(2) A relatively small number of voids form in the initial short period of less than 5 or 10 min, then the formation of voids ceases up to about 30 min. Thereafter, a second group of voids begin to form.

(3) The diameter of the bottom of the voids expands at a parabolic rate, keeping a linear relation with the scale thickness during oxidation.

(4) The number density of the initially-formed voids is highly affected by the temperature as well as the surface roughness of the specimen.

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Technical Paper

Vapor Phase Equilibrium of the Disproportionation Reaction of Indium Dichloride*

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Equilibrium of the disproportionation reaction of indium dichloride in the vapor phase, $\text{In}_2\text{Cl}_4(\text{g}) \rightleftharpoons \text{InCl}_3(\text{g}) + \text{InCl}(\text{g})$, has been studied by means of vapor pressure measurements and computer calculations. In the calculations, the vapor phase species of $\text{InCl}(\text{g})$, $\text{In}_2\text{Cl}_6(\text{g})$, $\text{InCl}_3(\text{g})$, $\text{In}_2\text{Cl}_4(\text{g})$, and $\text{Cl}_2(\text{g})$ were considered and each partial pressure was calculated by using the equilibrium constants previously reported. The temperature dependence of the equilibrium constant for the above reaction was obtained as $\log K_{p, \text{mm Hg}} = -\frac{7.463 \times 10^3}{T} + 9.658$. The vapor pressures of In_2Cl_3 and In_4Cl_7 were also investigated and it was found that the vapor phases from these compounds consist of same species as those from In_2Cl_4 .

1 Introduction

With the progress of technique for single crystal growth of III-V compound semiconductors by vapor phase chemical transport, the optimization of yield has been extensively studied by thermodynamic calculations for the vapor phase equilibria in the transport reaction system^{1)~7)}. In these studies, chemical species in vapor phase in the system should at first be accurately known. Therefore, we have investigated reactions between the metallic element as a constituent of compound semiconductor and halogen, and studied physical and chemical behaviors of the halides in the vapor phase^{8)~10)}.

In early works on the thermodynamic calculations, only predominant reactions in the system were considered. Although some species of fairly small amo-

unts, *e.g.* As_2 , P_2 , and the like, have been recently taken into account in the calculation, it seems that other species with unexpected high partial pressure have not yet been regarded.

In the studies on the reactions in the system $\text{In}-\text{Cl}_3$, the following equilibria were investigated^{8), 9)}.

Furthermore, in order to discuss the vapor phase reaction in a system containing indium and chlorine, the existence of indium dichloride in the vapor phase should be taken into account, but it has been overlooked in studies by many investigators. In our previous paper⁹⁾, it was pointed out that the compound exists as $\text{In}_2\text{Cl}_4(\text{g})$ rather than $\text{InCl}_2(\text{g})$, even in the vapor phase, and that it disproportionates with increasing temperature according to the equilibrium

The present work was intended to determine the

* Studies on the Vapor Phase Chemical Transport Reaction of III-V Compound Semiconductors (Part 5)

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equilibrium constant and the thermodynamic functions in the equilibrium, and also to confirm the result that the vapor phases from In_2Cl_3 and In_4Cl_7 consist of same species as those from In_2Cl_4 , using the equilibrium constant obtained above.

2 Experimental

A quartz Bourdon gauge, known as null manometer, was used to measure the temperature dependence of vapor pressure given by indium chlorides. Details of its construction and of the operation have been described in the previous papers^{(6), (8), (10)} and other references^{(11)~(13)}.

Metallic indium used was 99.9999% pure. Indium trichloride was used after distilling three or four times the commercially available product (99.99% pure). A known amount of the chloride was enclosed in a break tip ampoule with a similar process to that in the previous works^{(6), (9)}. In_2Cl_4 , In_2Cl_3 , and In_4Cl_7 were prepared by heating mixtures of metallic indium with the above indium trichloride in the mole ratio of $\text{In}:\text{InCl}_3=1:2$, $1:1$, and $5:7$, respectively.

3 Results and Discussion

3.1 Vapor pressure measurement and calculations

The pressure-temperature curves shown by indium dichloride are given in Fig. 1, in which different

moles of the substance was loaded in the unit volume of the sample chamber of the gauge in each run.

In each pressure-temperature curve in Fig. 1, a break point is observed, beyond which the total pressure, P_t , gradually increases with increasing temperature to approach the pressure approximated by the ideal gas law for twice the loaded moles of In_2Cl_4 , P_{ot} . The entire substance loaded is considered to be in the vapor phase in the region of gradual increase in pressure, as described in the previous papers^{(8), (9)}, and the possible chemical species in the system are $\text{InCl}(g)$, $\text{InCl}_3(g)$, $\text{In}_2\text{Cl}_6(g)$, $\text{In}_2\text{Cl}_4(g)$, $\text{Cl}_2(g)$, and $\text{Cl}(g)$. Among these species, the partial pressure of atomic chlorine was neglected since it was estimated to be extremely small as compared with those of the other species.

From the mutual relationship between partial pressures of entire chemical species, the following equations are obtained.

$$P_t = P_{\text{InCl}} + P_{\text{InCl}_3} + P_{\text{In}_2\text{Cl}_6} + P_{\text{In}_2\text{Cl}_4} + P_{\text{Cl}_2} \quad (4)$$

$$\frac{P_{\text{InCl}} + P_{\text{InCl}_3} + 2P_{\text{In}_2\text{Cl}_6} + 2P_{\text{In}_2\text{Cl}_4}}{P_{\text{InCl}} + 3P_{\text{InCl}_3} + 6P_{\text{In}_2\text{Cl}_6} + 4P_{\text{In}_2\text{Cl}_4} + 2P_{\text{Cl}_2}} = 1/2 \quad (5)$$

$$P_{ot} - P_t = P_{\text{In}_2\text{Cl}_4} + P_{\text{In}_2\text{Cl}_6} - P_{\text{Cl}_2} \quad (6)$$

$$K_{p1} = \frac{P_{\text{InCl}_3}^2}{P_{\text{In}_2\text{Cl}_6}} \quad (7)$$

$$K_{p2} = \frac{P_{\text{InCl}} \cdot P_{\text{Cl}_2}}{P_{\text{InCl}_3}} \quad (8)$$

where the temperature dependences of K_{p1} and K_{p2} have been determined as given by the following equations⁽⁹⁾.

$$\log K_{p1} \text{ mm Hg} = -\frac{6.645 \times 10^3}{T} + 10.10 \quad (9)$$

$$\log K_{p2} \text{ mm Hg} = -\frac{4.221 \times 10^3}{T} + 3.726 \quad (10)$$

From the above equations (4)–(8), a pair of biquadratic simultaneous equations for P_{InCl} and P_{InCl_3} were derived and it was solved by a FACOM 270–30 computer. One of which was adopted as the solution to conform to the system since the values of P_{InCl} and P_{InCl_3} are closed to those optically determined and the other was abandoned because it was far away from reasonable value. Thus, the partial pressures of each chemical species at various temperatures were calculated.

The equilibrium constant of the disproportionation reaction of $\text{In}_2\text{Cl}_4(g)$, which is represented by the equation (3), is given by

Fig. 1 Pressure-temperature curves shown by indium dichloride with various loaded moles per unit volume

- Run 1 : 4.380×10^{-6} mole/cm³ of In_2Cl_4
- Run 2 : 3.068×10^{-6} mole/cm³ of In_2Cl_4
- △— Run 3 : 1.523×10^{-6} mole/cm³ of In_2Cl_4

$$K_p = \frac{P_{\text{InCl}_3} \cdot P_{\text{InCl}}}{P_{\text{In}_2\text{Cl}_4}} \quad (11)$$

Substituting the calculated partial pressures of $P_{\text{In}_2\text{Cl}_4}$, P_{InCl} , and P_{InCl_3} into the equation (11), the equilibrium constants were calculated for various temperatures. The plots of $\log K_p$ vs. $1/T$ gave a linear relationship as shown in Fig. 2.

Fig. 2 Equilibrium constants for the disproportionation reaction,
 $\text{In}_2\text{Cl}_4(\text{g}) \rightleftharpoons \text{InCl}_3(\text{g}) + \text{InCl}(\text{g})$

—○— : Run 1
 —●— : Run 2
 —△— : Run 3

The temperature dependence of the equilibrium constant was given by the following equation

$$\log K_p \text{ mm Hg} = -\frac{7.463 \times 10^3}{T} + 9.658 \quad (12)$$

The thermodynamic quantities for the disproportionation reaction were calculated as follows :

$$\left. \begin{aligned} \Delta G^\circ &= 34.106 \times 10^3 - 30.975 T \text{ cal/mole} \\ \Delta H &= 34.106 \times 10^3 \text{ cal/mole} \\ \Delta S &= 30.975 \text{ e.u.} \end{aligned} \right\} \quad (13)$$

In the above calculations, atomic chlorine was not taken into account. A rough estimation for the partial pressure of atomic chlorine, for instance, gave about 0.001 and 0.17 mm Hg, when those of molecular chlorine were 0.121 and 1.60 mm Hg at 650° and 928°C, in the run 2, respectively. Thus, the partial pressure of atomic chlorine is within the experimental error and the values of the equilibrium constant are hardly affected even if atomic chlorine is considered in the calculation.

3.2 Partial pressure of each gaseous species in the system

Fig. 3 shows an example of the relationship bet-

ween the partial pressures of entire chemical species in the system and temperature, which were calculated for the run 2.

Fig. 3 Partial pressure of each chemical species in the system of disproportionation of $\text{In}_2\text{Cl}_4(\text{g})$ for run 2

—○— : $\text{In}_2\text{Cl}_4(\text{g})$, —△— : $\text{InCl}(\text{g})$
 —▲— : $\text{InCl}_3(\text{g})$, —◆— : $\text{Cl}_2(\text{g})$
 —□— : $\text{In}_2\text{Cl}_6(\text{g})$

It is of interest to observe, in Fig. 3, that the partial pressure of $\text{In}_2\text{Cl}_4(\text{g})$ is in the comparable order of those of $\text{InCl}(\text{g})$ and $\text{InCl}_3(\text{g})$, and much higher than those of $\text{In}_2\text{Cl}_6(\text{g})$ and $\text{Cl}_2(\text{g})$ even at the deposition temperature in the chemical transport of InAs, InP and the like. Particularly, in the chlorine transport of InSb, it should be noted that the partial pressure of $\text{In}_2\text{Cl}_4(\text{g})$ would play an important role in the equilibrium of the deposition reaction, since the reaction temperature must be kept at a moderate temperature due to its low melting point (525°C).

In Fig. 3, the partial pressures of each chemical species for the temperatures below the break point in the pressure-temperature curve were not shown. Below the break point where a liquid phase exists, it is impossible to express accurately the relationship between entire chemical species in the system, that is, the equation (5) does not hold, since the liquid forms a solution which dissolve more $\text{InCl}(1)$ than $\text{InCl}_3(1)^{19}$.

3.3 Vapor pressures of In_2Cl_3 and In_4Cl_7

Fedorov et al. reported the temperature dependences

of the vapor pressure of In_2Cl_3 and In_4Cl_7 ^{(14), (15)}. However the present authors observed that the absorption spectra for the vapor phases of these compounds were similar to those of In_2Cl_4 . When the optical densities of the bands at 242 and 315 $\text{m}\mu$ in the neighbourhood of each dew point (in the temperature range of 600–700°C), were compared with respect to equivalent mole of indium in each compound loaded in an optical cell, the intensities were arranged in the order of In_2Cl_4 , In_4Cl_7 , and In_2Cl_3 . Therefore, it was concluded that the two bands at 242 and 315 $\text{m}\mu$ are characteristic of In_2Cl_4 , and presumed that other two compounds also decompose to $\text{InCl}_3(\text{g})$ and $\text{InCl}(\text{g})$ via formation of $\text{In}_2\text{Cl}_4(1)$ according to the following reactions⁸⁾.

In the present work, the vapor pressures of these compounds were investigated. As shown in Fig. 4, the pressure-temperature curves of these compounds are similar to that of In_2Cl_4 .

Fig. 4 Pressure-temperature curves shown by In_2Cl_3 and In_4Cl_7

- : In_2Cl_3 , 4.097×10^{-6} mole/ cm^3
 —●— : In_4Cl_7 , 1.847×10^{-6} mole/ cm^3

The relationship between partial pressures in the system were formularized in a similar way to that in 3.1, under an assumption that the gradual increase in pressure beyond the break point in each curve is due to the disproportionation of $\text{In}_2\text{Cl}_4(\text{g})$ released from In_2Cl_3 and In_4Cl_7 . In the present case, the equation (5) should be modified to equate to 2/3 and 4/7 for In_2Cl_3 and In_4Cl_7 , respectively, corresponding to the atomic ratio of indium to chlorine in each compound.

The temperature dependences of the equilibrium constants of disproportionation reaction of $\text{In}_2\text{Cl}_4(\text{g})$ in the vapor phase systems from In_2Cl_3 and In_4Cl_7 were calculated as follows :

$$\text{for } \text{In}_2\text{Cl}_3, \log K_{p \text{ mm Hg}} = -\frac{7.763 \times 10^3}{T} + 10.038 \quad (16)$$

$$\text{for } \text{In}_4\text{Cl}_7, \log K_{p \text{ mm Hg}} = -\frac{7.866 \times 10^3}{T} + 9.996 \quad (17)$$

These values are in good agreement with the equation (12). The agreement shows that the assumption previously proposed is reasonable.

Temperature dependences of the vapor pressure of In_2Cl_3 and In_4Cl_7 have been reported as follows^{(14), (15)} :

$$\text{for } \text{In}_2\text{Cl}_3, \log P_{\text{mm Hg}} = -\frac{5310}{T} + 8.695 \quad (18)$$

$$\text{for } \text{In}_4\text{Cl}_7, \log P_{\text{mm Hg}} = -\frac{3581}{T} + 6.527 \quad (19)$$

However, the results obtained in the present work do not agree with the above equations. It was described in the previous papers that the temperature dependence of the vapor pressure of In_2Cl_4 varied with the loaded moles in the unit volume⁹⁾. In_2Cl_3 and In_4Cl_7 also disproportionate to form solutions consisting of $\text{InCl}_3(1)$, $\text{InCl}(1)$, and $\text{In}_2\text{Cl}_4(1)$, and keep a fixed composition at certain temperature. Therefore, the vapor pressure would depend upon the loaded moles in the unit volume.

4 Conclusion

Disproportionation reaction of indium dichloride in the vapor phase was studied. The following conclusions are deduced :

- (1) Temperature dependence of the equilibrium constant for the disproportionation reaction, $\text{In}_2\text{Cl}_4(\text{g}) \rightleftharpoons \text{InCl}_3(\text{g}) + \text{InCl}(\text{g})$, is given by

$$\log K_{p \text{ mm Hg}} = -\frac{7.463 \times 10^3}{T} + 9.658$$

and the thermodynamic quantities for the above reaction are calculated as follows :

$$\Delta G^\circ = 34.106 \times 10^3 - 30.975 T \text{ cal/mole}$$

$$\Delta H = 34.106 \text{ cal/mole}$$

$$\Delta S = 30.975 \text{ e.u.}$$

- (2) The vapor pressure given by In_2Cl_3 and In_4Cl_7

Cl₂ were investigated. The equilibrium constants of the disproportionation reaction of In₂Cl₄(g) were calculated, under an assumption that the gradual increase in pressure beyond the break point in each curve is due to the disproportionation of In₂Cl₄(g) released from In₂Cl₃ and In₄Cl₇. The results gave good agreement with that of In₂Cl₄ described in the conclusion (1). The fact supports the result of optical measurement previously reported.

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Technical Paper

Measurement of Concentration Profile at Cathode by a Microphotographic-colorimetry*

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Concentration profiles of aqueous nickel and cobalt chloride solutions, at the distance up to 300 mμ from the cathode, have been measured during the deposition by means of a new optical method such as microphotographic-colorimetry, which was devised to find precisely the variation of concentration of depositing ion in the electrolyte with electrolytic time. Monochromatic lights, 395 and 510 mμ, were selected spectrophotometrically for the determination of Ni²⁺ and Co²⁺ concentration, respectively. Horizontal electrodes in cathode-over-anode position were used in order to make the convection as little as possible. Current densities, D_k , at which no evolution of hydrogen occurred were applied; 7~15 mA/cm² for nickel, 10~30 mA/cm² for cobalt. The experimental values of metal concentration in cathode diffusion layer, in both aqueous nickel and cobalt solutions, were in good agreement with the calculated values in nonsteady state under mass transfer neglecting the convection at D_k below 10 mA/cm², though they deviated at D_k above 15 mA/cm². This optical method has great advantage in the application to study of cathode diffusion layer during the alloy deposition without hydrogen evolution.

1 Introduction

The knowledge of diffusion layer is important not only from theoretical point of view but also from practical one. Although various techniques, such as sampling^{1)~4)} and optical methods^{5)~6)}, have been used for studying the diffusion layer, the optical methods have great advantages from the following reasons: They do not disturb the depositing process and are

probably precise in determining the geometry of diffusion layer, and in determining small variations of metal concentration in diffusion layer. However, the usual optical methods which depend on a change in the index of refraction connected with the concentration of solution are not applicable to study of alloy deposition, since they do not give any information of the concentration of each substance. Indeed any data about cathode diffusion layer in alloy deposition have not been found except Brenner's data obtained by means of freezing method⁷⁾,

Thus, in this investigation a new optical method,

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