Oxygen Distribution between Molten B_2O_3 Flux and Indium or Gallium

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ABSTRACT

Oxygen behavior during single crystal growth of Ⅲ-V compound semiconductors by liquid encapsulated Czochralski(LEC) is very important in order to control impurity contents and stoichiometric composition. In this study, distribution of oxygen between molten B_2O_3 flux, and indium or gallium metal has been investigated.

1. INTRODUCTION

Ⅲ-V compound semiconductors have been applying to super high speed amplifier, optical device and LSI for portable personal telephone and personal digital assistant, since they have high electron mobility, wide band gap and high frequency characteristics. Liquid encapsulated Czochralski(LEC) method is mainly utilized for single crystals growth. In this process, liquid B_2O_3 flux is used as a liquid encapsulant in order to prevent V group elements in Ⅲ-V melts from vaporization. Therefore, for quality control of the products and reasonable process, it is very important to elucidate the reactions between Ⅲ-V melts and the crucible or B_2O_3 fluxes.

The authors have reported the fundamental thermodynamic properties concerning these reactions[1~4] such as solubilities of Ga_2O_3, In_2O_3 or Al_2O_3 in liquid B_2O_3 and the temperature dependence of oxygen solubility in liquid indium or gallium. In this paper, distribution of oxygen between molten B_2O_3 flux and indium or gallium metal has been described.

2. EXPERIMENTAL

Indium or gallium metal(Rasa Industries Co. Ltd.) and B_2O_3 flux were melted in a boron nitride crucible or silica crucible made of high purity quartz(T-2030, Toshiba Ceramics Co. Ltd.). The atmosphere was dried argon gas and the temperature was between 1273 K and 1423 K. Figure 1 shows schematically an experimental apparatus. At certain intervals of time, a small amount of sample was taken out from the molten flux and quenched. Finally after establishment of equilibrium, the crucible was quenched with liquid nitrogen. Obtained metal and flux samples were separated and cleaned up.

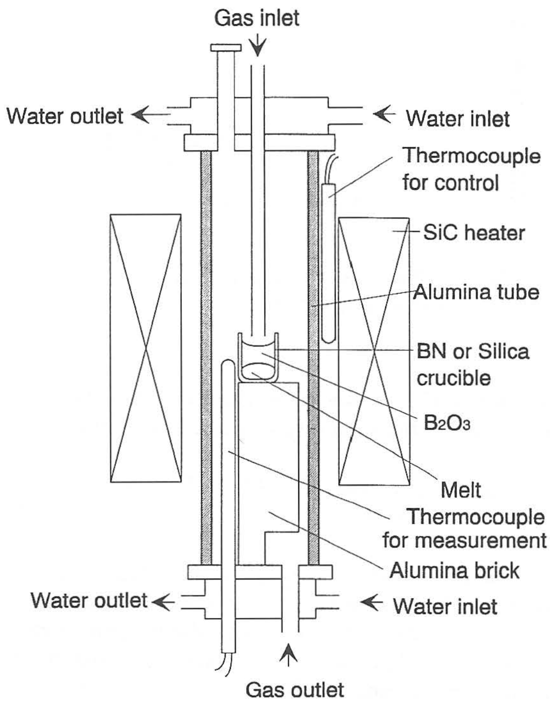

Fig. 1 Experimental apparatus.

The oxygen content in quenched indium or gallium metal was analyzed by the inert gas fusion-IR absorption method(LECO, TC436E). Indium or gallium contents in flux samples were determined by ICP atomic emission spectroscopy(ICP-AES). And also contents of silicon in metal and flux were determined by ICP-AES in order to consider contamination through the silica crucible.

3. EXPERIMENTAL RESULTS

3.1 Molten B_2O_3 and indium system

Figure 2 shows the contents of In_2O_3 in liquid B_2O_3 flux phase with time at 1373 K. In this figure, the solubility of In_2O_3 in liquid B_2O_3 is also shown with dotted line denoted as $In_2O_{3sat.}$, which was measured by the sampling method from the melts in a platinum crucible under dried argon atmosphere by the authors[1].

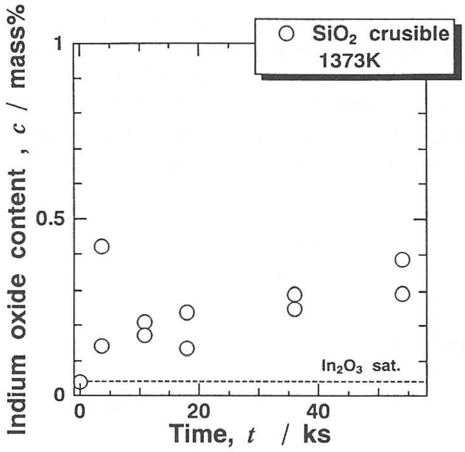

Fig. 2 Indium oxide content in the flux and time at 1373 K.

The value at 1373 K was calculated from the temperature dependency of the solubility expressed as follows:

$$\log(\mathrm{In_2O_3}\ \text{contents/mass\%}) = -9208/T + 5.32 \quad (1273\sim1573\ \mathrm{K}) \qquad (1)$$

The obtained contents of In_2O_3 are much higher than the solubility. This reason is not clear at the moment. In this study, since metal and flux coexist, the oxygen potential is much lower like as 7.0×10^{-13} atm than that during solubility measurement. Therefore, the suspension of metallic indium droplets or existence of lower valence indium ion might be considered in liquid B_2O_3 flux. Metallic indium dissolves easily in the dilute nitric acid aqueous solution(1:100) during preparation of the solution for ICP-AES and must be counted as a total indium oxide content. In order to check whether the suspension occurs or not, separation of suspended indium metal from indium oxide dissolved in liquid flux was tried by oxidation of the sample. It was confirmed by the preliminary experiment that the precipitated or suspended indium oxide is insoluble and only dissolved indium oxide is soluble in the dilute nitric acid aqueous solution. Decrease in indium oxide contents was observed after oxidation. Oxygen content in liquid indium was around 0.027~0.035 mass% at 1373 K. Oxygen solubility in liquid indium equilibrated with pure solid indium oxide was expressed by the following equations[3]:

$$\log(C_o/\text{mass\%, in In(l)}) = -6600/T + 3.77(\pm0.074) \quad (1073\sim1373\ \mathrm{K}) \qquad (2)$$

In this system, further experiments are necessary on the solubility of In_2O_3 in liquid B_2O_3 and determination of In_2O_3 in the flux sample.

3.2 Molten B_2O_3 and gallium system

In this system, the colorless and transparent flux phase was obtained after 28.8 ks that is the enough time for equilibration. It means no suspension of metallic gallium droplets. The relationship between oxygen content in liquid gallium and Ga_2O_3 content in liquid B_2O_3 flux at 1273 K is expressed in Fig. 3. For your reference, the temperature dependency of the solubility of Ga_2O_3 in liquid B_2O_3 or solubility of oxygen in liquid gallium is expressed by Eqs. (3) or (4), respectively[1,3].

$$\log(\mathrm{Ga_2O_3}\ \text{contents/mass\%}) = -4880/T + 3.95 \quad (973\sim1573\ \mathrm{K}) \qquad (3)$$

$$\log(C_o/\text{mass\%, in Ga(l)}) = -6200/T + 2.61(\pm0.119) \quad (1123\sim1523\ \mathrm{K}) \qquad (4)$$

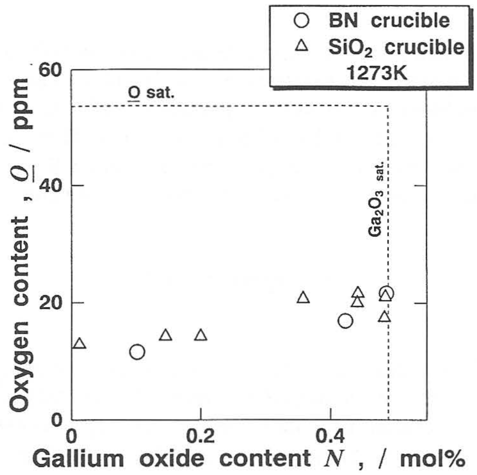

Fig. 3 Oxygen content in liquid gallium and Ga_2O_3 content in the flux at 1273 K.

4. DISCUSSION

In the present study, the equilibrium reactions between molten B_2O_3 flux and indium or gallium are expressed as follows:

$$2\mathrm{In(l)} + 3\underline{\mathrm{O}}(\text{in liquid In}) = \mathrm{In_2O_3}(\text{in liquid flux}) \qquad (5)$$

$$2\mathrm{Ga(l)} + 3\underline{\mathrm{O}}(\text{in liquid Ga}) = \mathrm{Ga_2O_3}(\text{in liquid flux}) \qquad (6)$$

Equilibrium constants, K's of these reactions are expressed by Eqs.(7) and (8).

$$K_{\mathrm{In_2O_3}} = a_{\mathrm{In_2O_3}}/a_{\mathrm{In}}^2 \cdot a_{\underline{\mathrm{O}}}^3 \qquad (7)$$

$$K_{\mathrm{Ga_2O_3}} = a_{\mathrm{Ga_2O_3}}/a_{\mathrm{Ga}}^2 \cdot a_{\underline{\mathrm{O}}}^3 \qquad (8)$$

where, $a_{In_2O_3}$ or $a_{Ga_2O_3}$ and a_{In}, a_{Ga} or a_{O} are referred to Raoult's law, and Henry's law in mass%, respectively. From these relations, in the present work the oxygen distribution ratio between liquid metal and flux could be defined by Eq.(9).

$$L_o \equiv (\text{mol\%}In_2O_3 \text{ or } Ga_2O_3)/[\text{mass\%}\underline{O}]^3 \qquad (9)$$

Figure 4 shows the oxygen distribution ratio between liquid gallium and B_2O_3 flux at 1273 K.

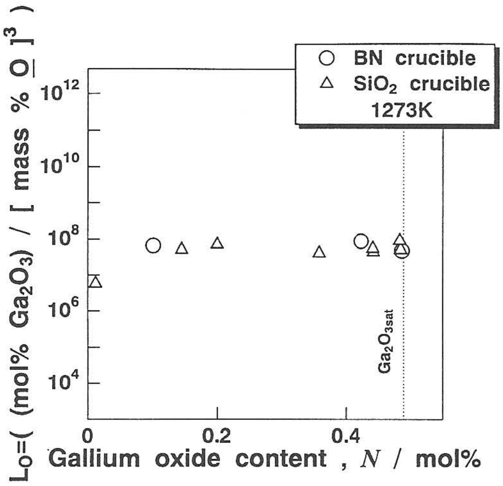

Fig. 4 Oxygen distribution between B_2O_3–Ga_2O_3 flux and liquid gallium at 1273 K.

Since contents of boron, silicon, and nitrogen contaminated from the crucible in liquid indium and gallium were less than the detection limit by ICP–AES, activity of indium or gallium metal could be assumed to be unity. Moreover, silica contents from the crucible in liquid flux were less than 1 mass%, and activity of indium or gallium oxide could be assumed to be unity. It is assumed that oxygen in liquid indium or gallium obeyed Henry's law(f_O = 1) since no data is available concerning the interaction parameters of oxygen in liquid indium or gallium metals. Then the activity of In_2O_3 or Ga_2O_3 in B_2O_3 flux is derived using the standard free energy changes of Eqs. (5) and (6) as expressed by Eqs. (10) and (11). These standard free energy changes were obtained by combining the standard free energy of formation of each oxide in the literatures[5,6] with the standard free energy of oxygen dissolution in liquid indium or gallium by the authors[2].

$$a_{In_2O_3} = [\text{mass\%}\underline{O}]^3\exp(-(-379500 + 149T)/RT) \qquad (10)$$

$$a_{Ga_2O_3} = [\text{mass\%}\underline{O}]^3\exp(-(-356000 + 217T)/RT) \qquad (11)$$

Figure 5 shows the activity of Ga_2O_3 in B_2O_3 flux at 1273 K. The broken line is Ga_2O_3 solubility in liquid B_2O_3.

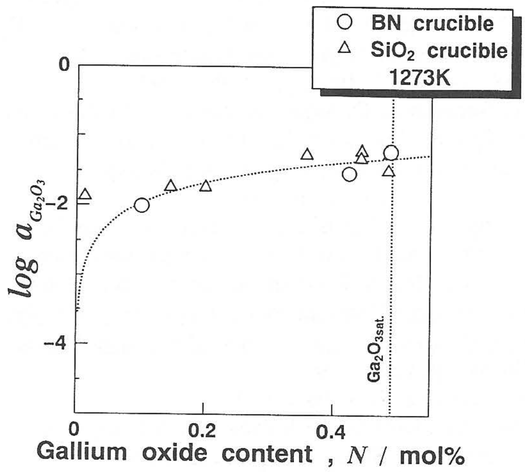

Fig. 5 Activities of Ga_2O_3 in the flux at 1273 K.

5. CONCLUSIONS

(1) Indium or gallium metal and B_2O_3 flux were melted in a boron nitride or silica crucible under dried argon gas at the temperature range between 1273 K and 1423 K. Oxygen distribution between liquid indium or gallium and liquid B_2O_3 flux was determined.

(2) The activities of In_2O_3 or Ga_2O_3 in liquid B_2O_3 flux were evaluated.

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