

Simple Thermodynamic Equations to Calculate Driving Force for $\text{In}_x\text{Ga}_{1-x}\text{As}$ Crystals which Grow from their Own Melt

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To evaluate thermodynamic driving force during the growth of InGaAs, simple two lattice excess enthalpy model was applied. It was found that the In-Ga-As system could be reduced to InAs-GaAs pseudo-binary system, keeping the validity of two lattice model. Differential lattice parameter model was applied to estimate excess enthalpy term for solid. Thermodynamic equations were constructed to calculate the thermodynamic driving force during crystallization processes. Reconstructed phase diagram using the present equation well explained the experimental phase relation data.

1. Introduction

$\text{In}_x\text{Ga}_{1-x}\text{As}$ is one of ternary 3-5 semiconductor systems but which is usually represented as InAs-GaAs pseudo-binary solid-solution system for convenience. Figure 1 shows InAs-GaAs equilibrium phase diagram based on experimentally obtained data¹⁾⁻⁷⁾. This diagram is a fundamental knowledge to grow crystals of desired composition. Since $\text{In}_x\text{Ga}_{1-x}\text{As}$ crystals show anisotropic growth characteristics such as existence of facets, we have to know kinetic parameters of crystal growth to obtain high quality crystals. Among the kinetic parameters, the most important parameter seems to be thermodynamic driving force. So, we have to evaluate the parameter as functions of temperature and concentration.

Some semi-empirical methods have been developed to reconstruct phase relations of the system, in which thermodynamic parameters have been selected to fit the experimental data^{8),9)}.

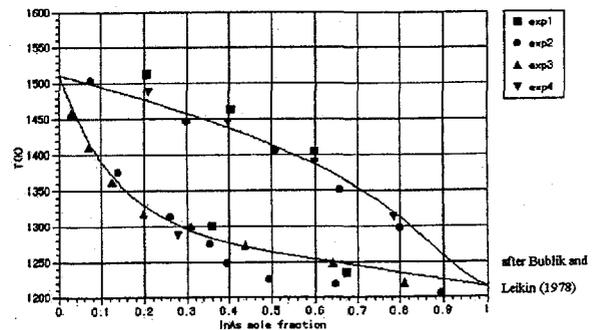


Fig1 Phase diagram for InAs-GaAs pseudo-binary system

More fundamental approach to reconstruct In-Ga-As system was developed by Strings^{10),11)} and Ma et.al¹²⁾ in which both liquid state and solid state have non-ideal characters. Their methods are useful to reconstruct phase diagrams but a little bit complicated to evaluate thermodynamic driving force. This paper describes a simple method to evaluate the driving force.

2. Two lattice model

InxGa1-xAs system is a solid solution system with wider compositional variations. In and Ga possesses same site in the crystal structure, and substitute each other. While As is never substituted by the other components. A convenient method to treat such type of solid solution is to utilize two sub-lattices^{15,16}).

First, we consider (A,B)(x,y) solid-solution crystal system to clarify the physical meaning of two lattice model. In the system, element A and B possesses same lattice site and substitute each other. Relationship between element x and y is similar to that of A and B. However, (A,B) and (x,y) never possess same lattice site. In this case, two sub-lattices are assumed, called lattice 1 and lattice 2, to calculate thermodynamic parameters. All nodes of lattice 1 are assumed to be filled with either element A or B. Lattice 2 also assumed to be filled with element x or y. No substitution between (A,B) and (x,y) is assumed.

Gibbs free energy of lattice 1 is represented as follows;

$$G^1 = \left[G_A^x p_A + G_B^x p_B + L_{AB}^x + RT(p_A \ln(p_A) + p_B \ln(p_B)) \right] p_x + \left[G_A^y p_A + G_B^y p_B + L_{AB}^y + RT(p_A \ln(p_A) + p_B \ln(p_B)) \right] p_y \quad [1]$$

where $G^1, G_A^x, G_B^x, G_A^y, G_B^y$ denotes total energy of lattice 1, partial molar energy of component A in pure component x, partial molar energy of component B in pure component x, partial molar energy of component A in pure component y, partial molar energy of component B in pure component y, respectively.

Molar fractions of A, B, x, y, denoted as p_A, p_B, p_x, p_y , satisfies following relationship, respectively.

$$p_A + p_B = 1 \quad [2a]$$

$$p_x + p_y = 1 \quad [2b]$$

Total energy of lattice 2 is also represented as follows;

$$G^2 = \left[G_x^A p_x + G_y^A p_y + L_w^A + RT(p_x \ln(p_x) + p_y \ln(p_y)) \right] p_A + \left[G_x^B p_x + G_y^B p_y + L_w^B + RT(p_x \ln(p_x) + p_y \ln(p_y)) \right] p_B \quad [3]$$

The total energy of (A,B)(x,y) is written as a sum of the energies of the sub-lattices; $G = G^1 + G^2$.

$$G = (G^1 + G^2) = G^{Ax} p_A p_x + G^{Bx} p_B p_x + G^{Ay} p_A p_y + G^{By} p_B p_y + [L_{AB}^x p_x + L_{AB}^y p_y] p_A p_B + [L_w^A p_A + L_w^B p_B] p_x p_y + RT[p_A \ln(p_A) + p_B \ln(p_B) + p_x \ln(p_x) + p_y \ln(p_y)] \quad [4]$$

Where, $G^{Ax}, G^{Ay}, G^{Bx}, G^{By}$ are free energies of phase Ax, Ay, Bx, By, respectively, and written as follows;

$$G^{Ax} = (G_A^x + G_x^A) \quad [5a]$$

$$G^{Ay} = (G_A^y + G_y^A) \quad [5b]$$

$$G^{Bx} = (G_B^x + G_x^B) \quad [5c]$$

$$G^{By} = (G_B^y + G_y^B) \quad [5d]$$

3. Simplification for InxGa1-xAs

Since InxGa1-xAs system is ternary, the equations are simplified to following form.

$$G^1 = \left[G_{In}^{Ax} p_{In} + G_{Ga}^{Ax} p_{Ga} + L_{InGa}^{Ax} + RT(p_{In} \ln(p_{In}) + p_{Ga} \ln(p_{Ga})) \right] \quad [6a]$$

$$G^2 = [G_{In}^{Ay}] p_{In} + [G_{Ga}^{Ay}] p_{Ga} \quad [6b]$$

The selected lattices are demonstrated in Fig.2.

So, the total energy of (In,Ga)As is written as follows.

$$G = (G^1 + G^2) = G^{InAs} p_{In} + G^{GaAs} p_{Ga} + [L_{InGa}^{As}] p_{In} p_{Ga} + RT[p_{In} \ln(p_{In}) + p_{Ga} \ln(p_{Ga})] \quad [7]$$

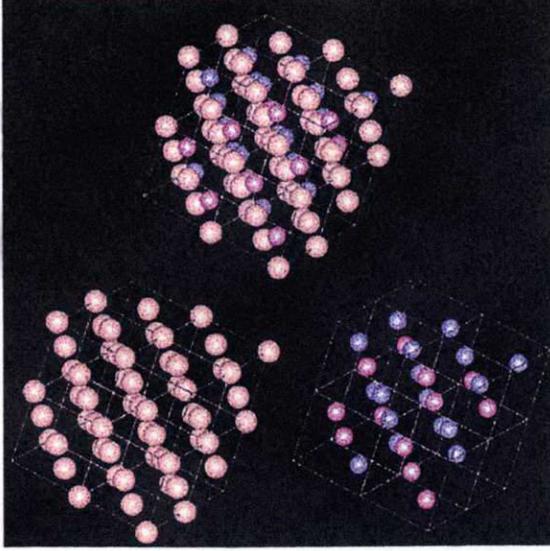


Fig.2 Two lattice model used for thermodynamic modelling of InAs-GaAs system

The form of eq.[7] is the same as that of binary excess enthalpy model, which has the following form.

$$G = G^{\text{InAs}} p_{\text{InAs}} + G^{\text{GaAs}} p_{\text{GaAs}} + \Omega_{\text{InGaAs}} p_{\text{InAs}} p_{\text{GaAs}} + RT \left[p_{\text{InAs}} \ln(p_{\text{InAs}}) + p_{\text{GaAs}} \ln(p_{\text{GaAs}}) \right] \quad [8]$$

So, we can treat In-Ga-As ternary system as InAs-GaAs binary solution system.

4. Thermodynamic driving force

Since $\text{In}_x\text{Ga}_{1-x}\text{As}$ liquid has metallic character, excess enthalpy term for liquid should be much smaller than that of solid solution. In this study, the excess enthalpy of the liquid is stated to be zero.

$$G_L = p_{\text{InAs},L} \mu_{\text{InAs},L} + p_{\text{GaAs},L} \mu_{\text{GaAs},L} = p_{\text{InAs},L} \mu_{\text{InAs},L}^0 + p_{\text{GaAs},L} \mu_{\text{GaAs},L}^0 + RT \left[p_{\text{InAs},L} \ln(p_{\text{InAs},L}) + p_{\text{GaAs},L} \ln(p_{\text{GaAs},L}) \right] \quad [9]$$

For the solid, we can not neglect the excess enthalpy term.

$$G_S = \mu_{\text{InAs},S}^0 p_{\text{InAs}} + \mu_{\text{GaAs},S}^0 p_{\text{GaAs}} + \Omega_{\text{InGaAs}} p_{\text{InAs}} p_{\text{GaAs}} + RT \left[p_{\text{InAs}} \ln(p_{\text{InAs}}) + p_{\text{GaAs}} \ln(p_{\text{GaAs}}) \right] \quad [10]$$

To calculate the eq.[10], we have to know the coefficient of excess enthalpy. For the purpose, we used DLP (differential lattice parameter) model developed by Stringfellow[10,11).

In DLP model, excess term is represented without the phase equilibrium data, as follows.

$$\Omega \cong 4.375K \frac{\Delta\alpha_0^2}{a^{4.5}} \quad [11]$$

Where, K is empirically determined coefficient between lattice constant and enthalpy of decomposition for semiconductors.

$$K = 5.279 \times 10^7 \text{ \AA}^{2.5} \quad [12]$$

So, chemical potentials of InAs and GaAs are written as follows.

1) Liquid state

$$\mu_{\text{InAs},L} = \mu_{\text{InAs},L}^0 + RT \ln(p_{\text{InAs},L}) \quad [13a]$$

$$\mu_{\text{GaAs},L} = \mu_{\text{GaAs},L}^0 + RT \ln(p_{\text{GaAs},L}) \quad [13b]$$

2) Solid state

$$\mu_{\text{InAs},S} = \mu_{\text{InAs},S}^0 + RT \ln(p_{\text{InAs},S}) + \Omega p_{\text{InAs},S} (1 - p_{\text{InAs},S}) \quad [13c]$$

$$\mu_{\text{GaAs},S} = \mu_{\text{GaAs},S}^0 + RT \ln(p_{\text{GaAs},S}) + \Omega p_{\text{GaAs},S} (1 - p_{\text{GaAs},S}) \quad [13d]$$

So, chemical potential differences between liquid state and solid state, $\Delta\mu$, are represented as follows.

$$\Delta\mu_{\text{InAs}} = \mu_{\text{InAs},L} - \mu_{\text{InAs},S} = \mu_{\text{InAs},L}^0 - \mu_{\text{InAs},S}^0 + RT \left[\ln(p_{\text{InAs},L}) - \ln(p_{\text{InAs},S}) \right] - \Omega p_{\text{InAs},S} (1 - p_{\text{InAs},S}) \quad [14a]$$

$$\Delta\mu_{\text{GaAs}} = \mu_{\text{GaAs},L} - \mu_{\text{GaAs},S} = \mu_{\text{GaAs},L}^0 - \mu_{\text{GaAs},S}^0 + RT \left[\ln(p_{\text{GaAs},L}) - \ln(p_{\text{GaAs},S}) \right] - \Omega p_{\text{GaAs},S} (1 - p_{\text{GaAs},S}) \quad [14b]$$

Moreover, the following equations are valid for pure InAs and GaAs.

$$\Delta\mu_{InAs}^0 = \mu_{InAs,L}^0 - \mu_{InAs,S}^0 = \frac{\Delta H_{M,InAs}}{T_{M,InAs}} (T_{M,InAs} - T) \quad [15a]$$

$$\Delta\mu_{GaAs}^0 = \mu_{GaAs,L}^0 - \mu_{GaAs,S}^0 = \frac{\Delta H_{M,GaAs}}{T_{M,GaAs}} (T_{M,GaAs} - T) \quad [15b]$$

Using eq.[15a] and eq.[15b], eq.[14a] and eq.[14b] are rewritten.

$$\Delta\mu_{InAs} = \frac{\Delta H_{M,InAs}}{T_{M,InAs}} (T_{M,InAs} - T) + RT \left[\ln(p_{InAs,L}) - \ln(p_{InAs,S}) \right] - \Omega p_{InAs,S} (1 - p_{InAs,S}) \quad [16a]$$

$$\Delta\mu_{GaAs} = \frac{\Delta H_{M,GaAs}}{T_{M,GaAs}} (T_{M,GaAs} - T) + RT \left[\ln(p_{GaAs,L}) - \ln(p_{GaAs,S}) \right] - \Omega p_{GaAs,S} (1 - p_{GaAs,S}) \quad [16b]$$

5. Phase diagram reconstruction

To evaluate the validity of above equations, we checked whether the equations reconstructed experimental phase diagram or not.

At liquidus temperature, chemical potential differences between liquid and solid must be equal to zero for both InAs and GaAs. So, the following relations must be satisfied at liquidus temperature, TL.

$$\mu_{InAs,L} - \mu_{InAs,S} = \frac{\Delta H_{M,InAs}}{T_{M,InAs}} (T_{M,InAs} - T_L) + RT_L \left[\ln(p_{InAs,L}) - \ln(p_{InAs,S}) \right] - \Omega p_{InAs,S} (1 - p_{InAs,S}) = 0 \quad [17a]$$

$$\mu_{GaAs,L} - \mu_{GaAs,S} = \frac{\Delta H_{M,GaAs}}{T_{M,GaAs}} (T_{M,GaAs} - T_L) + RT_L \left[\ln(p_{GaAs,L}) - \ln(p_{GaAs,S}) \right] - \Omega p_{GaAs,S} (1 - p_{GaAs,S}) = 0 \quad [17b]$$

Since $p_{InAs,L} + p_{GaAs,L} = p_{InAs,S} + p_{GaAs,S} = 1$, unknown parameters are InAs fraction in the liquid, $p_{InAs,L}$, InAs fraction in the solid, $p_{InAs,S}$, and liquidus temperature, T_L . So, we can calculate $(p_{InAs,L}, T_L)$ for desired $p_{InAs,S}$ using eq.[17a] and eq.[17b]. Since there were many latent heats data for both InAs and GaAs [13,14], we used averaged values, which are shown in Fig.3. Parameters used in the calculation are listed in Table 1.

Table1 Parameters used for calculation

Name	value	reference
InAs melting temperature(K)	1215	-
GaAs melting temperature(K)	1511	-
InAs enthalpy of melting(J/mol.)	110000	76986-140000
GaAs enthalpy of melting (J/mol.)	120000	87864-153000
InAs-GaAs coefficient of excess enthalpy (J/mol.)	12000	11794

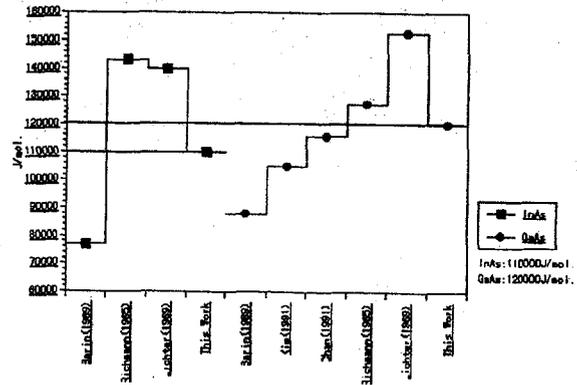


Fig.3 Latent heats of InAs and GaAs

Figure 4 shows an example to determine liquidus temperature and liquidus composition for desired solidus composition ($p_{InAs,S} = 0.2$). Calculated phase diagram is shown in Fig.5. In the figure, experimental data are also plotted. It is shown that the calculated curve well explains the experimental data, which means the validity of the present approach.

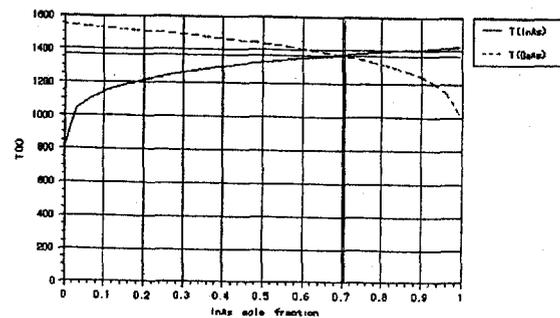


Fig.4 A method to determine liquidus temperature and liquid composition at desired solid composition

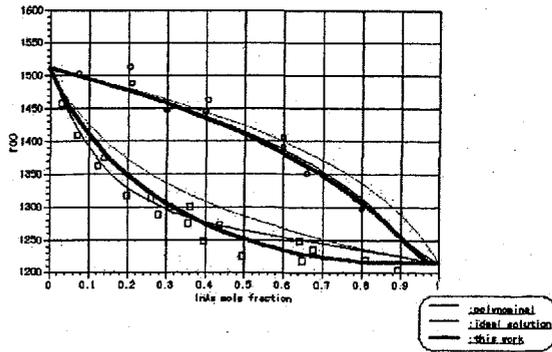


Fig.5 reconstructed InAs-GaAs phase diagram using thermodynamic parameters

6. Phase separation in sub solidus region

Since this model has excess enthalpy for solid solution, phase separation region is expected at sub solidus part. The phase separation region is defined by following equations.

$$G_{InGaAs}^{total}(x) \geq p_1 G_{InGaAs}^{total}(x_1) + p_2 G_{InGaAs}^{total}(x_2) \quad [18a]$$

$$\left. \frac{\partial G}{\partial x} \right|_{x=x_1} = \left. \frac{\partial G}{\partial x} \right|_{x=x_2} \quad [18b]$$

Inside the separation region, spinodal region is also expected, which is defined by the following equation.

$$\left. \frac{\partial^2 G}{\partial x^2} \right|_x \leq 0 \quad [19]$$

Free energies of the solid solution were calculated at sub solidus temperatures. Figure 6 shows some examples of calculated free energies at different temperatures.

Both calculated phase separation region and spinodal decomposition region are plotted in the phase diagram, shown in Fig.7.

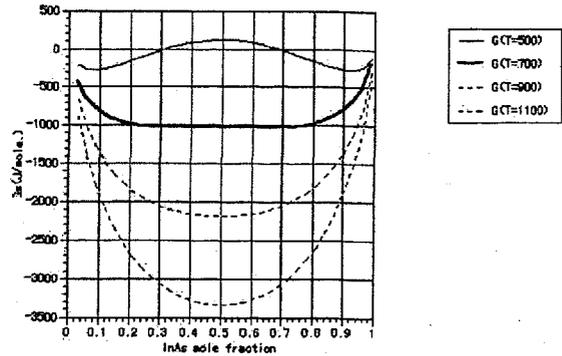


Fig.6 Calculated relative Gibbs free energies of solid, which indicate temperature effect of the energy

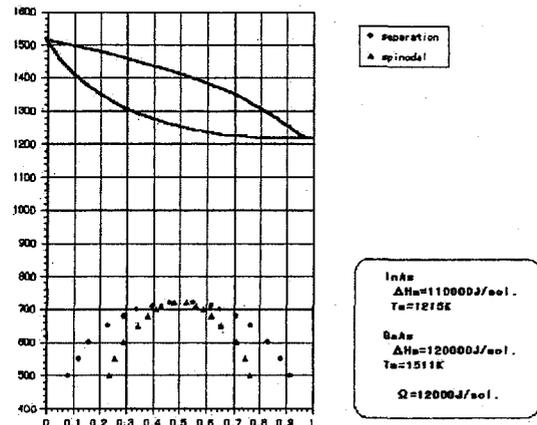


Fig.7 Calculated InAs-GaAs phase diagram which indicate a possibility of phase separation of solid at low temperature range

7. Summary

To evaluate thermodynamic driving force during the growth process of InGaAs, simple two lattice excess enthalpy model is applied. It was found that the In-Ga-As ternary system could be reduced to InAs-GaAs pseudo binary system, keeping the accuracy of two lattice model. DLP model was applied to estimate excess enthalpy term for the solid. The reconstructed phase diagram well explains the experimental phase equilibrium data. This result represents the validity of the present approach.

Thermodynamic driving force is a basic parameter for crystal growth research. The present work supplies one simple solution to evaluate the parameters.

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