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SOLUBILITY OF Ga_2O_3 OR In_2O_3 IN LIQUID B_2O_3

Djusman Sajuti*, Masahiro Yano**, Takayuki Narushima***,
and Yasutaka Iguchi***

* Graduate School, Tohoku University, Japan
** Graduate School, Tohoku University, Now Schlumberger K.K., Japan
*** Faculty of Engineering, Tohoku University, Japan

Synopsis: The solubility of Ga_2O_3 or In_2O_3 in liquid B_2O_3 has been measured by the sampling method in the temperature range of 973 to 1573 K. Gallium or indium contents in samples are analyzed by ICP atomic emission spectroscopy. The phase equilibrium in the binary system of Ga_2O_3–B_2O_3 or In_2O_3–B_2O_3 has been determined by x-ray diffraction and differential thermal analysis. The solid phase equilibrated with liquid phase was clarified.

Key words: LEC method, III group oxides, solubility, phase equilibrium, Ga_2O_3–B_2O_3, In_2O_3–B_2O_3, binary system

1. Introduction

Recently, single crystal of III–V compounds for semiconductor materials is 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 GaAs or InP for semiconductor materials are produced by the Czochralski pulling method. To prevent vaporization of As or P in the III–V melts during single crystal growth, 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 melts and B_2O_3 flux is very important. However, there are very few thermodynamic studies about these reactions.

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 has been measured and the solid phase equilibrated with liquid phase in the binary system of Ga_2O_3–B_2O_3 or In_2O_3–B_2O_3 has been investigated.

2. Experiments

Figure 1 shows a schematic diagram of the experimental apparatus. The specimens in Pt crucible were placed in the hot zone of the reaction tube with dried argon gas at a flow rate of 2.5×10^{-6} m^3/s. The temperature was controlled within ±2 K in the range between 973 and 1573 K by a PID controller and measured by a Pt/Pt–13%Rh thermocouple set inside of the reaction tube.

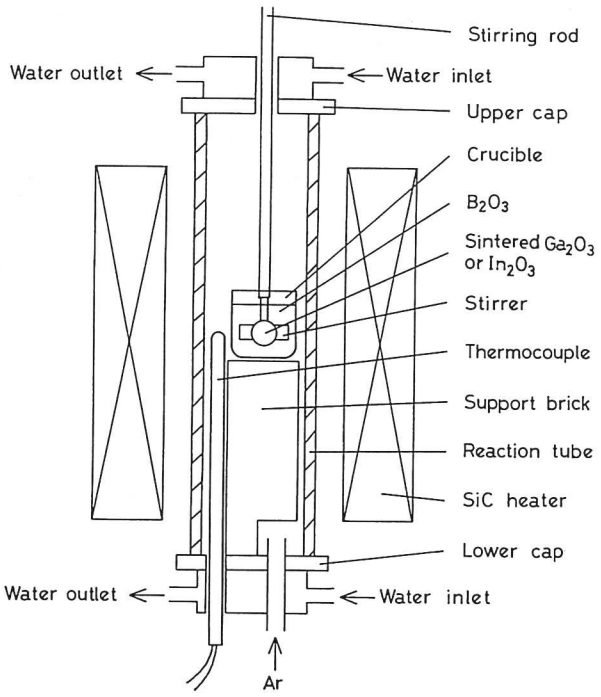

Fig. 1 Schematic diagram of experimental apparatus

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

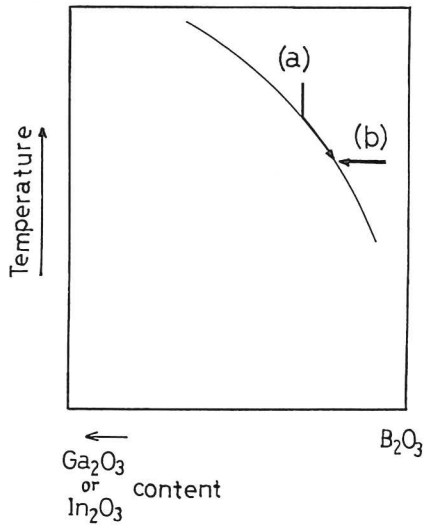

Fig. 2 Schematic illustration of principal process of dissolution
(a) supersaturation side
(b) undersaturation side

The experiments of supersaturation side were carried out by the precipitation of Ga_2O_3 or In_2O_3 in liquid B_2O_3 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 specified temperature, a part of the melts

were quenched by a Cu rod sampler cooled by water. The chemical analyses of the gallium or indium contents in 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 sample 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 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 of the melts.

The solid phase equilibrated with liquid phase was determined, firstly according to analysis of the precipitates in liquid phase from the experiments of 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. These precipitates and synthesized compounds were identified by x–ray diffraction (XRD). Thermal stability of the compounds was measured by differential thermal analysis (DTA) at a heating rate of 10 K/min in the atmospheric condition, using α Al_2O_3 as a reference specimen.

3. Results and discussion

3.1. Solubility measurements

The experimental results for the supersaturation side and undersaturation side in the Ga_2O_3–B_2O_3 binary system at the temperatures of 1273, 1323, and 1373 K are given in Table 1.

Table 1 Solubility of Ga_2O_3 in liquid B_2O_3 obtained by two different experimental methods

Temp. /K	Solubility of Ga_2O_3 in liquid B_2O_3 /mass%	
	supersaturation side	undersaturation side
1273	1.12	1.16
1323	1.61	1.73
1373	2.30	2.40

The both results are in good agreement with each other. These results indicate that the precipitate of Ga_2O_3–B_2O_3 compounds appeared in the experiments of supersaturation side has no effect on the Ga_2O_3 solubility, because it is difficult to dissolve in the dilute nitric acid solution during chemical analysis.

The logarithms of Ga_2O_3 concentrations in liquid B_2O_3 are plotted against the reciprocal of absolute temperature in Fig. 3. A linear relationship can be adequately approximated over the temperature range of the measurement. The temperature dependence of the solubility of Ga_2O_3 in liquid B_2O_3 is expressed as follows.

$$\log (Ga_2O_3 \text{ contents /mass\%}) = -4880/T + 3.95 \quad (973\text{~}1573\ K) \qquad (1)$$

Likewise, the solubility of In_2O_3 in liquid B_2O_3 as a function of the temperature is also expressed as follows.

$$\log (In_2O_3 \text{ contents /mass\%}) = -9208/T + 5.32 \quad (1273\text{~}1573\ K) \qquad (2)$$

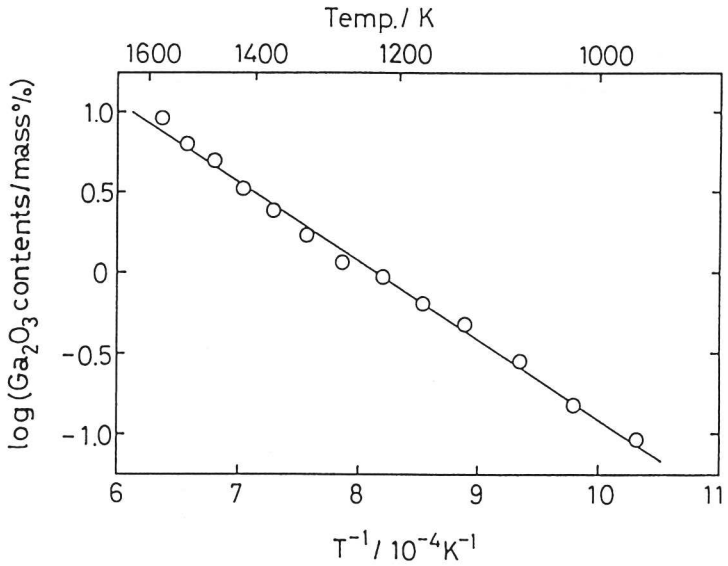

Fig. 3 Relation between solubility of Ga_2O_3 in liquid B_2O_3 and temperature

3.2. Phase equilibrium

3.2.1. Ga_2O_3–B_2O_3 binary system

Figure 4 (a) shows the XRD pattern for the precipitate in liquid phase appeared in the experiments of supersaturation side at 1423 to 1273 K. This diffraction pattern agreed well with the Ga_2O_3 spectrum from JCPDS.

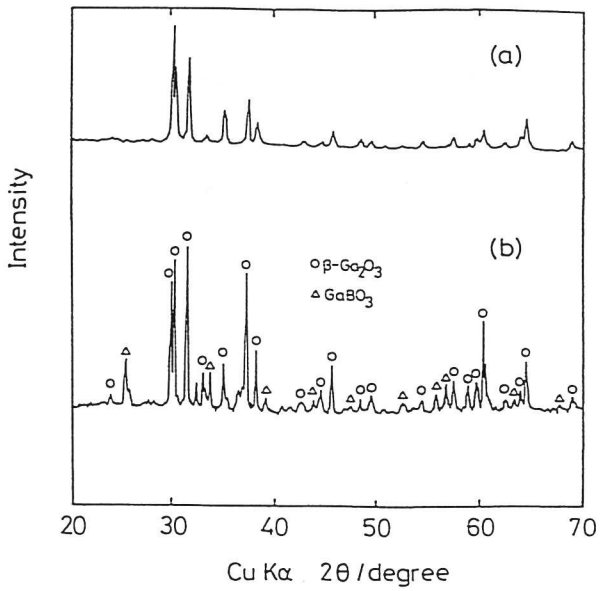

Fig. 4 X-ray diffraction patterns of Ga_2O_3–B_2O_3 binary system
(a) precipitate at limit of high temperature range
(b) precipitate at limit of low temperature range

Figure 4 (b) shows the XRD pattern of this precipitate obtained at 1273 to 973 K. As can be seen from this figure, the additional peaks besides the Ga_2O_3 peaks are appeared. It can be estimated that these additional peaks are caused by the precipitate phase of the Ga_2O_3–B_2O_3 binary system within the limit of low temperature range. This diffraction pattern agreed well with the $GaBO_3$ spectrum from JCPDS. It was checked by ICP analysis that Ga/B was equal to unity.

Figure 5 shows the result of DTA measurement for the $GaBO_3$ compound. As shown in this figure, a main endothermic peak which is caused by decomposition of the $GaBO_3$ compound is observed at temperature of 1191 K. This value is in essential agreement with the values of 1173±20 K given by Capponi et al. [4], 1123 K given by Blasse and Bril [5], and around of 1273 K given by Bither and Young [6].

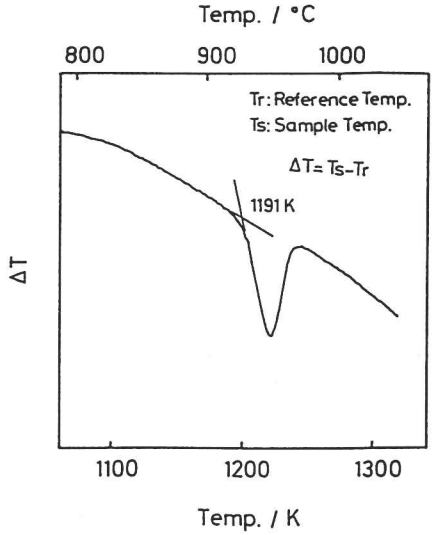

Fig. 5 Differential thermal analysis curve of $GaBO_3$ compound

From these results, since the solid phase equilibrated with the liquid phase was changed at 1191 K from $GaBO_3$ to Ga_2O_3, it would be predicted that the temperature dependence of Ga_2O_3 solubility was changed. But in Fig. 3, little change of the slope was observed.

3.2.2. In_2O_3–B_2O_3 binary system

In this study, $InBO_3$ compound is 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 216 or 252 ks in a sealed quartz tube. The sintered products are analyzed by XRD. The $InBO_3$ peaks are appeared at all of the composition range. Figure 6 shows the diffraction pattern of the spectrums of $InBO_3$ synthesized and that for JCPDS. As shown in this figure, the both spectrums are in good agreement with each other.

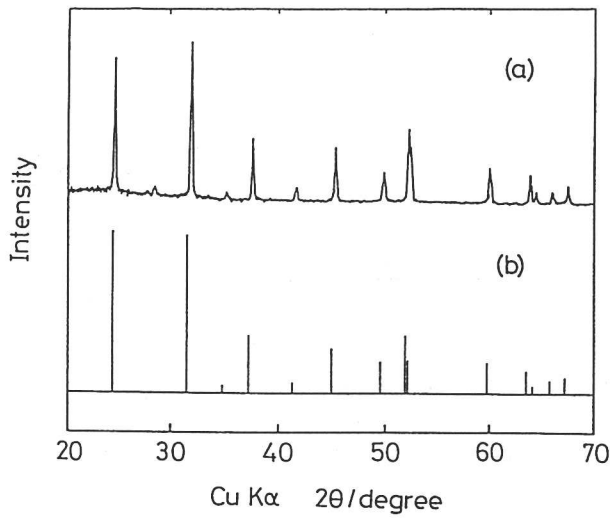

Fig. 6 X-ray diffraction patterns of $InBO_3$ compound
(a) synthesized from pure oxides of In_2O_3 and B_2O_3 powders
(b) from JCPDS

The thermal stability of the $InBO_3$ compound is measured by DTA, and no fusion or decomposition is observed at the temperature range up to 1773 K. It was reported by Levin et al. [7] 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 [8] found that after a few minutes at 1973 K the $InBO_3$ compound lost B_2O_3 to yield In_2O_3.

4. 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 dependence of the solubility of Ga_2O_3 or In_2O_3 in liquid B_2O_3 is expressed as follows, respectively.

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

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

(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 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.

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