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Behavior of Oxygen in Ga–As Melts with the Range of As Content up to 5 mass% Equilibrated with B_2O_3 Flux

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The equilibrium between Ga–As melt, containing arsenic up to 5 mass%, and B_2O_3 flux was investigated from 1273 to 1523 K in a silica ampoule. The effect of arsenic on equilibrium contents of oxygen, boron and silicon in the melt was investigated. The results were analyzed using interaction parameters. The equilibrium distribution ratio of oxygen between Ga–As melt and B_2O_3 flux decreased with the increase of temperature, Ga_2O_3 content in the flux and arsenic content in the melt. The activity of Ga_2O_3 in the B_2O_3 flux was determined in the temperature range from 1273 to 1523 K, which is relevant to the practical process of crystal growth of GaAs.

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1. Introduction

The liquid encapsulated Czochralski (LEC) and the vertical gradient freeze (VGF) methods with B_2O_3 flux as an encapsulant are employed to synthesize low cost and low dislocation density single crystals of III–V compound semiconductor,$^{1-3)}$ respectively. It is well known that the impurities and doping elements such as boron, hydrogen, silicon, carbon or oxygen were introduced into the single crystals via III–V melts$^{4-10)}$ in these processes. Understanding the redox reaction at the interface between III–V melt and a crucible or B_2O_3 flux is a key issue to control the contents of impurities and doping elements in the III–V melt. The equilibrium between III–V melt and B_2O_3 flux determines the oxygen potential of the III–V melt in the LEC and VGF processes. The present authors have studied the equilibrium between III-group metals and B_2O_3 flux and reported the activity of Ga_2O_3 in B_2O_3 flux at 1273 to 1373 K and the standard free energies of formation of complex III-group metal oxides$^{11)}$ as a fundamental study of the reaction between III–V melt and B_2O_3 flux. In our previous studies, however, the temperature range investigated for equilibrium study was lower than the melting point of GaAs (1511 K), and V-group elements were not included in the system. In the present work, the equilibrium between Ga–As melt with the range of arsenic content up to 5 mass% and B_2O_3 flux was examined in the temperature range from 1273 to 1523 K, and interaction parameters, oxygen distribution and Ga_2O_3 activity in B_2O_3 flux were obtained based on thermodynamic analysis.

2. Experimentals

Ga–As melt with the mass of 4 g and B_2O_3 flux with 2 g were equilibrated in a silica ampoule with an internal diameter of 13 mm and the height of 120 mm. Arsenic contents in the Ga–As melts were controlled in the range from 0 to 5 mass% by addition of GaAs with 5 N grade to pure gallium metal with 6 N grade. Before the equilibrium experiment in the silica ampoule, the B_2O_3 flux with the different contents of Ga_2O_3 was prepared by melting B_2O_3 powder with H_2O content less than 103 ppm and Ga_2O_3 powder in a platinum crucible. Ga_2O_3 contents in B_2O_3 flux were varied up to solubility limit at a respective temperature.$^{12)}$ The silica ampoule containing Ga–As alloy and B_2O_3 flux was evacuated to vacuum and sealed at room temperature, followed by heating in the temperature range from 1273 to 1523 K. The holding time at a respective temperature was 21.6 ks, which was the enough time period to attain equilibrium between Ga–As melt and B_2O_3 flux as already reported.$^{13)}$ After establishment of equilibrium, the liquid melt and flux in a silica ampoule were quenched with liquid nitrogen. Solidified alloy of Ga–As and B_2O_3 flux formed two layers, so that, were easily separated manually, followed by chemical analyses. Oxygen contents in the Ga–As alloy were measured by the inert gas fusion-IR absorption method (TC-436, LECO). The detailed procedures of the oxygen analysis have been reported elsewhere.$^{13)}$ Arsenic, boron and silicon contents in the Ga–As alloy were determined by the ICP mass spectroscopy (SPQ-9000, SII). The gallium contents in the flux were analyzed by ICP atomic emission spectroscopy (SPS1200A, SII).

3. Results and Discussion

3.1 Effect of arsenic content on the equilibrium contents of oxygen, boron and silicon in the Ga–As melt

The relationship between oxygen and arsenic contents in Ga–As melt equilibrated with B_2O_3 flux containing saturated Ga_2O_3 is shown in Fig. 1. The oxygen solubility increased with increasing arsenic contents in Ga–As melts at all the temperatures examined. The equilibrium reaction between Ga–As melt and B_2O_3 flux can be expressed by eq. (1).

$$2\mathrm{Ga}(l) + 3\underline{\mathrm{O}}(1\ \mathrm{mass\%\ in\ melt}) = \mathrm{Ga_2O_3(s)} \qquad (1)$$

The equilibrium constant of eq. (1) can be written as eq. (2).

$$K_{(1)} = \frac{a_{\mathrm{Ga_2O_3}}}{a_{\mathrm{Ga}}^2 \cdot a_{\underline{\mathrm{O}}}^3} = \frac{a_{\mathrm{Ga_2O_3}}}{a_{\mathrm{Ga}}^2 (f_{\underline{\mathrm{O}}} \cdot [C_{\underline{\mathrm{O}}}(\mathrm{mass\%})])^3} \qquad (2)$$

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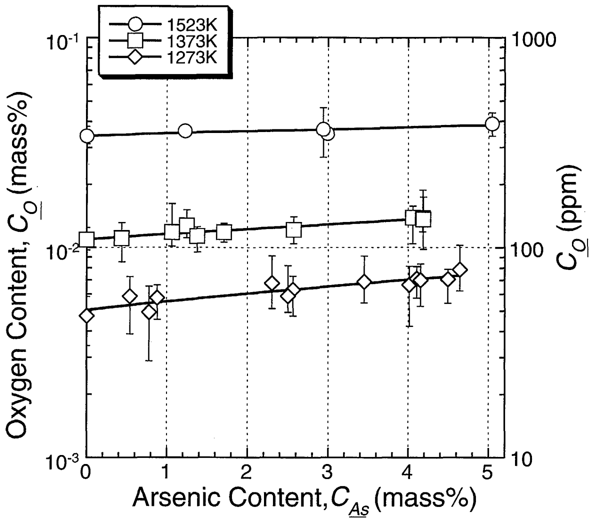

Fig. 1 Effect of arsenic on oxygen solubility in gallium-arsenic melt equilibrated with B_2O_3 flux.

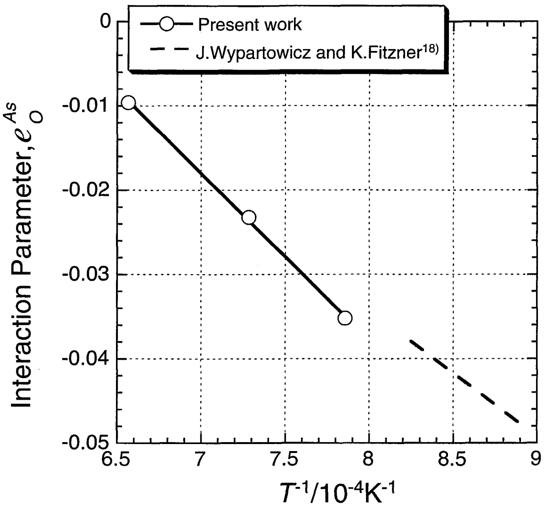

Fig. 2 Temperature dependence of interaction parameter ($e_{\mathrm{O}}^{\mathrm{As}}$).

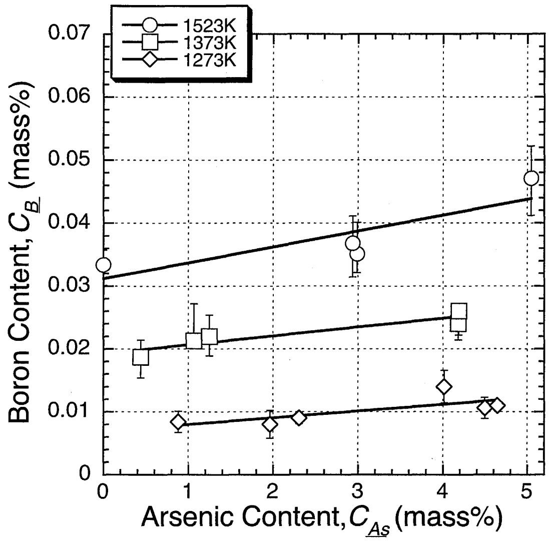

Fig. 3 Effect of arsenic on boron content in gallium-arsenic melt equilibrated with B_2O_3 flux.

a_{Ga} and $a_{\mathrm{Ga_2O_3}}$ are the activities of gallium and Ga_2O_3 referred to pure liquid gallium and pure solid Ga_2O_3, respectively. $a_{\underline{\mathrm{O}}}$ is the oxygen activity in Ga–As melt and its standard state in the melt is taken as 1 mass%. $f_{\underline{\mathrm{O}}}$ is the activity coefficient of oxygen in the melt. Yamaguchi *et al.*[14] measured the gallium activity in Ga–As melt in the temperature range between 1423 and 1573 K. According to their results, the gallium activity is 0.97 in the arsenic content of 5 mass% at 1573 K. Therefore, it was assumed in the present work that the gallium activity is unity. $a_{\mathrm{Ga_2O_3}}$ can also be assumed to be unity because B_2O_3 flux was saturated with solid Ga_2O_3 that is the phase coexisted with B_2O_3 flux in the present temperature range.[12] Then, $\boldsymbol{K}_{(1)}$ can be rewritten as eq. (3).

$$\boldsymbol{K}_{(1)} = \frac{1}{(f_{\underline{\mathrm{O}}} \cdot [C_{\underline{\mathrm{O}}}(\text{mass\%})])^3} \tag{3}$$

Equation (3) gives eq. (4).

$$-1/3 \log \boldsymbol{K}_{(1)} = \log f_{\underline{\mathrm{O}}} + \log[C_{\underline{\mathrm{O}}}(\text{mass\%})] \tag{4}$$

The activity coefficient of oxygen in Ga–As melt can be expressed by eq. (5) using interaction parameters, $e_{\mathrm{O}}^{\mathrm{As}}$, $e_{\mathrm{O}}^{\mathrm{O}}$, $e_{\mathrm{O}}^{\mathrm{B}}$ and $e_{\mathrm{O}}^{\mathrm{Si}}$.

$$\begin{aligned}\log f_{\underline{\mathrm{O}}} &= e_{\mathrm{O}}^{\mathrm{As}}[C_{\underline{\mathrm{As}}}(\text{mass\%})] + e_{\mathrm{O}}^{\mathrm{O}}[C_{\underline{\mathrm{O}}}(\text{mass\%})] \\ &\quad + e_{\mathrm{O}}^{\mathrm{B}}[C_{\underline{\mathrm{B}}}(\text{mass\%})] + e_{\mathrm{O}}^{\mathrm{Si}}[C_{\underline{\mathrm{Si}}}(\text{mass\%})]\end{aligned} \tag{5}$$

Since the equilibrium contents of oxygen, boron and silicon in the Ga–As melt are much lower than arsenic content, eq. (5) can be approximated by eq. (6).

$$\log f_{\underline{\mathrm{O}}} = e_{\mathrm{O}}^{\mathrm{As}}[C_{\underline{\mathrm{As}}}(\text{mass\%})] \tag{6}$$

When eq. (6) is substituted in eq. (4), eq. (7) can be obtained.

$$\log[C_{\underline{\mathrm{O}}}(\text{mass\%})] = -1/3 \log \boldsymbol{K}_{(1)} - e_{\mathrm{O}}^{\mathrm{As}}[C_{\underline{\mathrm{As}}}(\text{mass\%})] \tag{7}$$

Then, the interaction parameter ($e_{\mathrm{O}}^{\mathrm{As}}$) can be calculated using the slope of the lines in Fig. 1. It is well known that an interaction parameter depends on the inverse of the temperature.[15–17] Equation (8) could be obtained assuming a linear relationship between the interaction parameter and $1/T$ as shown in Fig. 2.

$$e_{\mathrm{O}}^{\mathrm{As}} = 0.12 - 1.98 \times 10^2/T \quad (1273\text{–}1523\,\mathrm{K}) \tag{8}$$

The present values of $e_{\mathrm{O}}^{\mathrm{As}}$ are compared with those reported by Wypartowicz and Fitzner[18] in Fig. 2. They measured $e_{\mathrm{O}}^{\mathrm{As}}$ in the temperature range from 1123 to 1223 K by the electromotive force method with the range of arsenic content from 3 to 7 mass%. Our results are in good agreement with their extrapolated values to higher temperatures.

Figures 3 and 4 show boron and silicon contents in the Ga–As, respectively. Both of boron and silicon contents slightly increased as arsenic contents in the Ga–As melt increased. The equilibrium reaction between B_2O_3 flux and boron in Ga–As melt is represented by eq. (9).

$$B_2O_3(l) = 2\underline{\mathrm{B}}(1\ \text{mass\% in melt}) + 3\underline{\mathrm{O}}(1\ \text{mass\% in melt}) \tag{9}$$

The equilibrium constant of eq. (9) can be written as eq. (10).

$$\boldsymbol{K}_{(9)} = \frac{a_{\underline{\mathrm{B}}}^2 \cdot a_{\underline{\mathrm{O}}}^3}{a_{\mathrm{B_2O_3}}} \tag{10}$$

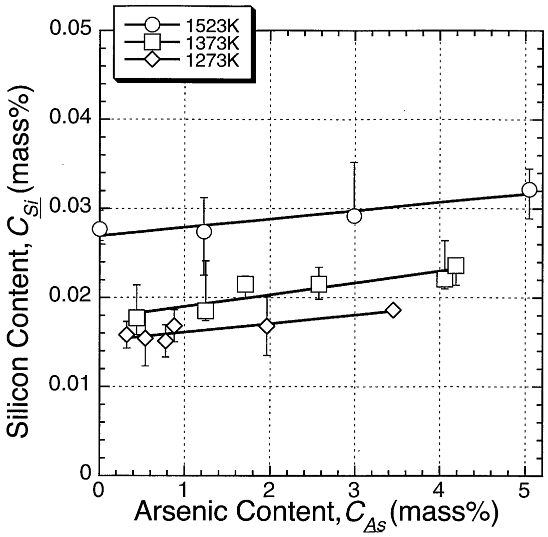

Fig. 4 Effect of arsenic on silicon content in gallium-arsenic melt equilibrated with B_2O_3 flux.

$\boldsymbol{a}_{\underline{B}}$ is the boron activity in Ga–As melt and its standard state is taken as 1 mass% in Ga–As melt. $\boldsymbol{a}_{B_2O_3}$ is the activity of B_2O_3 in the flux and can be assumed to be unity because SiO_2 and arsenic contents in the B_2O_3 flux were less than 3 mass% and the detection limit of ICP atomic emission spectroscopy, respectively. Then, eq. (10) can be represented by eq. (11).

$$\boldsymbol{K}_{(9)} = \boldsymbol{a}_{\underline{B}}^2 \boldsymbol{a}_{\underline{O}}^3 = (f_{\underline{B}} \cdot [C_{\underline{B}}(\text{mass\%})])^2 (f_{\underline{O}} \cdot [C_{\underline{O}}(\text{mass\%})])^3 \tag{11}$$

$f_{\underline{B}}$ is the activity coefficient of boron in Ga–As melt. Equation (12) can be derived from eq. (11).

$$\log \boldsymbol{K}'_{(9)} = \log \boldsymbol{K}_{(9)} - 2\log f_{\underline{B}} - 3\log f_{\underline{O}} \tag{12}$$

where $\boldsymbol{K}'_{(9)}$ is an apparent equilibrium constant and shown by eq. (13).

$$\log \boldsymbol{K}'_{(9)} = \log[C_{\underline{B}}(\text{mass\%})]^2[C_{\underline{O}}(\text{mass\%})]^3 \tag{13}$$

$f_{\underline{B}}$ can be expressed by eq. (14) using an interaction parameter, $e_{\mathrm{B}}^{\mathrm{As}}$, because oxygen, boron and silicon contents in Ga–As melt are much lower than the arsenic content.

$$\log f_{\underline{B}} = e_{\mathrm{B}}^{\mathrm{As}}[C_{\underline{As}}(\text{mass\%})] \tag{14}$$

Substituting eq. (6) and (14) for $\log f_{\underline{O}}$ and $\log f_{\underline{B}}$ in eq. (12) gives eq. (15).

$$\log \boldsymbol{K}'_{(9)} = \log \boldsymbol{K}_{(9)} - (2e_{\mathrm{B}}^{\mathrm{As}} + 3e_{\mathrm{O}}^{\mathrm{As}})[C_{\underline{As}}(\text{mass\%})] \tag{15}$$

The relationship between $\log \boldsymbol{K}'_{(9)}$ and $C_{\underline{As}}$ is shown in Fig. 5. The value of $2e_{\mathrm{B}}^{\mathrm{As}}+3e_{\mathrm{O}}^{\mathrm{As}}$ can be calculated assuming the linear relationship between $\log \boldsymbol{K}'_{(9)}$ and $C_{\underline{As}}$. The value of $e_{\mathrm{B}}^{\mathrm{As}}$ could be evaluated to be -0.03 in the temperature range between 1273 and 1523 K using eq. (8) as the value of $e_{\mathrm{O}}^{\mathrm{As}}$. As for silicon, the equilibrium reaction between silica ampoule and silicon in Ga–As melt can be shown by eq. (16)

$$SiO_2(s) = \underline{Si}(1\ \text{mass\% in melt}) + 2\underline{O}(1\ \text{mass\% in melt}) \tag{16}$$

The activity of silica can be assumed to be unity because the melt coexisted with silica ampoule. Then the equilibrium constant of eq. (16) is expressed by eq. (17)

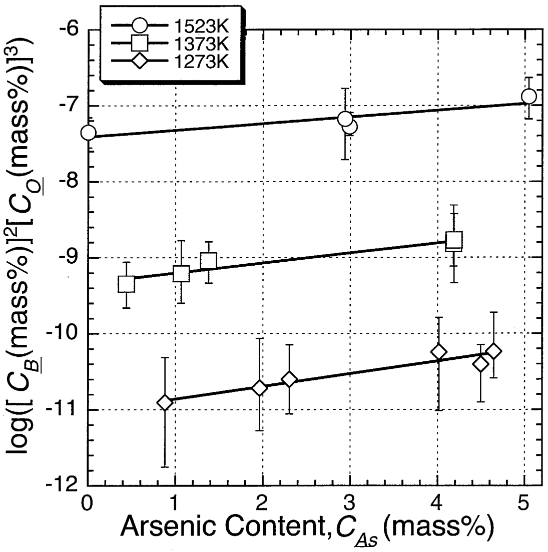

Fig. 5 Effect of arsenic on the apparent equilibrium constant ($\boldsymbol{K}'_{(9)}$) in gallium-arsenic melt equilibrated with B_2O_3 flux.

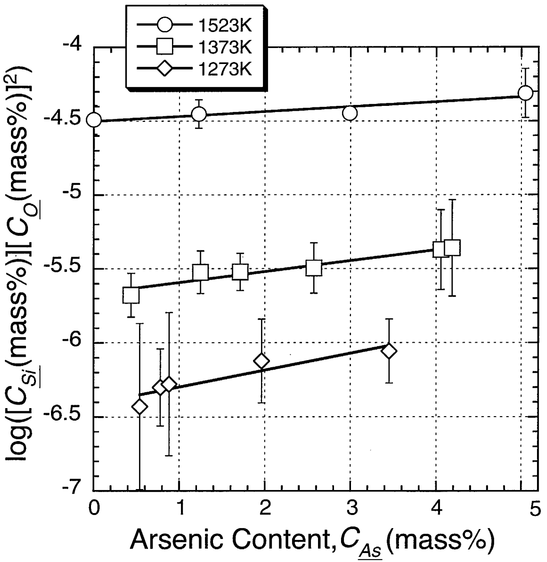

Fig. 6 Effect of arsenic on the apparent equilibrium constant ($K'_{(16)}$) in gallium-arsenic melt equilibrated with B_2O_3 flux.

$$\boldsymbol{K}_{(16)} = \boldsymbol{a}_{\underline{Si}} \cdot \boldsymbol{a}_{\underline{O}}^2 = (f_{\underline{Si}} \cdot [C_{\underline{Si}}(\text{mass\%})])(f_{\underline{O}} \cdot [C_{\underline{O}}(\text{mass\%})])^2 \tag{17}$$

where $\boldsymbol{a}_{\underline{Si}}$ and $f_{\underline{Si}}$ are the activity of silicon and the activity coefficient of silicon in Ga–As melt, respectively. The apparent equilibrium constant of eq. (16) can be expressed by eq. (18).

$$\begin{aligned}\log \boldsymbol{K}'_{(16)} &= \log[C_{\underline{Si}}(\text{mass\%})][C_{\underline{O}}(\text{mass\%})]^2 \\ &= \log \boldsymbol{K}_{(16)} - (e_{\mathrm{Si}}^{\mathrm{As}} + 2e_{\mathrm{O}}^{\mathrm{As}})[C_{\underline{As}}(\text{mass\%})]\end{aligned} \tag{18}$$

Figure 6 shows the relationship between the apparent equilibrium constant of eq. (16) and $e_{\mathrm{Si}}^{\mathrm{As}} + 2e_{\mathrm{O}}^{\mathrm{As}}$. The value of $e_{\mathrm{Si}}^{\mathrm{As}}$ at a respective temperature was obtained using the result of Fig. 6 and the value of $e_{\mathrm{O}}^{\mathrm{As}}$. Then, the temperature dependence of $e_{\mathrm{Si}}^{\mathrm{As}}$ value was expressed by eq. (19).

$$e_{\mathrm{Si}}^{\mathrm{As}} = 0.13\text{–}2.11 \times 10^2/T \quad (1273\text{–}1523\ \mathrm{K}) \tag{19}$$

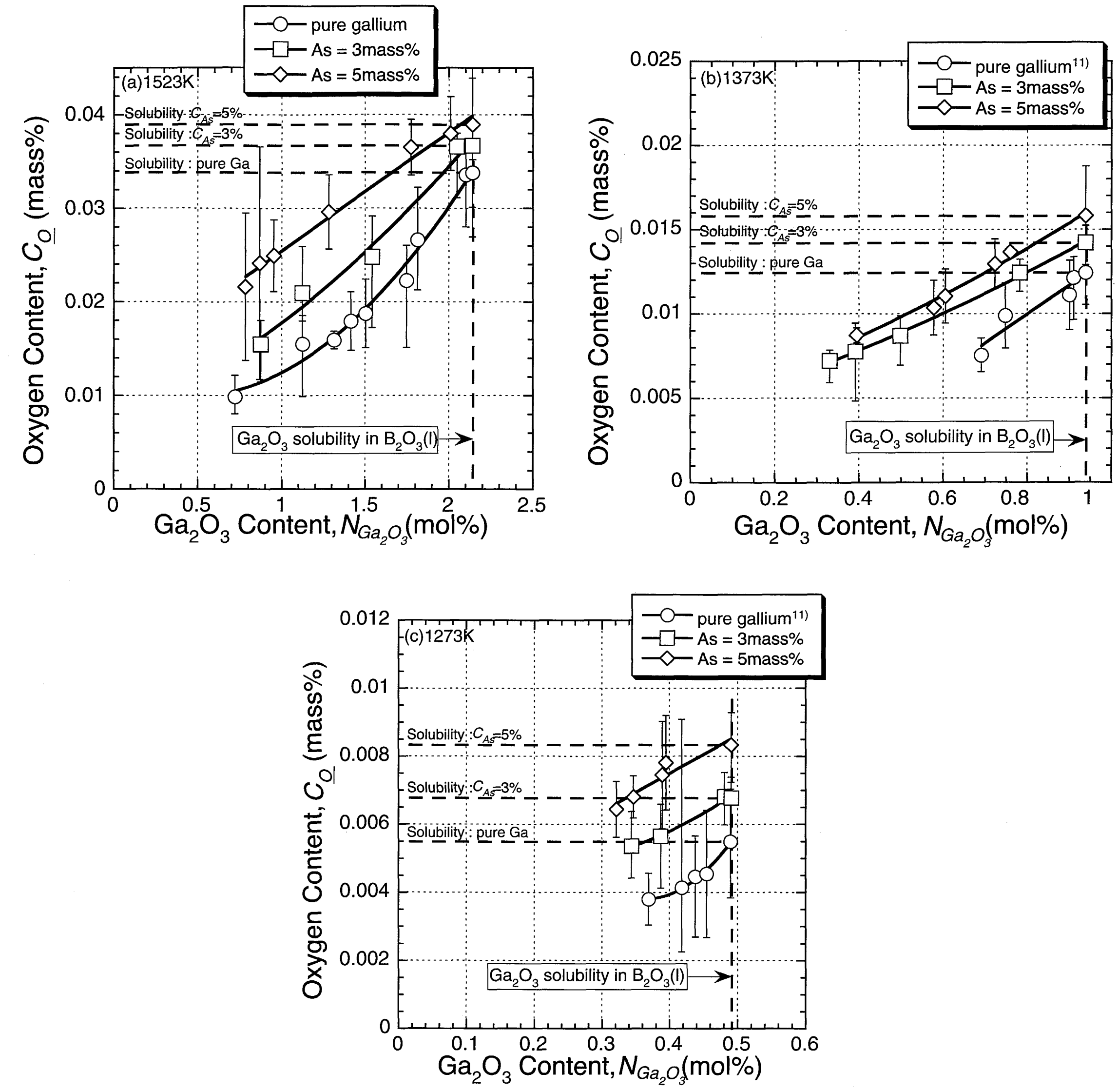

Fig. 7 Oxygen contents in gallium-arsenic melt equilibrated with B_2O_3 flux. (a) 1523 K, (b) 1373 K, (c) 1273 K.

3.2 Distribution of oxygen between B_2O_3 flux and Ga–As melt

The oxygen contents in Ga–As melt equilibrated with B_2O_3 flux containing unsaturated Ga_2O_3 at 1523, 1373 and 1273 K are shown in Figs. 7(a), (b) and (c), respectively. The solubilities of Ga_2O_3 in B_2O_3 flux and oxygen in Ga–As melt are demonstrated in these figures, which were reported by the present authors.[12)] The distribution ratio of oxygen ($L_{\underline{O}}$) is defined by eq. (20) in the present work.[11)]

$$L_{\underline{O}} = \frac{N_{Ga_2O_3}}{[C_{\underline{O}}(\text{mass\%})]^3} \tag{20}$$

The values of $L_{\underline{O}}$ at 1523, 1373 and 1273 K are shown in Figs. 8(a), (b) and (c), respectively. It was found that $L_{\underline{O}}$ decreased with the increase of the temperature, Ga_2O_3 contents in the flux and arsenic contents in the melt. $a_{Ga_2O_3}$ can be expressed by eq. (21).

$$a_{Ga_2O_3} = [f_{\underline{O}} \cdot C_{\underline{O}}(\text{mass\%})]^3 \exp\left(-\frac{\Delta G^\circ_{(1)}}{RT}\right) \tag{21}$$

where R is the gas constant and $\Delta G^\circ_{(1)}$ is the standard free energy change of eq. (1), which was reported to be expressed by eq. (22) as the present authors reported.[13)]

$$\Delta G^\circ_{(1)} = -356000 + 149T\,(J) \tag{22}$$

The values of Ga_2O_3 activity in B_2O_3 flux calculated with eqs. (21), (22) and the oxygen contents in the melt (see Fig. 7) are shown in Fig. 9. The activity of Ga_2O_3 is important thermodynamic data for controlling the oxygen potential at the interface between B_2O_3 flux and III–V melt in LEC and VGF processes for crystal growth of GaAs. The Ga_2O_3 activity in B_2O_3 flux was obtained experimentally in the wide temperature range for the first time.

4. Conclusion

The oxygen, boron and silicon contents in Ga–As melt with the range of arsenic content up to 5 mass% equilibrated with B_2O_3 flux were measured in the temperature range of 1273 to 1523 K, yielding the following findings.

(1) The interaction parameters in Ga–As melt were deter-

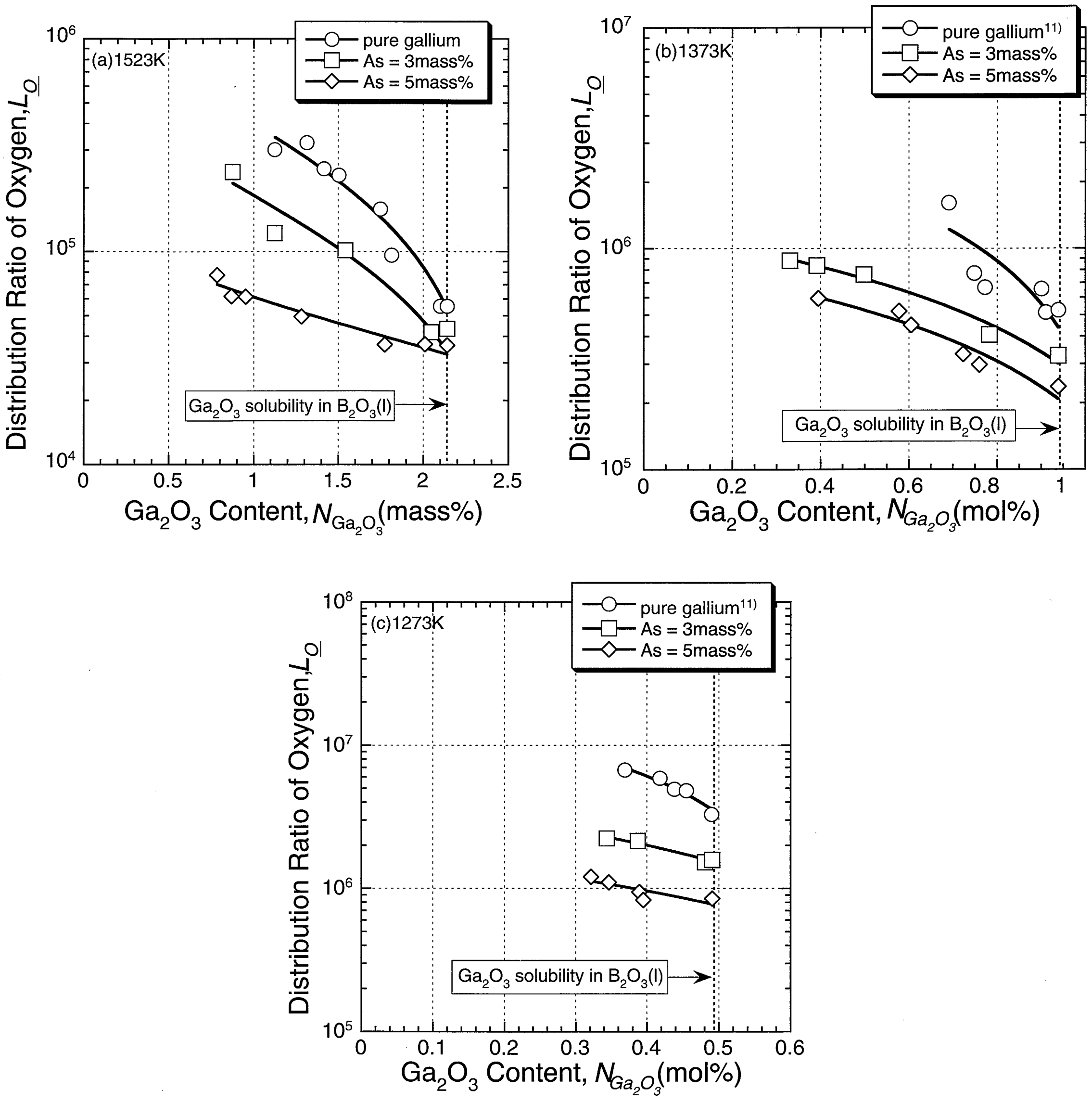

Fig. 8 The distribution ratio of oxygen between B_2O_3 flux and gallium-arsenic melt. (a) 1523 K, (b) 1373 K, (c) 1273 K.

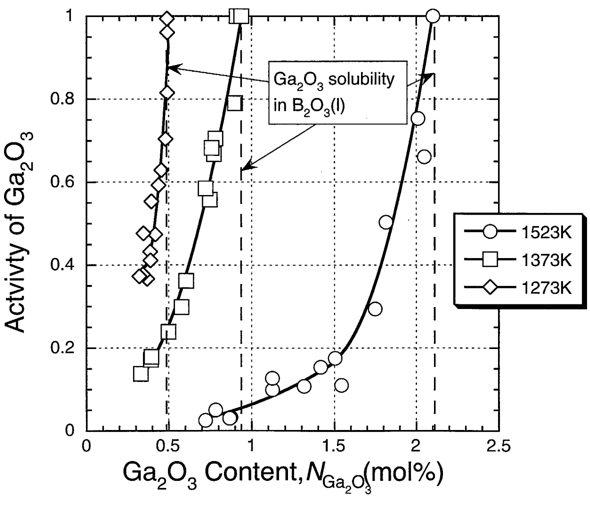

Fig. 9 Activity of Ga_2O_3 in B_2O_3 flux.

mined as follows:

$$e_{O}^{As} = 0.12\text{–}1.98 \times 10^2/T \quad (1273\text{–}1537\,\mathrm{K})$$

$$e_{B}^{As} = -0.03 \quad (1273\text{–}1537\,\mathrm{K})$$

$$e_{Si}^{As} = 0.13\text{–}2.11 \times 10^2/T \quad (1273\text{–}1537\,\mathrm{K})$$

(2) The equilibrium distribution ratio of oxygen between Ga–As melt and B_2O_3 flux decreased with the increases of the temperature, Ga_2O_3 contents and arsenic contents.

(3) The activity of Ga_2O_3 in the B_2O_3 flux was obtained in the temperature range adopted in practical process of crystal growth of GaAs.

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