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Phase Diagrams of the Ga_2O_3–B_2O_3 and In_2O_3–B_2O_3 Binary Systems

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The solubility of Ga_2O_3 or In_2O_3 in liquid B_2O_3 which is used as a flux for pulling single crystal of III-V compounds has been measured by the sampling method in the temperature range of 973 to 1573 K. The gallium or indium contents in the samples were analyzed by ICP atomic emission spectroscopy. The phase equilibrium in the Ga_2O_3–B_2O_3 or In_2O_3–B_2O_3 binary system has been determined by X-ray diffraction and differential thermal analysis for the precipitates in liquid phase or the binary compounds which were synthesized from pure oxides. The solid phase equilibrated with liquid phase was clarified. The phase diagrams of the Ga_2O_3–B_2O_3 and In_2O_3–B_2O_3 binary systems were constructed.

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I. Introduction

Recently, single crystals of III-V compounds for semiconductor materials are of interest in the electronic industry. Many of the III-V compound semiconductors have excellent electrical and optical properties. These semiconductors, such as GaAs and InP, are used mainly for high-speed LSI, microwave, and photonic applications. At the present time, most single crystals of GaAs or InP for semiconductor materials are produced by the Czochralski pulling method. To prevent vaporization of arsenic or phosphorus in the III-V melt during single crystal growth, the liquid encapsulated Czochralski (LEC) method is employed. In the LEC process, molten boron oxide (B_2O_3) is used as the liquid encapsulant because of its transparency in the visible, low vapor pressure, low density, and low melting point[(1)-(3)]. In order to control the contents of impurities and a stoichiometric composition during single crystal growth of III-V compounds, the knowledge about the reactions between III-V melt and B_2O_3 flux is very important. To be successful in this effort, a better understanding of the phase diagram is necessary. However, there are very few thermodynamic studies about these reactions and both the phase diagrams of the Ga_2O_3–B_2O_3 and In_2O_3–B_2O_3 binary systems have not been yet reported.

In the present work, as a first-step of these studies, the solubility of Ga_2O_3 or In_2O_3 in liquid B_2O_3 and the solid phase equilibrated with liquid phase in the Ga_2O_3–B_2O_3 or In_2O_3–B_2O_3 binary system have been investigated. From these results, the phase diagrams of the Ga_2O_3–B_2O_3 and In_2O_3–B_2O_3 binary systems are presented.

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II. Experiments

Figure 1 shows a schematic diagram of the experimental apparatus. The specimens in a platinum crucible were placed in the hot zone of the reaction tube flowing dried argon gas. The temperature was controlled within ±2 K in the range between 973 and 1573 K by a PID controller and measured by a Pt/Pt13Rh thermocouple set inside of the reaction tube.

The solubility of Ga_2O_3 or In_2O_3 in liquid B_2O_3 was measured by the sampling method. These measurements were approached by the following two different methods,

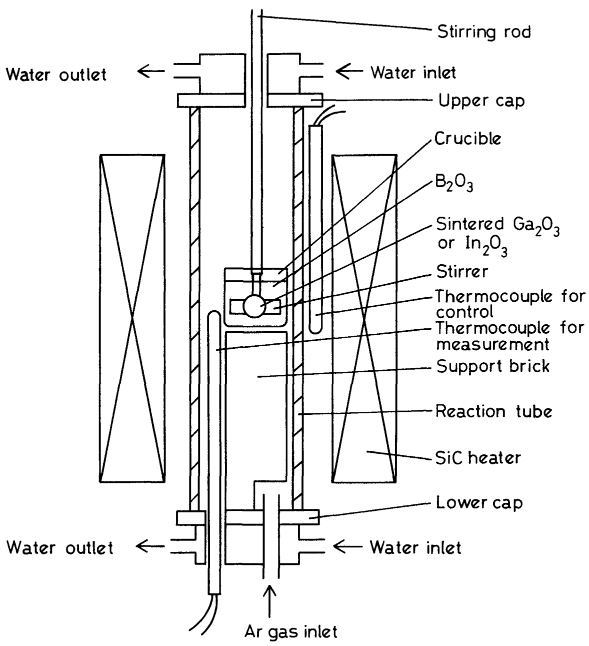

Fig. 1 Schematic diagram of the experimental apparatus.

the experiments of supersaturation side and undersaturation side as shown schematically in Fig. 2.

The experiments of supersaturation side were carried out under Ga_2O_3 or In_2O_3 supersaturated condition. The crucible containing the powder mixture of B_2O_3 and Ga_2O_3 or In_2O_3 pure oxides in the required proportions was heated up to 50 K higher than the desired measurement temperatures and kept at this temperature for 72 ks. The dissolution process was carried out with stirring to accelerate its reaction. After stirring was stopped, the temperature was lowered to the desired temperature. At the specified temperature, a part of the melt was quenched by a Cu rod sampler cooled by water. The chemical analysis of the gallium or indium contents in the samples, after dissolved in the dilute nitric acid solution, were made by ICP atomic emission spectroscopy. After constant concentration of Ga_2O_3 or In_2O_3 was obtained, the melt temperature was lowered to the next experimental temperature. In every experimental run, the solubility measurements can be made at 3 or 4 different temperatures.

At the experiments of undersaturation side, the sintered disk of Ga_2O_3 or In_2O_3 attached to a Pt-10%Rh stirrer was dipped into liquid B_2O_3. During the dissolution process, the Ga_2O_3 or In_2O_3 concentrations increase until equilibrium is achieved. The equilibrium was checked by the sampling a small amount of the melt.

The solid phase equilibrated with liquid phase was determined, firstly according to analysis of the precipitates in the liquid phase from the experiments of the supersaturation side. However this technique is not effective for the phase equilibrium determination in the In_2O_3–B_2O_3 binary system, because the solubility value of In_2O_3 was very low. Instead, synthesis of compounds in the In_2O_3–B_2O_3 binary system was tried by using pure oxides of In_2O_3 and B_2O_3 powders at several compositions in the experimental temperature range of the solubility measurement. These precipitates and synthesized compounds were identified by X-ray diffraction (XRD). The thermal stability of these binary compounds was measured by differential thermal analysis (DTA) at a heating rate of 0.17 K/s in the atmospheric condition, using α-Al_2O_3 as a reference specimen.

III. Results and Discussion

1. Solubility measurements

(1) Ga_2O_3–B_2O_3 binary system

Figures 3 (a) and (b) show the experimental results for the supersaturation side at temperature range from 1423 to 1273 K, and the undersaturation side at temperature of 1273 K in the Ga_2O_3–B_2O_3 binary system, respectively. As can be seen from these figures, for example at 1273 K, both results are in good agreement with each other. These results indicate that the precipitate of Ga_2O_3–B_2O_3 binary compounds appeared in the experiments of supersaturation side has no effect on the analytical value of the Ga_2O_3 solubility, because it was difficult to dissolve in the dilute nitric acid solution during sample preparation for chemical analysis. The results obtained by two different experimental methods at the temperatures of 1273, 1323, and 1373 K are also summarized in Table 1.

The logarithms of Ga_2O_3 concentrations in liquid B_2O_3

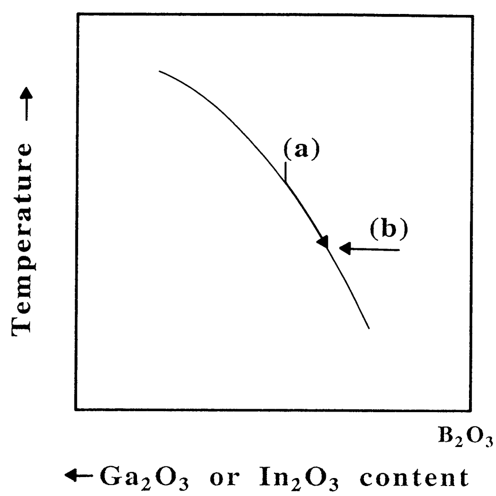

Fig. 2 Schematic illustration of the principal process of dissolution (a) supersaturation side and (b) undersaturation side.

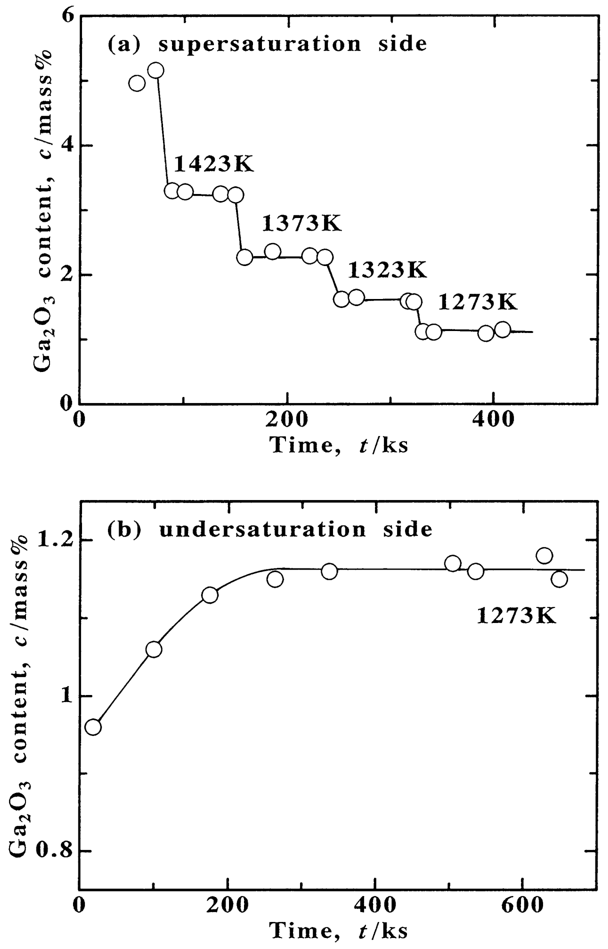

Fig. 3 Change of the Ga_2O_3 content in liquid B_2O_3 with time (a) supersaturation side and (b) undersaturation side.

Table 1 Solubility of Ga_2O_3 in liquid B_2O_3. (temperature in K and solubility in mass%)

Temperature	Experimental method	Solubility value
1273	supersaturation side	1.12±0.03
	undersaturation side	1.16±0.01
1323	supersaturation side	1.61±0.03
	undersaturation side	1.73±0.03
1373	supersaturation side	2.30±0.05
	undersaturation side	2.40±0.03

are plotted against the reciprocal of absolute temperature in Fig. 4. A linear relationship could be approximated over the temperature range of the measurement. The temperature dependency of the solubility of Ga_2O_3 in liquid B_2O_3 is expressed as follows.

$$\log (Ga_2O_3 \text{ contents/mass\%}) = -4880/T + 3.95 \pm 0.05 \quad (973\sim1573\text{ K}) \qquad (1)$$

(2) In_2O_3-B_2O_3 binary system

Figures 5(a) and (b) show the experimental results for the supersaturation side and the undersaturation side at the temperature of 1473 K in the In_2O_3-B_2O_3 binary system, respectively. As can be seen from these figures, both results are in good agreement with each other. These results indicate that the precipitate of In_2O_3-B_2O_3 binary compounds appeared in the experiments of supersaturation side has no effect on the analytical value of the In_2O_3 solubility, because the In_2O_3 dissolved in liquid B_2O_3 and both the undissolved In_2O_3 or In_2O_3-B_2O_3 binary compounds precipitated in the experiments of supersaturation side could be selectively dissolved in a certain concentration of dilute nitric acid solution during sample preparation for chemical analysis. If the specimen was dissolved in the pure water and then filtered, the value of the indium content in the specimen was equal to zero. This condition indicated that the indium ions in the specimen dissolve into the pure water as

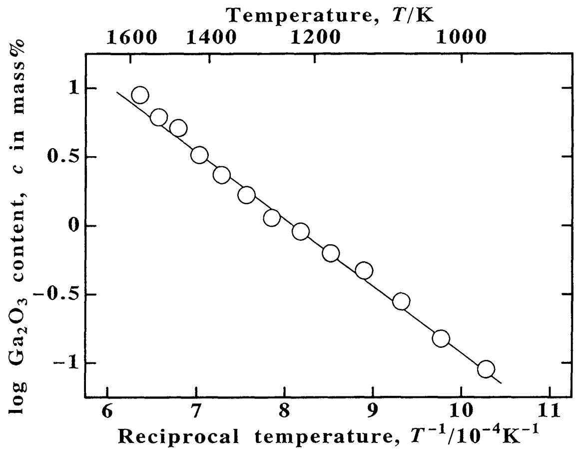

Fig. 4 Temperature dependency of the solubility of Ga_2O_3 in liquid B_2O_3.

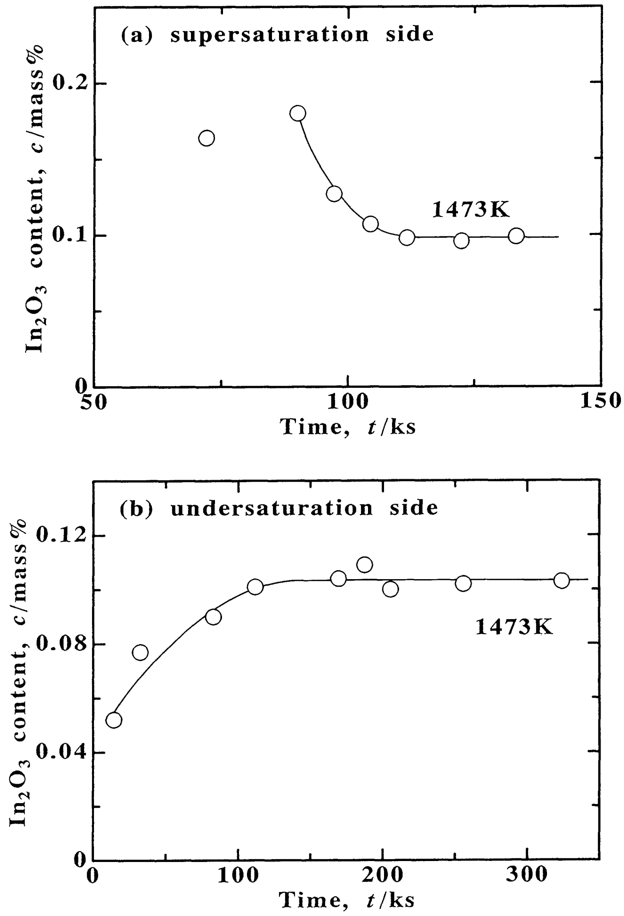

Fig. 5 Change of the In_2O_3 content in liquid B_2O_3 with time (a) supersaturation side and (b) undersaturation side.

a hydrate oxide for the pH of solution greater than 2.24[4]. For that, the specimens were dissolved in the dilute nitric acid solution at the concentration of 1:200 (pH of solution less than 2) during chemical analysis. Analytical values of the indium content in the specimen are very consistent after dissolution in the dilute nitric acid solution and filtration. It was confirmed that both the $InBO_3$ compound and undissolved In_2O_3 (see the next section) were difficult to dissolve in the dilute nitric acid solution.

The logarithms of In_2O_3 concentrations in liquid B_2O_3 are plotted against the reciprocal of absolute temperature in Fig. 6. A linear relationship could be adequately approximated over the temperature range of the measurement. The solubility of In_2O_3 in liquid B_2O_3 as a function of the temperature is expressed as follows.

$$\log (In_2O_3 \text{ contents/mass\%}) = -9208/T + 5.32 \pm 0.09 \quad (1273\sim1573\text{ K}) \qquad (2)$$

2. Phase equilibrium

(1) Ga_2O_3-B_2O_3 binary system

The precipitates in the liquid phase appeared in the experiments of supersaturation side at the temperature range from 1423 to 1273 K were identified as Ga_2O_3 by XRD analysis, whereas the diffraction pattern of the

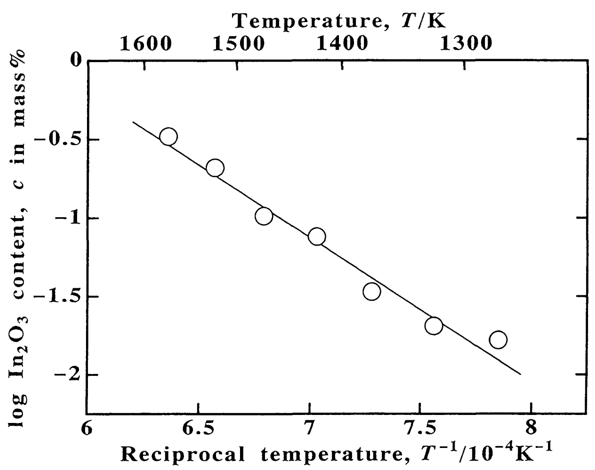

Fig. 6 Temperature dependency of the solubility of In_2O_3 in liquid B_2O_3.

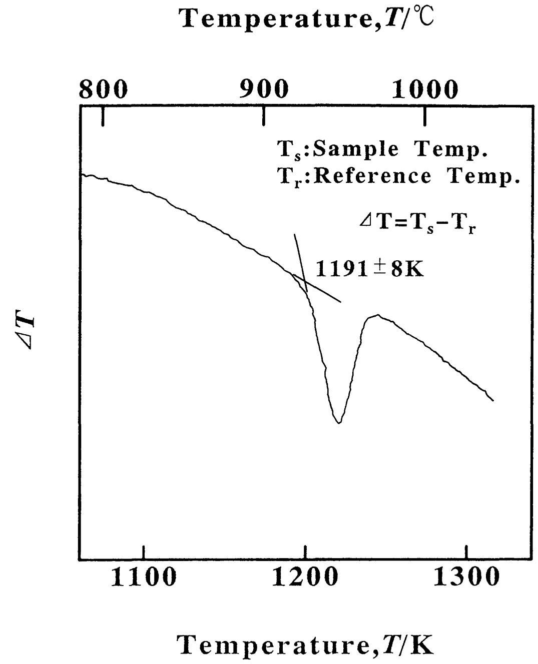

Fig. 7 Differential thermal analysis curve of the $GaBO_3$ compound.

precipitates obtained in the temperature range from 1273 to 973 K showed the additional peaks besides the Ga_2O_3 peaks. It can be estimated that these additional peaks are caused by the precipitated phase of the Ga_2O_3–B_2O_3 binary system within the limit of low temperature. These additional peaks agreed well with the $GaBO_3$ spectrums from JCPDS file[(5)]. It was checked by ICP analysis that the ratio of gallium to boron of this precipitate was equal to unity.

Figure 7 shows the result of DTA measurement for the $GaBO_3$ compound. As shown in this figure, an endothermic peak caused by decomposition of the $GaBO_3$ is observed at the temperature of 1191 ± 8 K. The decomposition temperature of $GaBO_3$ compound was reported by several investigators using DTA measurement method, but detailed information concerning its measurement procedure or determination method was not explained. The present value is within the range of 1123 to 1273 K, which were previously reported[(6)–(8)].

From these results, since the solid phase equilibrated with the liquid phase changed at 1191 ± 8 K from $GaBO_3$ to Ga_2O_3, it would be predicted that the temperature dependency of Ga_2O_3 solubility might change. But in Fig. 4, little change of the slope was observed above and below the decomposition temperature. It may be considered that its enthalpy change of decomposition for eq. (3) is small and therefore its effect does not appear.

$$2GaBO_3(s) = Ga_2O_3(s) + B_2O_3(l) \quad (3)$$

(2) In_2O_3–B_2O_3 binary system

In this study, the compounds in the In_2O_3–B_2O_3 binary system were synthesized by sintering of pure In_2O_3 and B_2O_3 powders in the composition range of 1:1 to 1:8 at 1173 or 1273 K for 252 or 216 ks in a sealed quartz tube. The synthesized compounds were identified by XRD analysis. The peaks which agreed well with the $InBO_3$ spectrums from JCPDS file[(9)] were observed in the whole composition range.

The thermal stability of the synthesized $InBO_3$ compound was measured by DTA, and no phase transition, fusion or decomposition was observed in the temperature range up to 1773 K. It was reported by Levin *et al.*[(10)] that the $InBO_3$ compound melts at 1883 ± 30 K. During a study of the structural relations among double oxides of trivalent elements, Keith and Roy[(11)] found that after a few min at 1973 K the $InBO_3$ compound lost B_2O_3 and yielded In_2O_3.

3. Phase diagram

According to these results, the phase diagrams of the Ga_2O_3–B_2O_3 and In_2O_3–B_2O_3 binary systems were shown in Figs. 8(a) and (b), respectively. The decomposition temperature of $InBO_3$ compound obtained by Levin *et al.* was used. The liquidus compositions at B_2O_3 side were determined from the solubility measurements. The $GaBO_3$ and $InBO_3$ compounds were confirmed at the Ga_2O_3–B_2O_3 and In_2O_3–B_2O_3 binary systems, respectively. The liquidus curve is shown rising continuously from the melting point of B_2O_3 at 753 K. The other compounds in these binary systems, except the $GaBO_3$ and $InBO_3$ compounds, have not been reported and could not be observed in the present work. Therefore, the phase diagrams shown in Figs. 8(a) and (b) are considered to be appropriate at the present time. Since both the phase diagrams of the Ga_2O_3–B_2O_3 and In_2O_3–B_2O_3 binary systems have not been yet reported, this work could not be compared with another data.

IV. Conclusions

From the studies of the reaction between Ga_2O_3 or In_2O_3 and B_2O_3, the following conclusions are obtained:

(1) The temperature dependency of the solubility of Ga_2O_3 or In_2O_3 in liquid B_2O_3 is expressed as follows,

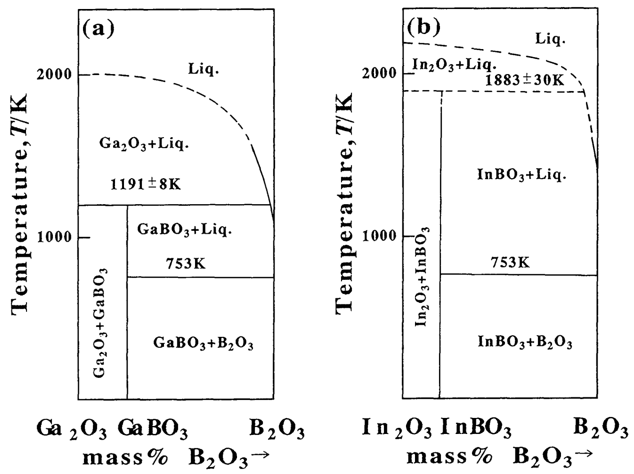

Fig. 8 Phase diagrams of the (a) Ga_2O_3–B_2O_3 and (b) In_2O_3–B_2O_3 binary systems.

respectively.

$$\log(Ga_2O_3\ \text{contents/mass\%}) = -4880/T + 3.95 \pm 0.05 \quad (973 \sim 1573\ \text{K})$$

$$\log(In_2O_3\ \text{contents/mass\%}) = -9208/T + 5.32 \pm 0.09 \quad (1273 \sim 1573\ \text{K})$$

(2) The solid phases equilibrated with the liquid phase in the Ga_2O_3–B_2O_3 binary system were $GaBO_3$ below 1191 K, and Ga_2O_3 above 1191 K. The $GaBO_3$ compound decomposed to Ga_2O_3 and liquid B_2O_3 at 1191 ± 8 K. In the In_2O_3–B_2O_3 binary system, the solid phase equilibrated with the liquid phase was $InBO_3$. The $InBO_3$ compound was found to be thermally stable up to 1773 K.

(3) From results (1) and (2), the phase diagrams of the Ga_2O_3–B_2O_3 and In_2O_3–B_2O_3 binary systems could be constructed.

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