K.

silicon to a GaAs melt increased the maximum content of boron in the resulting GaAs single crystals. Boron contents ranging from $5 \times 10^{17} \text{ cm}^{-3}$ (1.7 mass ppm) to $1.9 \times 10^{19} \text{ cm}^{-3}$ (64 mass ppm) have been reported for Si-doped GaAs single crystal.^{23,26–30} The mechanism of boron incorporation can be explained by the following reaction:^{29,30}

That is, the reduction of B₂O₃ by silicon increases the boron content of the GaAs melt, and then boron in the melt is incorporated in the GaAs single crystal during growth. Boron content of less than 10^{16} cm^{-3} in Si-doped GaAs single crystal grown by the horizontal Bridgman method has been reported.^{27,28} This suggests that the presence of B₂O₃ flux is essential for the increase of boron content in Si-doped GaAs single crystals, and confirms the validity of the mechanism related to eq. (8).

The boron content of a GaAs melt can be estimated by using the distribution coefficient for boron and the maximum boron content of a GaAs crystal. The distribution coefficient for boron was found to lie in the range between 0.3 and 0.7 by calculation from the initial boron content of a GaAs melt and the boron content of the GaAs single crystal at each solidified fraction volume.³¹ Assuming that the distribution coefficient for boron in GaAs is 0.5, the boron content of a GaAs melt was estimated to be 2×10^{17} – $2 \times 10^{18} \text{ cm}^{-3}$ (0.68–6.8 mass ppm) and 5.0×10^{18} – $3.8 \times 10^{19} \text{ cm}^{-3}$ (17–128 mass ppm) for the LEC process with undoped and Si-doped GaAs, respectively. The boron content of a GaAs melt equilibrated with B₂O₃ flux and BN is compared with the estimated value using the distribution coefficient for boron in Fig. 8. The calculated values of boron and nitrogen contents using ChemSage¹⁴ are included in the figure. Although the calculated values are much lower than those obtained in the present work and estimated using the distribution coefficient, the trend that the boron content decreased with increasing nitrogen content agrees with the present result. The filled circle in Fig. 8 denotes the boron content of a GaAs melt

Fig. 8 Comparison of the present and the reported values of boron and nitrogen contents of a GaAs melt equilibrated with B₂O₃ flux.

Fig. 9 Silicon content of the melt of Ga-As alloy equilibrated with SiO₂ and B₂O₃ flux at 1523 K.

coexisted with silica (see the stoichiometric composition of Ga-As alloy in Fig. 7). Since the nitrogen content of GaAs after melting with silica is expected to be very low, the plot is located on the left side in the figure. Figure 9 shows the silicon content of the melt of Ga-As alloy equilibrated with B₂O₃ flux and silica. A silicon content of around $4.6 \times 10^{19} \text{ cm}^{-3}$ (400 mass ppm) was obtained at the stoichiometric composition of Ga-As alloy, which was much larger than that of the GaAs melt equilibrated with BN ($< 1 \text{ mass ppm}$, $1.1 \times 10^{17} \text{ cm}^{-3}$). Therefore, reaction (8) proceeded to the right and the boron content of the GaAs melt increased.

3.3 Comparison with the contents of boron and nitrogen in the residue after crystal growth

Since the distribution coefficients of boron and nitrogen are less than unity, boron and nitrogen in the residue after the industrial LEC crystal growth process may be close to the

Fig. 10 Comparison of the boron and nitrogen contents of GaAs melts equilibrated with B_2O_3 flux and a BN crucible.

equilibrium level with BN. The boron and nitrogen contents of the residue after LEC crystal growth of GaAs were measured. Figure 10 compares the present results with those obtained from this residue analysis. In order to control the boron and nitrogen contents of the melt during the crystal growth, the N_2 gas pressure in the crystal growth chamber was varied. The values of boron and nitrogen contents and the slope of the line obtained in the residue agreed well with the present laboratory data.

4. Conclusions

The relationship between the boron and nitrogen contents of GaAs and InP melts equilibrated with B_2O_3 flux was examined at 1523 and 1373 K, respectively. The following results were obtained:

(1) The boron content decreased with increasing nitrogen content of the GaAs and InP melts coexisted with BN. The solubility products of BN in the GaAs and InP melts ($K'_{(3)} = [C_B/\text{mass\%}] \cdot [C_N/\text{mass\%}]$) were expressed as follows.

$$\text{GaAs: } \log K'_{(3)} = 0.863 \log[C_N/\text{mass\%}] - 3.21 \\ (1523 \text{ K, } \log[C_N/\text{mass\%}] : -5.3 \sim -3.5)$$

$$\text{InP: } \log K'_{(3)} = 0.927 \log[C_N/\text{mass\%}] - 3.50 \\ (1373 \text{ K, } \log[C_N/\text{mass\%}] : -5.0 \sim -3.6)$$

(2) The boron content of a GaAs melt coexisted with silica was higher than that of one coexisted with BN. It is thought that the reduction of B_2O_3 by silicon that was introduced into the melt from silica led the increase in boron content.

(3) The relationship between boron and nitrogen contents in GaAs melts equilibrated with B_2O_3 flux and BN agreed well with that in the residue after the LEC crystal growth process for GaAs.

Acknowledgments

The authors thank Mr. Hisanori Koda, former graduate student at Tohoku University, for his assistance in the melt experiments. The authors are indebted to Mr. K. Tayama for his cooperation in the nitrogen analysis, and thank Mr. S. Kagaya and Mr. R. Nakamura for their continuous encouragement throughout this study.

REFERENCES

- 1) A. Kawasaki: *Electronic Materials and Parts* **34** (1995) 28–33.
- 2) J. Nishio and K. Terashima: *J. Crystal Growth* **96** (1989) 605–608.
- 3) J. Nishio and H. Fujita: *J. Crystal Growth* **134** (1993) 97–104.
- 4) J. D. Oberstar, B. G. Streetman, J. E. Baker, P. Williams, R. L. Henry and E. M. Awiggard: *J. Crystal Growth* **54** (1981) 443–448.
- 5) Y. Itoh, Y. Kadota, T. Nozaki, H. Fukushima and K. Takeda: *Jpn. J. Appl. Phys.* **28** (1989) 210–211.
- 6) T. Kikuta, H. Emori, T. Fukuda and K. Ishida: *J. Crystal Growth* **76** (1986) 517–520.
- 7) J. Osaka, F. Hyuga, T. Kobayashi, Y. Yamada and F. Orito: *Appl. Phys. Lett.* **50** (1987) 191–193.
- 8) H. Emori, T. Kikuta, T. Inada, T. Obokata and T. Fukuda: *Jpn. J. Appl. Phys.* **24** (1985) L291–L293.
- 9) L. Fisher, U. Lambert, G. Nagel, H. Rüfer and E. Tomzig: *J. Crystal Growth* **153** (1995) 90–96.
- 10) K. Terashima, J. Nishio, S. Washizuka and M. Watanabe: *J. Crystal Growth* **84** (1987) 247–252.
- 11) P. J. Doering, B. Freidenreich, R. J. Tobin, P. J. Pearah, J. P. Tower and R. M. Ware: *Proceedings of the 6th Conference on Semi-insulating III-V Materials*, edited by A. G. Milnes and C. J. Miner, Philadelphia, PA, (1991) pp. 173–181.
- 12) M. Seifert, M. Neubert, W. Ulrich, B. Wiedermann, J. Donecker, J. Kluge, E. Wolf, D. Klinger and P. Rodolph: *J. Crystal Growth* **158** (1996) 409–417.
- 13) C. Gärtner, T. Flade, M. Jurisch, A. Köhler, J. Korb, U. Kretzer and B. Weinert: *J. Crystal Growth* **198/199** (1999) 355.
- 14) J. Korb, T. Flade, M. Jurisch, A. Köhler, Th. Reinhold and B. Weinert: *J. Crystal Growth* **198/199** (1999) 343.
- 15) W. A. Oates and H. Wenzl: *J. Crystal Growth* **191** (1998) 3033–312.
- 16) K. Tajima, Y. Hino, T. Narushima and Y. Iguchi: *Mater. Trans., JIM* **41** (2000) 714–718.
- 17) D. Sajuti, M. Yano, T. Narushima and Y. Iguchi: *Mater. Trans., JIM* **34** (1993) 1195–1199.
- 18) K. Wagatsuma: *Metals and Technology* **72** (2002) 770–776.
- 19) S. Itoh, H. Yamaguchi, T. Hobo and T. Kobayashi: *Tetsu-to-Hagané* **99** (2002) 575–579.
- 20) M. Saito: *Bunseki Kagaku* **48** (1999) 77–86.
- 21) Standard RSF file, VG Elemental.
- 22) J. Nishio and H. Fujimoto: *J. Crystal Growth* **141** (1994) 249–255.
- 23) Y. Homma and Y. Ishii: *J. Appl. Phys.* **56** (1984) 1892–1894.
- 24) C. G. Hopkins, V. R. Deline, R. J. Blattner, C. A. Evans, Jr. and T. J. Magee: *Appl. Phys. Lett.* **36** (1980) 989–990.
- 25) L. B. Ta, H. M. Hobgood and R. N. Thomas: *Appl. Phys. Lett.* **41** (1982) 1091–1093.
- 26) O. Pätzold, G. Gärtner and G. Irmer: *Phys. Status Solidi B*, **232** (2002) 314–322.
- 27) I. C. Bassignana, D. A. Macquistan, G. C. Hillier, R. Streater, D. Beckett, A. Majeed and C. Miner: *J. Crystal Growth* **178** (1997) 445–458.
- 28) F. Orito, H. Okada, M. Nakajima, T. Fukuda and K. Tajimura: *J. Electron. Mater.* **15** (1986) 87–90.
- 29) G. Frigerio, C. Mucchino, J. L. Weyher, L. Zanotti and C. Paorici: *J. Crystal Growth* **99** (1990) 685–691.
- 30) K. Hashio, S. Sawada, M. Tatsumi, K. Fujita and S. Akai: *J. Crystal Growth* **173** (1997) 33–41.
- 31) T. Yamada, R. Toba and R. Nakamura: unpublished work.