

# CALCULATION OF PHASE DIAGRAM FOR PSEUDOBINARY GaAs-InAs<sup>①</sup>

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## ABSTRACT

The phase diagram for the pseudobinary GaAs-InAs has been calculated using the optimized thermodynamic data on accounting the influence of the elastic energy, which is induced by the mismatch of the growing lattice with the substrate in the process of epitaxy. The result shows that the miscibility gap in the solid phase of this system would be restrained by this elastic energy.

**Key words:** GaAs-InAs III - V compound calculation of phase diagram miscibility gap

## 1 INTRODUCTION

The phase diagram of pseudobinary GaAs-InAs has been reported in some literature<sup>[1-7]</sup>. It belongs to the system with complete miscibility in liquid phase and with miscibility gap in solid state. But when the III - V semi-conductor compounds are produced in the process of epitaxy and the growing lattice parameter is different from that of the substrate, deformation of the lattice occurs in certain layers of the product. The comparison of the calculated phase diagram with the experimental results for the ternary Ga-In-As shows that the addition of elastic energy in Gibbs energy is necessary for above case. In this paper we present the influence of the elastic energy upon the phase diagram of the pseudobinary GaAs-InAs, especially upon the miscibility gap of the solid solution of this system.

## 2 CALCULATED PHASE DIAGRAM OF PSEUDOBINARY GaAs - InAs WITH- OUT ELASTIC ENERGY

The thermodynamic parameters for the system

of Ga-In-As were optimized by the CALPHAD technique<sup>[7]</sup>. Redlich-Kister formula was used for expressing excess Gibbs energy of both liquid and solid, where the liquid is considered as ternary Ga-In-As and the solid as pseudobinary GaAs-InAs. The total Gibbs energy was expressed as follows;

$$G^l = \sum_{i=1}^3 x_i^l ({}^0G_i^l + RT \ln x_i^l) + \sum_{i=1}^3 \sum_{j=1}^3 \sum_{\mu=0}^N \alpha_{ij}^l x_i^l x_j^l (x_i^l - x_j^l)^\mu + \beta^l x_1^l x_2^l x_3^l \quad (1)$$

$$G^s = x_2^s {}^0G_2^s + x_3^s {}^0G_3^s + RT(x_2^s \ln a x_2^s + x_3^s \ln a x_3^s) + x_2^s x_3^s \sum_{\mu=0}^N \Omega_\mu^s (x_2^s - x_3^s)^\mu \quad (2)$$

where  $x_i^l$  is mole fraction of component  $i$  in liquid;  ${}^0G_i^l$  is standard Gibbs energy of component  $i$  in liquid;  $\alpha_{ij}^l$  is the interactive coefficient of component  $i$  and  $j$  in liquid;  $\beta^l$  is ternary interactive coefficient in liquid;  ${}^0G_2^s$  and  ${}^0G_3^s$  are standard Gibbs energy of GaAs and InAs in solid, respectively;  $x_2^s$  and  $x_3^s$  are mole fractions of GaAs and InAs in solid, respectively;  $\Omega_\mu^s (\mu = 0 \sim N)$  is interactive coefficient of GaAs and InAs in solid.

${}^0G_1^l$ ,  ${}^0G_2^s$ ,  ${}^0G_3^s$ ,  $\alpha_{ij}^l$ ,  $\beta^l$  and  $\Omega_\mu^s$  are functions of temperature expressed as  $F(T)$  in formula (3). All coefficients are listed in Table 1.

$$F(T) = a - bT + cT(1 - \ln T)$$

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$$- (d/2)T^2 - (e/2)T - (f/6)T^3 \quad (3)$$

**Table 1 Parameters of the thermodynamic expressions for ternary Ga-In-As(J/mol)**

	a	b	c
${}^0G_i^s$	As 24 843. 7	22. 736 33	0. 010 181
	Ga 5 526. 1	18. 340 17	-0. 002 089
	In 3 274. 3	7. 610 5	-0. 001 694
${}^0G_i^l$	GaAs -86 202. 7	-7. 937 49	-0. 722 254
	InAs -65423. 5	5. 81122	5. 579762
	d	e	f
${}^0G_i^s$	As -0. 000 009 1	0. 0	0. 0
	Ga -0. 000 007 4	0. 0	0. 0
	In -0. 000 002 4	0. 0	0. 0
${}^0G_i^l$	GaAs -0. 002 890 4	-468 784	4. 041 6 × 10 <sup>-6</sup>
	InAs 0. 011 118 6	-539 074	-1. 352 9 × 10 <sup>-6</sup>
$\beta^l$	-11 859		
$\Omega_b$	30 797. 7 - 8. 266 8T		
	As-Ga	-3150. 5 - 20. 782 8T	
$\alpha_j$	Ga-In	4 450. 5 + 1. 191 85T + 0. 259 43(x <sub>Ga</sub> - x <sub>In</sub> )	
	In-As	-18 866. 8 - 10. 497 64T	

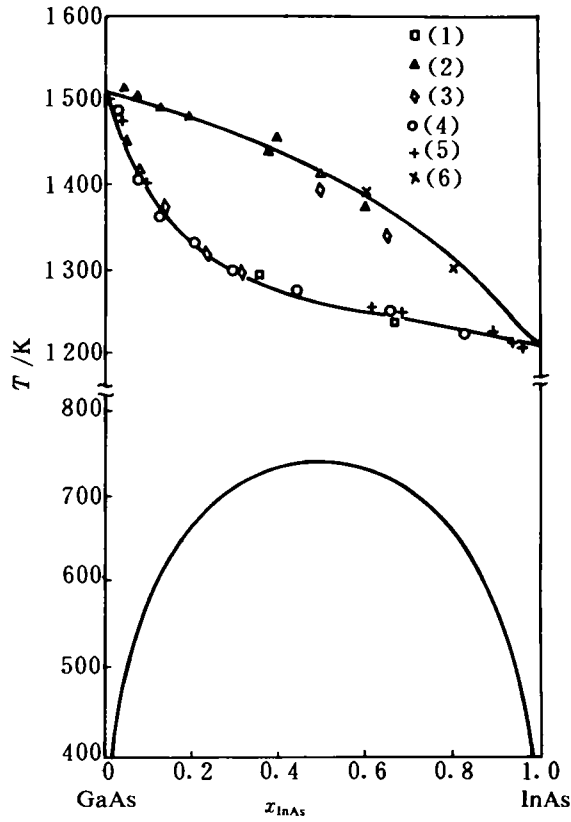
The phase diagram of pseudobinary GaAs-InAs based on the above thermodynamic data is calculated with Thermo-Calc program. The result is compared with the experimental results and shown in Fig. 1. It can be seen from Fig. 1 that the calculated liquidus and solidus agree well with most of the experimental points. From the optimized parameters in Table 1, we know that the solid of this system is a solid solution with positive deviation from ideal solution. That is to say it would exhibit miscibility gap below certain temperature. The temperature, where the miscibility gap begins to occur, is called critical temperature  $T_c$ . For the present system, the composition of the miscibility gap can be derived by solving equation (4).  $T_c$  and the corresponding composition can be derived by solving equations (5) and (6) simultaneously<sup>[9, 10]</sup>.

$$\frac{\partial [G^s - (x_{GaAs}^s G_{GaAs}^s + x_{InAs}^s G_{InAs}^s)]}{\partial x_{InAs}} = 0 \quad (4)$$

$$\frac{\partial^2 [G^s - (x_{GaAs}^s G_{GaAs}^s + x_{InAs}^s G_{InAs}^s)]}{\partial x_{InAs}^2} = 0 \quad (5)$$

$$\frac{\partial^3 [G^s - (x_{GaAs}^s G_{GaAs}^s + x_{InAs}^s G_{InAs}^s)]}{\partial x_{InAs}^3} = 0 \quad (6)$$

The calculated miscibility gap in solid of the GaAs-InAs system is shown in Fig. 1. The critical temperature  $T_c$  and critical composition  $x_{InAs}$  are 741. 9 K and 0. 50, respectively.



**Fig. 1 GaAs-InAs pseudobinary phase diagram**  
(calculated value)

### 3 INFLUENCE OF ELASTIC STRAIN ENERGY OF CRYSTAL ON MISCIBILITY GAP FORMATION

It should be pointed out that the experimental points in Fig. 1 are all obtained under the condition of pseudobinary equilibrium, where the substrate is not used and there is no lattice deformation. The study on the ternary of Ga-In-As<sup>[7]</sup> indicated that the calculated equilibrium results are quite different from the experimental ones obtained under liquid epitaxy. The reason is that there is lattice elastic energy induced by the mismatch of the lattices between the growing layer and the substrate and this term of the energy must be added into the thermodynamic model.

From molecular mechanics, the lattice elastic energy for cubic crystal of white zinc type can be

calculated by formula (7)<sup>[11]</sup>:

$$E_{el} = \left( \frac{a - a_0}{a_0} \right)^2 \sigma \quad (7)$$

where  $\sigma$  is shear stress;  $a$  and  $a_0$  are lattice parameters of epitaxial and substrate molecules respectively;  $\sigma$  and  $a$  are functions of composition.

$$a = a_1 x_1^s + a_2 x_2^s \quad (8)$$

$$\sigma = \sigma_1 x_1^s + \sigma_2 x_2^s \quad (9)$$

where  $x_i^s$  is mole fraction in solid; subscript 1 indicates GaAs and subscript 2 indicates InAs;  $\sigma_1$ ,  $\sigma_2$  can be derived from basic mechanic properties, such as shear modulus, Poisson coefficient, Young's modulus, etc<sup>[12]</sup>.

When  $T = 920$  K and substrate is InP,  $a_1 = 56.772$  nm,  $a_2 = 60.757$  nm,  $a_0 = 58.853$  nm. On (100) plane,  $\sigma_1 = 3.355 \times 10^6$  J/mol,  $\sigma_2 = 3.1354 \times 10^6$  J/mol; and on (111) plane,  $\sigma_1 = 4.7153 \times 10^6$  J/mol,  $\sigma_2 = 4.4061 \times 10^6$  J/mol.

Thus the relationship between lattice elastic strain energy and composition can be expressed as:

$$E_{el} = \left( \frac{x_{GaAs}^s a_1 + x_{InAs}^s a_2 - a_0}{a_0} \right)^2 \times (\sigma_1 x_{GaAs}^s + \sigma_2 x_{InAs}^s) \quad (10)$$

In order to use Thermo-Calc program for calculating the phase diagram, formula (10) was transformed into the Redlich-Kister form as Eq. (11):

$$E_{el} = Ax_{GaAs}^s + Bx_{InAs}^s + x_{GaAs}^s x_{InAs}^s [C + D(1 - 2x_{GaAs}^s)] \quad (11)$$

where  $A = \sigma_1 \left( \frac{a_1 - a_0}{a_0} \right)^2$ ;  $B = \sigma_2 \left( \frac{a_2 - a_0}{a_0} \right)^2$ ;

$$C = \left( \frac{a_1 - a_0}{2a_0^2} \right) [\sigma_2 (3a_2 + a_1 - 4a_0) - \sigma_1 (3a_1 + a_2 - 4a_0)];$$

$$D = \left( \frac{\sigma_2 - \sigma_1}{2} \right) \left( \frac{a_1 - a_2}{a_0} \right)^2$$

All coefficients used in (11) were calculated and listed in Table 2.

Table 2 Coefficients in expression (11)

Substrate	A	B	C	D
InP(111)	5895.5	4611.6	-20972.8	-708.8
InP(100)	4195.5	3281.6	-14916.8	-504.8

After adding lattice elastic energy, the molar Gibbs energy can be represented as:

$$G = x_{GaAs} (G_{GaAs}^0 + A) + x_{InAs} (G_{InAs}^0 + B) + x_{GaAs} RT \ln x_{GaAs} + x_{InAs} RT \ln x_{InAs} + x_{GaAs} x_{InAs} \times [(\Omega_0 + C) + D(x_{GaAs} - x_{InAs})] \quad (12)$$

From equation (12) and Fig. 2, it can be seen that coefficients  $A$ ,  $B$  stand for the contribution of lattice elastic strain energy to Gibbs energy of pure GaAs and InAs and  $C$ ,  $D$  stand for the contribution of lattice elastic energy to mixing Gibbs energy.

So the mixing molar Gibbs energy for the pseudobinary GaAs-InAs can be expressed as:

$$G^{mix} = G^s - (x_{GaAs}^s G_{GaAs}^s + x_{InAs}^s G_{InAs}^s) - (Ax_{GaAs}^s + Bx_{InAs}^s) \quad (13)$$

According to the calculation by solving Eqs. (4), (5), (6), the critical point of miscibility gap is  $x_{InAs} = 0.4$ ,  $T_c = 75$  K for the substrate InP (100); and  $T_c < 0$  for the substrate InP (111). This fact can be explained by the change of Gibbs energy curve while elastic energy contribution is added. In Fig. 2 the solid line represents the case in which only the chemical factors are considered and the dotted line represents that with elastic energy at the temperatures between 600 °C and 800 °C. The solid line energy represents the typical form combining two concave curves. According to the common tangent principle, the conjugated equilibrium compositions of miscibility gap are just located between the two minima of this curve. Two knees of this curve, corresponding to  $\frac{\partial^2 G^{mix}}{\partial x_{InAs}^2} = 0$ , are the equili-

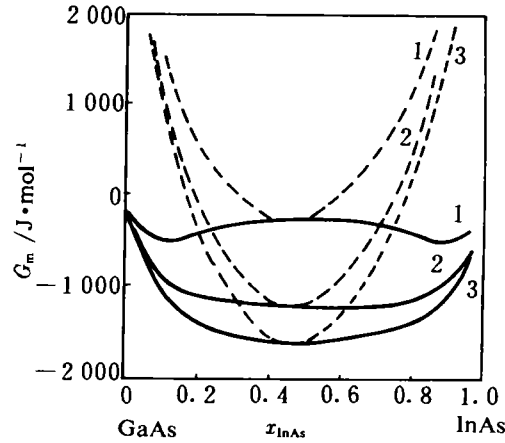


Fig. 2 Molar Gibbs energy—composition curve in solid of GaAs-InAs

Solid line—without elastic energy;

Dotted line—with elastic energy;

Substrate—InP(100);

1—600 K; 2—741 K; 3—800 K

brum composition of spinodal line. With the temperature increasing, the two minima close and combine into one at last, which is just corresponding to the critical point  $T_c$  and  $x_c$ . When the contribution of elastic energy is added into the total Gibbs energy as shown by the dotted line in Fig. 2, the curve becomes a concave curve with only one minimum. The calculated results show that while using epitaxial method to produce III - V compound, the miscibility gap would be restrained by lattice elastic energy induced by the mismatch of epitaxial layer and substrate crystal.

#### 4 CONCLUSION

The phase diagram of pseudobinary GaAs-InAs was studied using the thermodynamic and phase equilibrium information available. The calculated results show that, when using epitaxial method to produce III - V compound, the lattice elastic strain energy of epitaxial layer induced by the mismatch of epitaxial layer and substrate lattice has great restraint effect on the formation of miscibility

gap.

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(From page 24) into froth core from swirl layer, and the second one is axially moving upwards into froth core from the centre of liquid column. In both routes, the bubbles always bear buoyancy which is due to the pressure gradient in liquid as a driving force.

#### 5 CONCLUSIONS

(1) The pressure in liquid column increases radially from the centre to the circumference with a fixed axial position. In the upper section of ASH, where the froth core and swirl layer occupy, the pressure drops radially to a minimum and then increases. The pressure in outer helical flow is larger than that in inner helical flow.

(2) The pressure in the fluid below the end of vortex finder, including froth core, swirl layer and liquid column, increases axially with increasing axial coordinate  $z$ .

(3) The driving force for bubbles including mineralized bubbles to enter froth core is mainly

contributed by the centripetal buoyancy and the upward buoyancy which are both due to the pressure gradients in fluid. Pressure distribution heavily affects the magnitude of the driving force. There are two routes for bubbles including mineralized bubbles to enter froth core, the first one is radially moving inwards into froth core from swirl layer, and the second one is axially moving upwards into froth core from the centre of liquid column.

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