Thermodynamic Analysis for Vapor Growth of $In_{1-x}Ga_xP$ and $In_{1-x}Ga_xAs$ Crystals

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Abstract. **The open tube vapor growth process of $In_{1-x}Ga_xP$ and $In_{1-x}Ga_xAs$ crystal in the In-Ga- Cl- H- P and In-Ga- Cl- As systems is analyzed by a chemical equilibrium model, and the relation between growth condition and crystal composition is discussed.**

Keywords: **vapor-phase growth, vapor-phase epitaxy, $In_{1-x}Ga_xP$ and $In_{1-x}Ga_xAs$, ternary systems .**

I. INTRODUCTION.

$In_{1-x}Ga_xP$ and $In_{1-x}Ga_xAs$ alloys have received much attention as materials for laser and detector diodes in long-distance fiber-optical communication system. The alloys lattice-matched to InP substrates can be grown by vapor-phase epitaxy. For the preparation of these alloys, it is essential to know fundamentally the growth aspects of $In_{1-x}Ga_xP$ and $In_{1-x}Ga_xAs$ alloys from the vapor phase. The thermodynamic calculation provide a useful tool for prediction of the deposit composition. The purpose of this paper is to describe the detailed analysis of the $In_{1-x}Ga_xP$ and $In_{1-x}Ga_xAs$ vapor growth.

II.THERMODYNAMIC ANALYSIS. CALCULATION PROCEDURE.

In this report the equilibrium partial pressures of gaseous species were calculated by taking account of the activities of the binary compounds in the alloys.

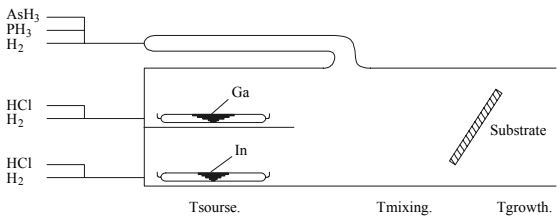

Fig.1. Schematic diagram.

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Calculation about thermodynamic data show that in the Ga-In-P-H_2-HCl and Ga-In-As-H_2-HCl systems within the temperature range 600-900^{0}C possible stable species are following 9 species: CaCl, InCl, P_4 (As_4), P_2 (P_4), $InCl_2$, $InCl_3$, HCl, $CaCl_3$ and H_2.

Figure 1 show schematic diagram of the VPE system.

The chemical reactions which connect all the species at the deposition zone are[2]:

$$2InCl+0,5P_4(As_4)+H_2=2InP(As)_{alloy.}+2HCl \quad (1)$$
$$2GaCl+0,5P_4(As_4)+H_2=2GaP(As)_{alloy.}+2HCl \quad (2)$$
$$GaCl+2HCl = GaCl_3+H_2 \quad (3)$$
$$InCl+2HCl =InCl_3+H_2 \quad (4)$$
$$2InCl+2HCl =2InCl_2+H_2 \quad (5)$$
$$P_4(As_4)=2P_4(As_4) \quad (6)$$

where:$GaP(As)_{alloy}$, $InP(As)_{alloy}$ stand for the binary compounds in the $In_{1-x}Ga_xP$ and $In_{1-x}Ga_xAs$ alloy.

The equlilibrium equations for these reactions are as follows:

$$K_1 = a_{InP}(a_{InAs})^2 P_{HCl}^2 /P_{InCl}^2 P_{P4(AS4)}^{1/2} P_{H2} \quad (7)$$
$$K_2 = a_{GaP}(a_{GaAs})^2 P_{HCl}^2 /P_{GaCl}^2 P_{P4(AS4)}^{1/2} P_{H2} \quad (8)$$
$$K_3 = P_{GaCl3}P_{H2} /P_{GaCl} P_{HCl}^2 \quad (9)$$
$$K_4= P_{InCl3} P_{HCl} /P_{InCl}P_{HCl}^2 \quad (10)$$
$$K_5= P_{InCl2}^2 P_{H2} /P_{InCl}^2P_{HCl}^2 \quad (11)$$
$$K_6= P_{P2(AS2)}^2 /P_{P4(As4)} \quad (12)$$
$$P_{GaCl}+P_{InCl}+P_{P4(AS4)}+P_{P2(As2)}+P_{InCl2}+P_{InCl3}+P_{GaCl3}+P_{HCl}+P_{H2}=1 \quad (13)$$
$$A=(P_{InCl}+ 2P_{InCl2}+ 3P_{InCl3} + P_{GaCl} +3P_{GaCl3}+P_{HCl})(2P_{H2}+ P_{HCl})^{-1} \quad (14)$$
$$B=[(P_{InCl}+P_{InCl2}+P_{InCl3}+P_{GaCl}+P_{GaCl3})-(4P_{P4(As4)}+2P_{P2(As2)})](2P_{H2}+P_{HCl})^{-1} \quad (15)$$

where: $a_{GaP}(a_{GaAs})$ and $a_{InP}(a_{InAs})$ are the activities of InP(InAs) and GaP(GaAs) in the alloy. Equation (7) to (12) are obtained from the equilibrium condition.

A(eq.14) is the atomic ratio of the number of chlorine atoms to the number of hydrogen atoms in the system which is conserved throughout the reaction tube. B (eq.15) is the ratio of the number of group III atoms minus the number of

group V atoms to the number of hydrogen. Eq(13) expresses that the total pressure equals 1 atmosphere in the open tube process.

The activities in the solid phase can be expressed as:

For InGaP:

$$a_{InP}(T,x) = x.\left\{\frac{\beta(T,x)-1+2.x}{x.[\beta(T,x)+1]}\right\}^{\frac{Z}{2}} \quad (16)$$

$$a_{GaP}(T,x) = (1-x).\left\{\frac{\beta(T,x)+1-2.x}{(1-x).[\beta(T,x)+1]}\right\}^{\frac{Z}{2}} \quad (17)$$

$$\beta(T,x) = \sqrt{1+4x.\left(1-x\left[\eta^2(T)-1\right]\right)} \quad (18)$$

$$\eta(T) = e^{\frac{\Omega}{Z.R.T}} \quad (19)$$

For InGaAs:

$$a_1(T,x) = xe^{\frac{a(1-x)^2}{RT}} \quad (20)$$

$$a_2(t,x) = (1-x)e^{\frac{ax^2}{RT}} \quad (21)$$

where:
x is the mole fraction of InP and InAs in the alloy
Ω is the interaction parameter (2000 cal/mol)
a is interactive parameter
R is (8,319 $m^3.Pa.mol^{-1}.K^{-1}$)
T is the temperature
Z is 12
For eq 7-12 the equilibrium constant are:

$$\lg K_i(T) = \text{const}\, a_i \frac{1000}{T} + \text{const}\, b_i \quad (21)$$

The calculations can easily be carried out with a computer, so that a large number of various combinations of pertinent variable cold be tested.

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III.RESULTS

The equilibrium partial pressures of gaseous species over $In_{1-x}Ga_xP$ and $In_{1-x}Ga_xAs$ alloys are shown in figs 2 to 12.

Fig.2 shows the partial pressures of the $InCl_2$ as a function of the parameter A. Increasing A, the partial pressures of the $InCl_2$ increase.

The partial pressures of $InCl_2$ is shown as function of temperature (Fig.3).

The partial pressures are shown as function of temperature (fig.4) and the alloy composition fig.5. It is seen thet predominant species are CaCl, InCl, P_4, P_2, and HCl and thet the partial pressure of InCl is considerably larger then that of CaCl.

Fig.6, 10, 11, 12 to 13 shows the variation of GaCl, P_4,H_2, InCl, $InCl_2$ as a function of alloy composition for various temperature.

Fig.7 shows the variation of log partial pressure of P_4 as a function of log parameter A for various B.

Fig.8 shows the variation of log partial pressure of $InCl_3$ as a function of parameter X for various B.

Fig.9 shows the variation of partial pressure of InCl as a function of parameter x, temperature for various B.

IV. SUMMARY.

Taking InGaP as an example, vapor growth by open tube process of ternary III-V compounds was analyzed thermodynamically. For this purpose, chemical equilibria of $In_{1-x}Ga_xP$-H_2-HCl-P_4 system was calculated.

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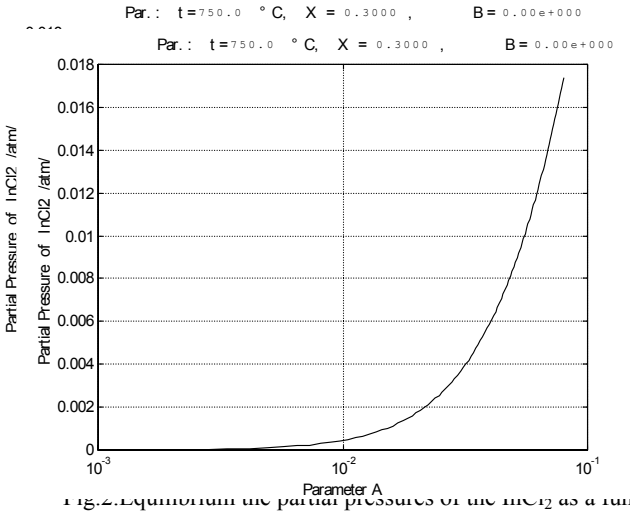

Fig.2.Equilibrium the partial pressures of the $InCl_2$ as a function of the parameter A.

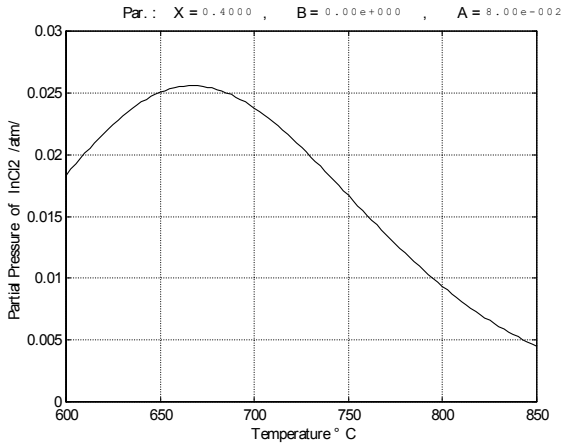

Fig.3.Equilibrium the partial pressures of the $InCl_2$ as a function of the temperature ^0C

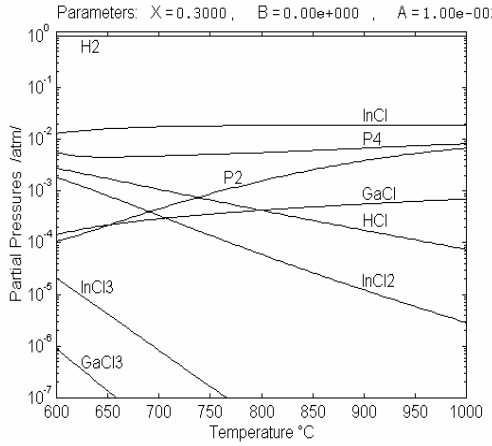

Fig.4-Equilibrium the partial pressures of the various species as a function of the temperature.

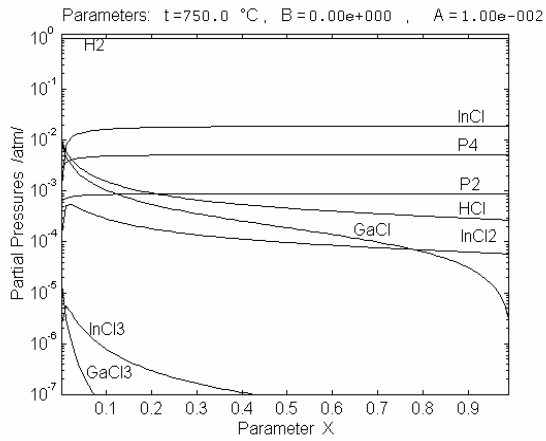

Fig.5 shows the variation of the partial pressures of the gaseous species with the parameter x.

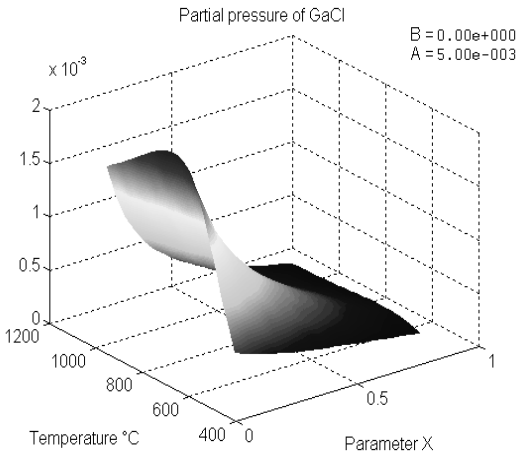

Fig.6 shows the variation of GaCl, as a function of alloy composition for various temperature.

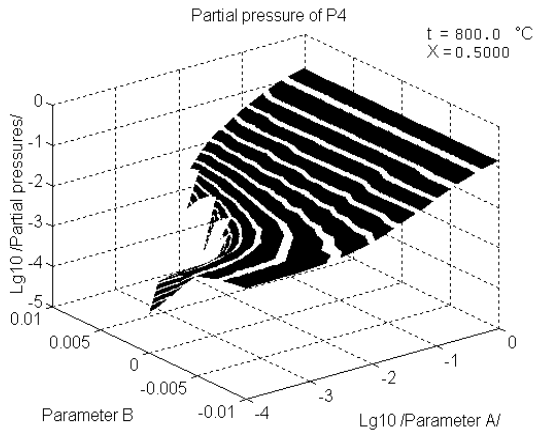

Fig.7. shows the variation of log partial pressure of P_4 as a function of log parameter A for various B.

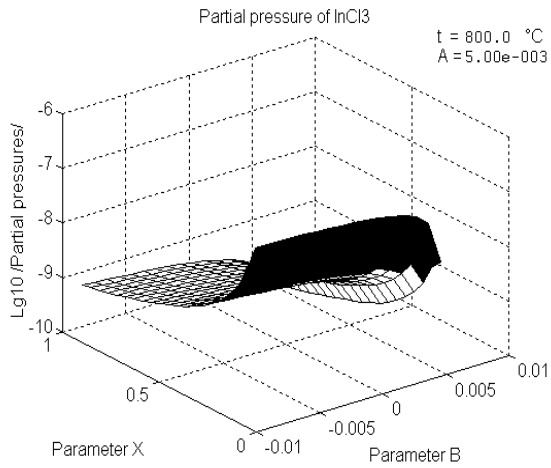

Fig.8 shows the variation of log partial pressure of $InCl_3$ as a function of parameter X for various B.

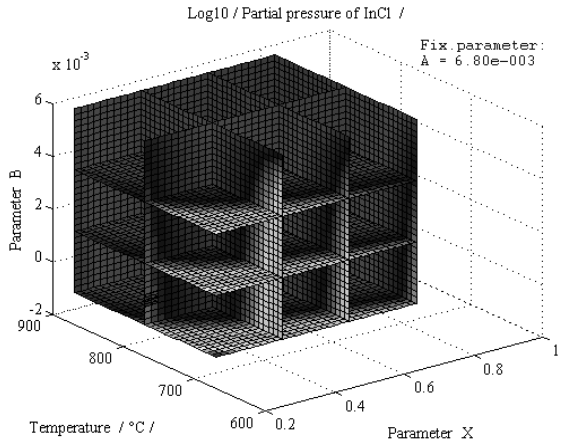

Fig.9 shows the variation of log partial pressure of InCl as a function of parameter X for various B.

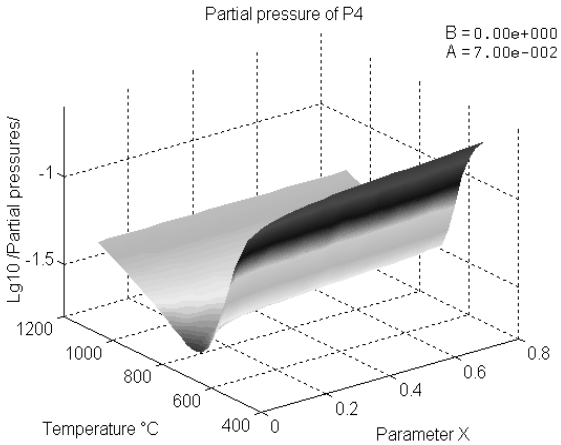

Fig.10 shows the variation of P_4, as a function of alloy composition for various temperature.

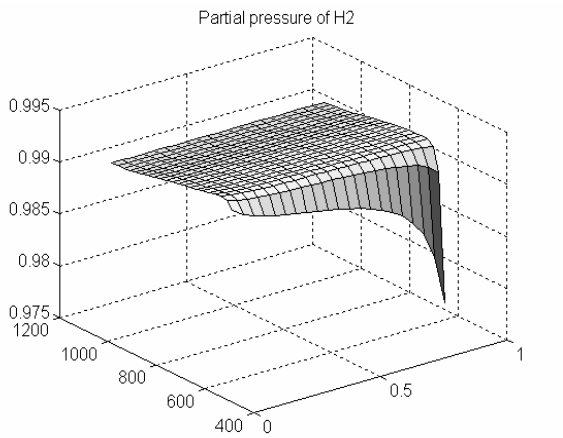

Fig.11 shows the variation of H_2, as a function of alloy composition for various temperature.

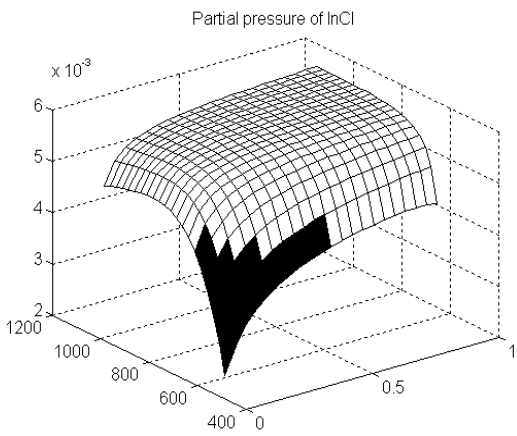

Fig.12 shows the variation of InCl, as a function of alloy composition for various temperature.

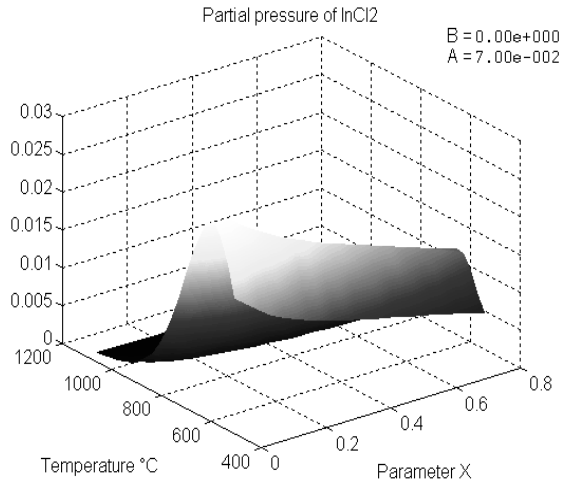

Fig.12 shows the variation of $InCl_2$ as a function of alloy composition for various temperatu