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THERMODYNAMIC ANALYSIS OF THE MOVPE GROWTH OF QUATERNARY III–V ALLOY SEMICONDUCTORS

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A chemical equilibrium model is applied to the MOVPE growth of quaternary III–V alloys. The equilibrium partial pressures and the diagram of solid composition versus input mole ratio are computed for InGaAsP, GaAlAsP, InAlAsP, InGaAsSb, AlGaInP, AlGaInAs, and InAsSbP alloys. It is shown that under normal growth conditions (V/III > 1), the incorporation of the group III elements into the solid phase is a linear function of the input mole ratio of the group III metalorganic sources, while that of the group V elements differs significantly from the input vapor phase content. For several alloys, the vapor–solid distribution relation is discussed in comparison with the experimental data reported in the literature.

1. Introduction

The epitaxial growth of quaternary III–V alloys is very important, because the alloys involve key materials for many applications. Metalorganic vapor phase epitaxy (MOVPE) is investigated as one of the most attractive methods for the preparation of epitaxial layers. However, studies of the growth mechanism of quaternary alloys are scarce and most of the work has been done empirically.

This work is a continuation of our thermodynamic studies of MOVPE. As pointed out by Stringfellow [1,2], thermodynamics provides very useful information. For instance, it has been shown that the equilibrium model predicts the alloy composition and growth rate of MOVPE [1–6]. While these studies clarified the thermodynamic characteristics of binary compounds and ternary alloys, those of quaternary alloys have been left without detailed investigation.

The purpose of this paper is to describe a thermodynamic analysis of quaternary alloys grown by MOVPE. In order to calculate the equilibrium partial pressure, a previously developed computation method [5,6] has been extended to the growth system of quaternary alloys. For several alloys, the vapor–solid distribution relation is discussed in comparison with experimental data reported in the literature. It will be seen that the present analysis provides an efficient guide for the MOVPE growth of quaternary alloys.

2. Calculation procedure

The following 10 species are chosen as the necessary vapor species in analyzing the MOVPE growth of $In_{1-x}Ga_xAs_yP_{1-y}$: Ga, In, As_4, As_2, P_4, P_2, AsH_3, PH_3, H_2, and C_2H_6. Here, we describe the growth of $In_{1-x}Ga_xAs_yP_{1-y}$ alloys using triethylgallium (TEGa), triethylindium (TEIn), AsH_3 and PH_3, as an example of quaternary systems. Of course, the calculation of other systems such as III–III–III–V and III–V–V–V alloys can be done with a similar procedure. The input TEGa and TEIn are decomposed irreversibly according to the following homogeneous reaction near the vapor–solid interface [7,8]:

$$Ga(C_2H_5)_3(g) + \tfrac{3}{2}H_2(g) \rightarrow Ga(g) + 3\,C_2H_6(g), \quad (1)$$

$$In(C_2H_5)_3(g) + \tfrac{3}{2}H_2(g) \rightarrow In(g) + 3\,C_2H_6(g). \quad (2)$$

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The chemical reactions which connect all the species at the vapor–solid interface are:

$$Ga(g) + \tfrac{1}{4}As_4(g) = GaAs(alloy), \quad (3)$$

$$In(g) + \tfrac{1}{4}As_4(g) = InAs(alloy), \quad (4)$$

$$Ga(g) + \tfrac{1}{4}P_4(g) = GaP(alloy), \quad (5)$$

$$In(g) + \tfrac{1}{4}P_4(g) = InP(alloy), \quad (6)$$

$$As_4(g) = 2\,As_2(g), \quad (7)$$

$$P_4(g) = 2\,P_2(g), \quad (8)$$

$$AsH_3(g) = \tfrac{1}{2}As_2(g) + \tfrac{3}{2}H_2(g), \quad (9)$$

$$PH_3(g) = \tfrac{1}{2}P_2(g) + \tfrac{3}{2}H_2(g), \quad (10)$$

where GaAs(alloy), InAs(alloy), GaP(alloy), and InP(alloy) stand for the binary compounds in the $In_{1-x}Ga_xAs_yP_{1-y}$ alloy. Thus, the equilibrium equations for these reactions are as follows:

$$K_1 = a_{GaAs}/P_{Ga}P_{As_4}^{1/4}, \quad (11)$$

$$K_2 = a_{InAs}/P_{In}P_{As_4}^{1/4}, \quad (12)$$

$$K_3 = a_{GaP}/P_{Ga}P_{P_4}^{1/4}, \quad (13)$$

$$K_4 = a_{InP}/P_{In}P_{P_4}^{1/4}, \quad (14)$$

$$K_5 = P_{As_2}^2/P_{As_4}, \quad (15)$$

$$K_6 = P_{P_2}^2/P_{P_4}, \quad (16)$$

$$K_7 = P_{As_2}^{1/2}P_{H_2}^{3/2}/P_{AsH_3}, \quad (17)$$

$$K_8 = P_{P_2}^{1/2}P_{H_2}^{3/2}/P_{PH_3}, \quad (18)$$

where a_{GaAs}, a_{InAs}, a_{GaP}, and a_{InP} are the activities of the binary compounds in the alloy. The total pressure of the system is expressed as follows:

$$\sum P_i = P_{Ga} + P_{In} + P_{As_4} + P_{As_2} + P_{AsH_3} + P_{P_4} + P_{P_2} + P_{PH_3} + P_{H_2} + P_{C_2H_6}. \quad (19)$$

From conservation constraints we have

$$P_{III}^0 - (P_{Ga} + P_{In}) = P_V^0 - 4(P_{As_4} + P_{P_4}) - 2(P_{As_2} + P_{P_2}) - (P_{AsH_3} + P_{PH_3}), \quad (20)$$

$$P_{C_2H_6} = 3P_{III}^0, \quad (21)$$

where P_{III}^0 and P_V^0 are the input partial pressure of group III and group V species. Eq. (20) expresses the fact that the deposition occurs in the ratio of 1 to 1 for group III and group V elements.

The mole fractions x and y in $In_{1-x}Ga_xAs_yP_{1-y}$ alloy are given by the following equations:

$$x = (P_{Ga}^0 - P_{Ga})\left[(P_{Ga}^0 - P_{Ga}) + (P_{In}^0 - P_{In})\right]^{-1}, \quad (22)$$

$$y = (P_{As}^0 - 4P_{As_4} - 2P_{As_2} - P_{AsH_3}) \times \left[(P_{As}^0 - 4P_{As_4} - 2P_{As_2} - P_{AsH_3}) + (P_P^0 - 4P_{P_4} - 2P_{P_2} - P_{PH_3})\right]^{-1}. \quad (23)$$

The equilibrium partial pressures were calculated by using a method similar to that developed previously [5]. Most of the calculations were carried out at a total pressure of 1 atm. The values of the equilibrium constants were the same as those in our previous paper [5]. For a detailed calculation procedure for the quaternary alloy of III–III–V–V systems, the paper on halogen transport VPE [9] should be consulted. The activity coefficients in the alloy were calculated with the delta lattice parameter (DLP) model proposed by Stringfellow [10].

3. Results and discussion

3.1. III–III–V–V systems

As InGaAsP alloys are used most widely in this system, we describe mainly the alloys lattice-matched to InP. Figs. 1 to 3 show the equilibrium partial pressures of gaseous species over InGaAsP alloys. The general features of the equilibrium partial pressures are found to be quite similar to those of the GaAs and InP systems [6]. For instance, the equilibrium partial pressures of C_2H_6 and PH_3 are high. The partial pressures of the group III elements are extremely low under normal growth conditions (V/III > 1). This is a remarkable feature generally obtained in MOVPE growth. Under these conditions, we have $P_{Ga} \approx 0$

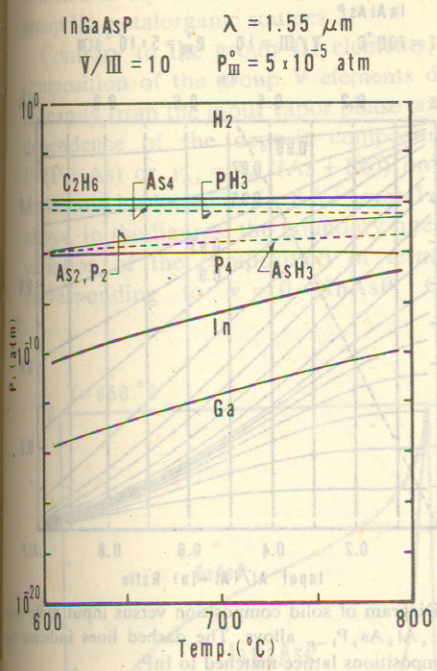

Fig. 1. The equilibrium partial pressures of gaseous species over InGaAsP ($\lambda = 1.55$ μm) as a function of temperature.

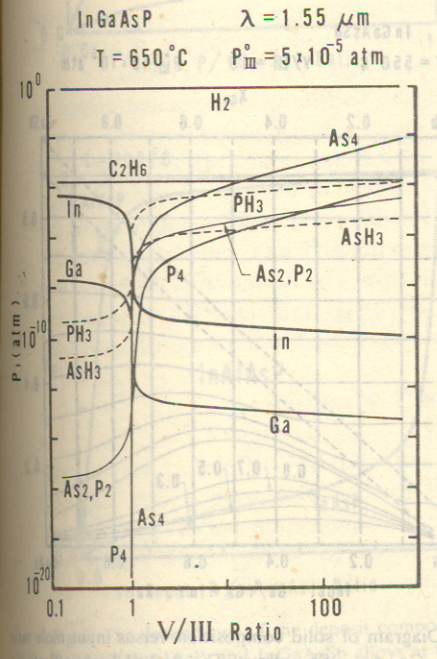

Fig. 2. The equilibrium partial pressures over InGaAsP ($\lambda = 1.55$ μm) as a function of V/III ratio.

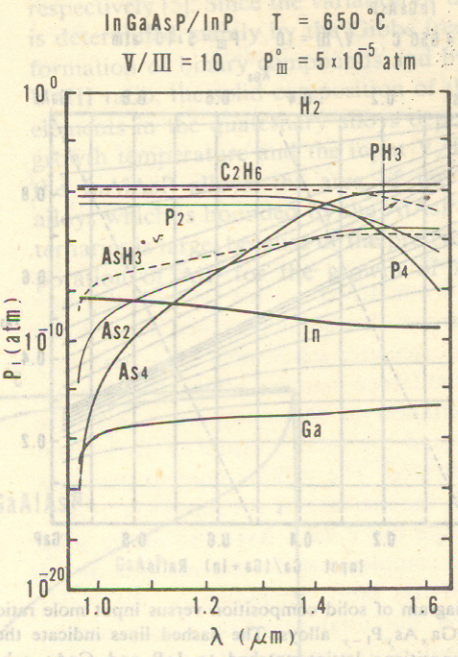

Fig. 3. The equilibrium partial pressures over InGaAsP/InP as a function of wavelength.

and $P_{In} \approx 0$. Inserting these values, eq. (22) becomes:

$$x = P^{0}_{Ga} / \left(P^{0}_{Ga} + P^{0}_{In} \right). \qquad (24)$$

Thus, the solid composition of the group III elements becomes a linear function of the input mole ratio of the group III metalorganic sources [3,5]. This contrasts markedly with hydride and chloride VPE [9,11]. It is worthwhile noting that this linear relation holds in all quaternary systems and agrees with the experimental observations [12,13].

Figs. 4 to 7 show the diagrams of solid composition versus input mole ratio for several quaternary alloys. The dashed lines indicate the allow compositions lattice-matched to the respective binary compounds. From these diagrams, we can predict the input mole ratios necessary for the preparation of an alloy of the desired composition. The preferential deposition of AlP in GaAlAsP alloys and InAs in InGaAsSb alloys is seen. As described above, we find that in all alloy systems the solid composition of the group III

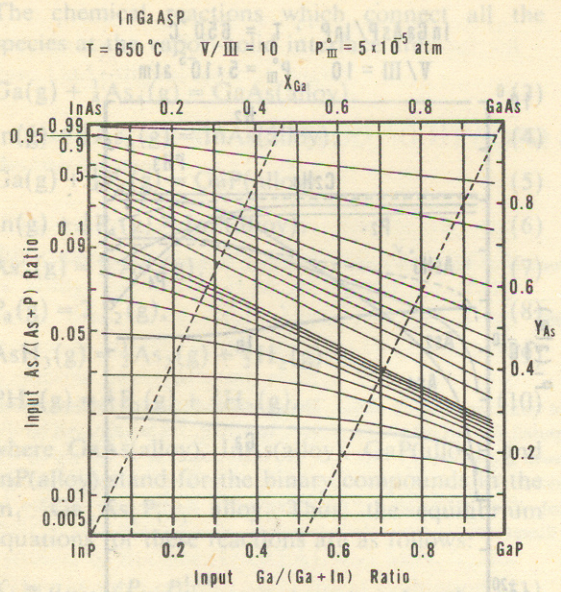

Fig. 4. Diagram of solid composition versus input mole ratio for $In_{1-x}Ga_xAs_yP_{1-y}$ alloys. The dashed lines indicate the alloy compositions lattice-matched to InP and GaAs substrates.

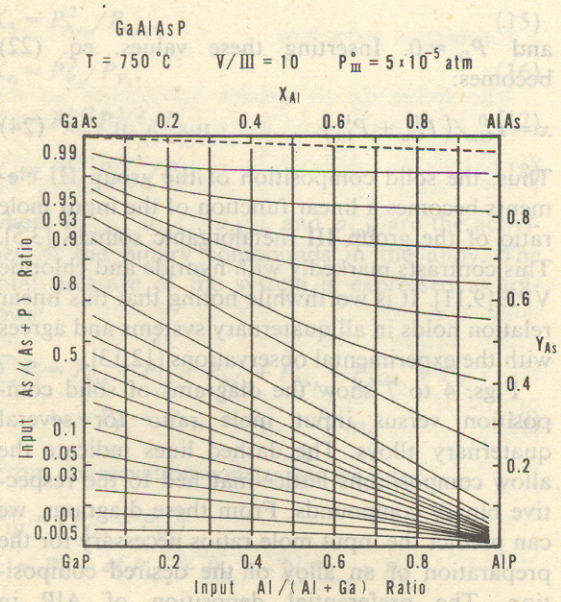

Fig. 5. Diagram of solid composition versus input mole ratio for $Ga_{1-x}Al_xAs_yP_{1-y}$ alloys. The dashed lines indicate the alloy compositions lattice-matched to GaAs.

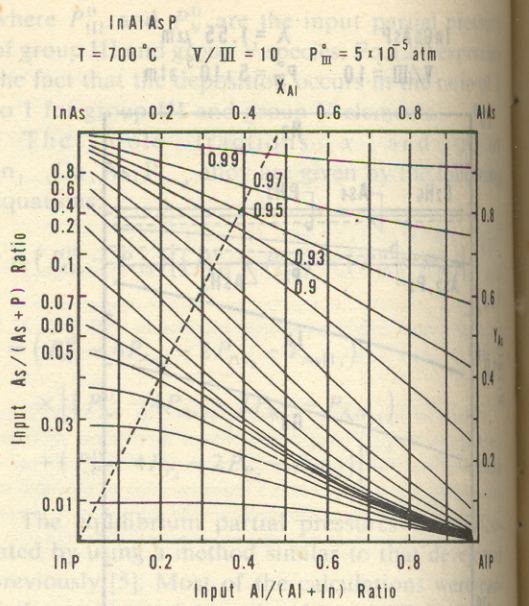

Fig. 6. Diagram of solid composition versus input mole ratio for $In_{1-x}Al_xAs_yP_{1-y}$ alloys. The dashed lines indicate the alloy compositions lattice-matched to InP.

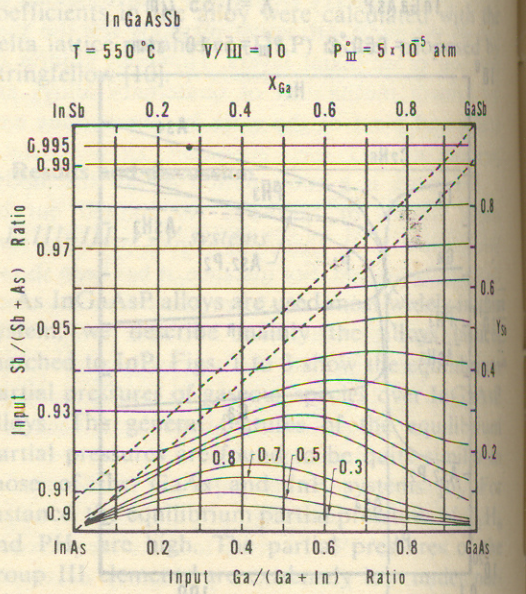

Fig. 7. Diagram of solid composition versus input mole ratio for $In_{1-x}Ga_xAs_{1-y}Sb_y$ alloys. The dashed lines indicate the alloy compositions lattice-matched to InAs and GaSb.

elements is equal to the input mole ratio of the group III metalorganic sources.

Contrary to the group III elements, the solid composition of the group V elements differs significantly from the input vapor phase content. The dependence of the deposit composition ($y_P = P/(P+As)$ or $y_{As} = As/(As+Sb)$) on the input mole ratio is plotted in fig. 8 for several quaternary alloys. In the figures, the boundary lines show the variation of the composition of ternary alloys, corresponding to $x = 0$ (InAsP, GaAsP or GaAsSb) and $x = 1$ (GaAsP, AlAsP or InAsSb), respectively [5]. Since the variation of these curves is determined mainly by the Gibbs free energy of formation of binary compounds and by the input V/III ratio, the solid composition of the group V elements in the quaternary alloys depends on the growth temperature and the input V/III ratio. In the InAlAsP alloys, the area of the quaternary alloys which is bounded by the AlAsP and InAsP ternaries is large, because of the preferential incorporation of AlP for the growth of AlAsP, and

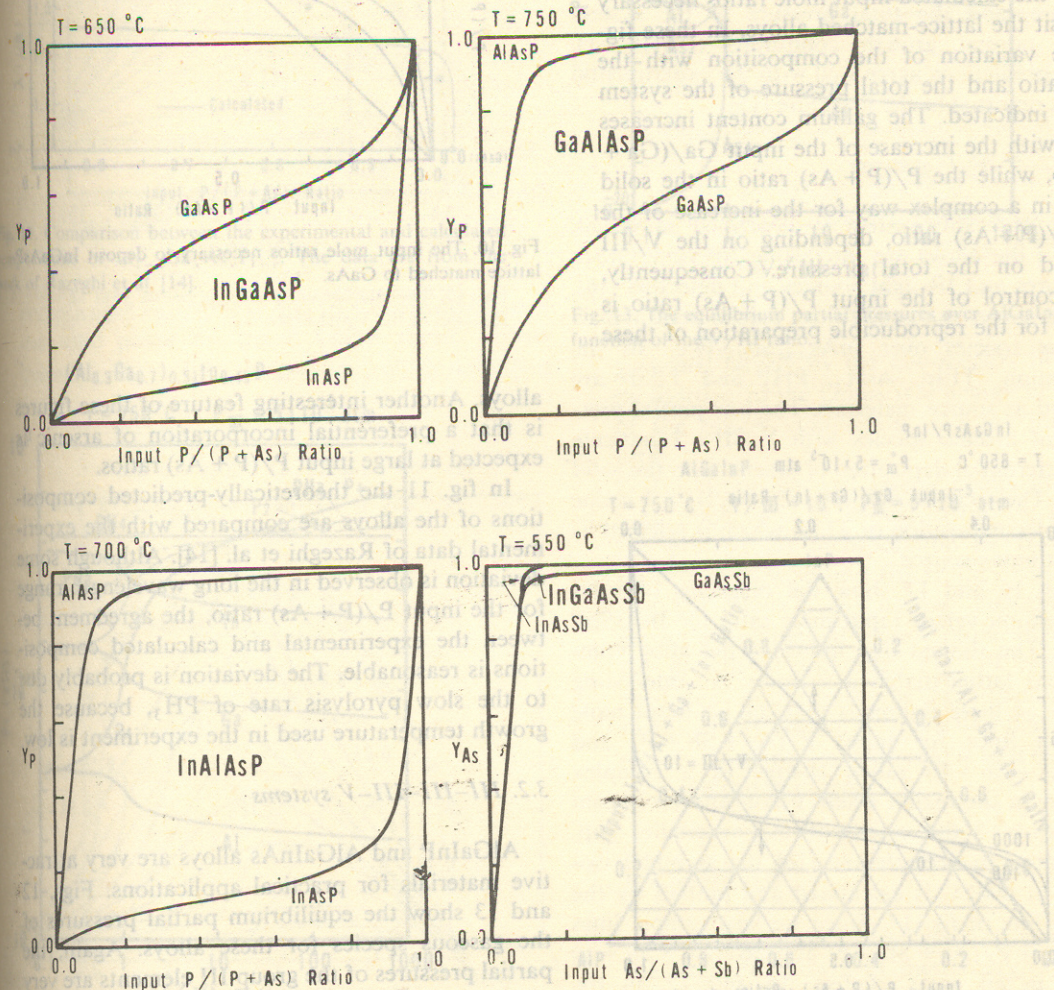

Fig. 8. The dependence of the deposit composition ($y_P = P/(P+As)$ or $y_{As} = As/(As+Sb)$) on the input mole ratio for InGaAsP, GaAlAsP, InAlAsP, and InGaAsSb alloys at the following conditions: V/III = 10, $P^0_{III} = 5\times10^{-5}$ atm.