

ORIENTATION-DEPENDENT PHASE EQUILIBRIA IN $\text{In}_{1-x}\text{Ga}_x\text{As}$: A MODEL INCLUDING SURFACE ENERGIES†

SOBHANA SRINIVASA
NCERT, New Delhi 110 016, India

and

PALLAB K. BHATTACHARYA
Solid State Electronics Laboratory, Department of Electrical Engineering and Computer Science,
University of Michigan, Ann Arbor, MI 48109, U.S.A.

(Received 9 July 1984; accepted 30 August 1984)

Abstract—Orientation-dependent growth phenomena have been observed for liquid-phase epitaxial $\text{In}_{1-x}\text{Ga}_x\text{As}$ and other ternary and quaternary III-V semiconductors. The data cannot be explained by existing regular solution phase equilibria models. In this study we have used the quasi-regular solution formulation to derive a model which also considers equilibrium between the growing surface and the bulk solid under it. Orientation-dependent parameters characterizing the growing surface in the (100) and (111) directions have been included. The model is demonstrated for growth of $\text{In}_{1-x}\text{Ga}_x\text{As}$ at 650 and 621°C. Excellent agreement is obtained with data for growth of the ternary on (111)B InP substrates, whereas some adjustment of the parameters are necessary to obtain similar agreement in case of growth on (100)-oriented substrates.

1. INTRODUCTION

The ternary alloy $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ lattice-matched to InP is an important semiconductor for use in the fabrication of long-wavelength optoelectronic devices. High-quality epitaxial layers of this material, suitable for the fabrication of optical sources and detectors, are being fabricated by liquid-phase epitaxy (LPE). Several anomalous features have been observed in the LPE growth of the ternary semiconductor and, in general, for the growth of the quaternary $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ alloys lattice-matched to InP. Many authors have recently reported that the distribution coefficient, growth rate and surface morphology of the epitaxial layers of the alloys are strongly dependent on the substrate orientation. This is the result of different solid compositions being in equilibrium with the same liquid composition for (100) and (111)B substrate orientations. The importance of strain energy in the phase equilibria of $\text{In}_{1-x}\text{Ga}_x\text{As}$ /InP and other important ternary and quaternary alloy semiconductors has been recently demonstrated by us [1], de Cremoux [2] and Quillec *et al.* [3]. With the inclusion of a lattice strain energy term in the Jordan-Ilegems-Panish regular solution model [4], we were able to obtain an excellent agreement with the experimental solidus isotherm of $\text{In}_{1-x}\text{Ga}_x\text{As}$ for growth on (100)-oriented InP substrates. The orientation-dependent strain coefficient for the (111) direction included in the model is not adequate to explain the measured solidus isotherm for growth of

$\text{In}_{1-x}\text{Ga}_x\text{As}$ on (111)B InP substrates. This is comprehensible, since this orientation dependence exists even at the lattice-matching composition, whereas the role of strain energy is dependent on the degree of lattice mismatch.

In this study we wish to present a phase equilibria model for the LPE growth of $\text{In}_{1-x}\text{Ga}_x\text{As}$. It is demonstrated that the solidus isotherm of $\text{In}_{1-x}\text{Ga}_x\text{As}$ grown on (111) InP, in close agreement with the measured one, can be calculated.

2. THEORY

An examination of the arrangement of atoms in different crystal planes will suggest that properties of the crystal surfaces are strongly dependent on the crystallographic orientation. Therefore, any model aimed at explaining orientation-dependent isotherms should take into account surface excess thermodynamic quantities as a function of coordination numbers, number of bonds and bond energies which can distinguish between the different orientations. We have considered the equilibria between various phases as follows: (a) the (liquid) melt is in equilibrium with a (solid) surface phase; (b) the surface phase is in equilibrium with the solid (bulk) phase. In effect, the orientation dependence will be taken into account in the surface energies and coordination numbers of surface atoms. A model for a ternary alloy system is being developed here.

It is being assumed that the experimentally observed solid composition corresponds to the composition of the solid surface in equilibrium with the bulk. Previously reported solidus data obtained theoretically

† This work was done while the authors were at the Department of Electrical Engineering, Oregon State University, Corvallis, Oregon 97331, U.S.A.

correspond to the bulk in equilibrium with the liquid where the effect of the surface phase has been neglected. The continued existence of a surface phase after initiation of epitaxial growth is being assumed in this model and needs explanation. When a multi-component liquid–solid system is in equilibrium, the free-energy change associated with the transfer of material from one phase to the other is zero. If the equilibrium solid phase is replaced by another similar phase, consisting of the same components, but in different proportions, the equilibrium is disturbed and the free-energy change is not zero. This provides the driving force for attaining a new equilibrium. Equilibrium is attained by solid-state diffusion, and hence this surface phase is also termed a diffusion layer. It has been shown that this diffusion layer can be strained if the lattice constant of the growing solid solution markedly differs from that of the substrate. This may be true for $\text{In}_{1-x}\text{Ga}_x\text{As}/\text{InP}$ growth. It is also necessary to assume a few monolayers in the surface phase to ensure its thermodynamic continuity with the bulk phase.

The chemical potential of the binary molecules AC and BC (e.g. GaAs, InAs) in the surface of a ternary solid solution $\text{A}_x\text{B}_{1-x}\text{C}$ in the regular solution formulation can be written as [5]

$$\mu_{\text{AC}}^{\text{surf}} = \mu_{\text{AC}}^{0,\text{surf}} + RT \ln x' + \alpha_{\text{A}_x\text{B}_{1-x}\text{C}} L(1-x')^2 + \alpha_{\text{A}_x\text{B}_{1-x}\text{C}} M(1-x')^2 = S_{\text{A}_x\text{B}_{1-x}\text{C}} A, \quad (1a)$$

$$\mu_{\text{BC}}^{\text{surf}} = \mu_{\text{BC}}^{0,\text{surf}} + RT \ln (1-x') + \alpha_{\text{A}_x\text{B}_{1-x}\text{C}} L(x')^2 + \alpha_{\text{A}_x\text{B}_{1-x}\text{C}} Mx'^2 - S_{\text{A}_x\text{B}_{1-x}\text{C}} A, \quad (1b)$$

where the symbols μ , R and T have their usual meanings. The superscript '0' refers to an ideal surface in which no relaxation or atomic arrangement occurs. The symbol x' refers to the solid-surface-phase composition and corresponds to x in the bulk of the epitaxial layer. The solid interaction parameter for interaction between the solids AC and BC is denoted by $\alpha_{\text{A}_x\text{B}_{1-x}\text{C}}$ (henceforth to be written as α), and $S_{\text{A}_x\text{B}_{1-x}\text{C}}$ (henceforth to be written as S) is the surface free energy per unit area of $\text{A}_x\text{B}_{1-x}\text{C}$. A is the molar surface area of $\text{A}_x\text{B}_{1-x}\text{C}$, and SA the total surface free energy of the ternary solid. L is the ratio of the number of lateral bonds made by an atom to the total number of first nearest neighbors, and M the ratio of the number of vertical bonds made by an atom to each adjacent plane of atoms to the total number of first nearest neighbors. A representation of this scheme is shown in Fig. 1. A broken bond model of the melt–solid interface is shown. More exactly, the lateral and vertical bonds of the surface layer are perturbed by the interfacial discontinuity. This change provides the enthalpy of the surface formation. In the nearest neighbor approximation $L = 1/3$, $M = 1/3$ for the (100) orientation, and $L = 1/2$, $M = 1/4$ for the (111) orientation. We have, however, used the values of L and M corresponding

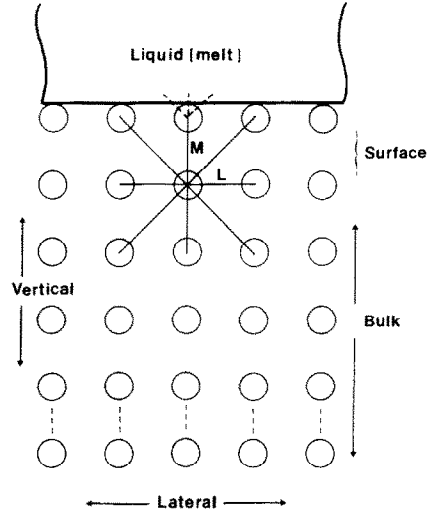


Fig. 1. A representation of the growing semiconductor surface in equilibrium with the melt.

to effective neighbors [6], for which $L = 0.3$ and $M = 0.4$ for both (100) and (111) orientations.

Treating the ternary solid in the bulk phase as a simple solution of the constituent binaries, we can express the chemical potentials of the latter as [5]

$$\mu_{\text{AC}}^{\text{bulk}} = \mu_{\text{AC}}^{0,\text{bulk}} + RT \ln x + \alpha(1-x)^2, \quad (2a)$$

$$\mu_{\text{BC}}^{\text{bulk}} = \mu_{\text{BC}}^{0,\text{bulk}} + RT \ln (1-x) + \alpha x^2. \quad (2b)$$

Under conditions of equilibrium between surface and bulk phase, the following equations can be written:

$$\mu_{\text{AC}}^{\text{surf}} = \mu_{\text{AC}}^{\text{bulk}} \quad (3a)$$

and

$$\mu_{\text{BC}}^{\text{surf}} = \mu_{\text{BC}}^{\text{bulk}}. \quad (3b)$$

Also, for pure compounds AC and BC, the relations

$$\mu_{\text{AC}}^{0,\text{surf}} - \mu_{\text{AC}}^{0,\text{bulk}} = S_{\text{AC}} A_{\text{AC}} \quad (4a)$$

and

$$\mu_{\text{BC}}^{0,\text{surf}} - \mu_{\text{BC}}^{0,\text{bulk}} = S_{\text{BC}} A_{\text{BC}} \quad (4b)$$

are true. Here $S_{\text{AC(BC)}}$ and $A_{\text{AC(BC)}}$ are the surface free energies and molar areas of the binaries AC and BC. Using eqns (3) and (4) in eqns (1) and (2), we obtain relations

$$S_{\text{AC}} A_{\text{AC}} = RT \ln x + \alpha(1-x)^2 - RT \ln x' - \alpha L(1-x')^2 - \alpha M(1-x')^2 + SA, \quad (5a)$$

and

$$S_{\text{BC}} A_{\text{BC}} = RT \ln (1-x) + \alpha x^2 - RT \ln (1-x') - \alpha L(x')^2 - \alpha Mx'^2 + SA. \quad (5b)$$

Eliminating the quantity SA between these equations, we obtain a relation between x and x' as follows:

$$\ln \left[\frac{x'(1-x)}{x(1-x')} \right] + \beta[L(1-2x') + (M-1)(1-2x)] - \frac{1}{RT}(S_{BC}A_{BC} - S_{AC}A_{AC}) = 0, \quad (6)$$

where $\beta = \alpha/RT$.

The equilibria between the liquid (melt) and the surface (solid) phase can be written as [4, 5]

$$\mu_{AC}^{\text{surf}} = \mu'_{AC} = \mu_A^0 + RT \ln \gamma'_A x'_A + \mu_C^0 + RT \ln \gamma'_C x'_C, \quad (7a)$$

where the symbols have the same meaning as in Ref. [4]. Combining eqn (12) of Ref. [4] and eqns (4) and (7) above, the following relations can be written:

$$\mu_{AC}^{\text{surf}} - \mu_{AC}^0 = RT \ln \gamma_{AC}^{\text{surf}} x' = Q_{AC} - S_{AC}A_{AC}, \quad (8a)$$

$$\begin{aligned} \mu_{BC}^{\text{surf}} - \mu_{BC}^0 &= RT \ln \gamma_{BC}^{\text{surf}} (1-x') \\ &= Q_{BC} - S_{BC}A_{BC}. \end{aligned} \quad (8b)$$

From eqn (1), with $M = 0$, and eqn (8), the liquid-(solid) surface-phase equilibria can be expressed as

$$\ln \left(\frac{x'}{1-x'} \right) + \beta[L(1-2x')] - \frac{1}{RT} [(S_{BC}A_{BC} - S_{AC}A_{AC}) + (Q_{AC} - Q_{BC})] = 0, \quad (9)$$

which is similar to eqn (6) derived above for surface-bulk equilibria. If the effect of the surface phase is neglected in these equations by substituting $\mu^{\text{surf}} = \mu^{\text{bulk}}$ and letting the surface energies reduce to zero, the familiar solid-liquid equilibrium equation of Ref. [4] is obtained.

We have solved eqn (6) for x' after including the effect of strain in the bulk solid [1] through additional chemical potential terms corresponding to strain energy. Then the final surface-bulk-phase equilibrium equation can be expressed as

$$\begin{aligned} \ln \left[\frac{x'(1-x)}{x(1-x')} \right] + \beta[L(1-2x') + (M-1)(1-2x)] \\ - \frac{1}{RT} [S_{BC}A_{BC} - S_{AC}A_{AC}] \\ + \frac{2\sigma}{RTa_0^2} (a - a_0)(a_{BC} - a_{AC}) = 0, \end{aligned} \quad (10)$$

Table 1. Parameters used in phase equilibria calculations

Parameter	Reference	InAs	GaAs
Lattice constant (Å)	15	6.0584	5.65321
Density (gm-cm ⁻³)	15	5.70	5.316
Surface energy			
per unit area (erg-cm ⁻²)	16	(100) 1400 (111) 840	2200 1300
Stiffness constant			
c ₄₄ (dyne-cm ⁻²)	15	3.96x10 ¹¹	5.94x10 ¹¹
Solid interaction			
parameter $\alpha_{\text{InAs-GaAs}}$ (cal-mole ⁻¹)	8	2990	
Lattice constant of substrate (InP) (Å)		5.86875	
Molar surface area	17	A = fN ^{1/3} (M/ρ) ^{2/3}	

where σ is the strain coefficient and a , a_0 , a_{AC} and a_{BC} are, respectively, the lattice constants of the growing ternary $A_xB_{1-x}C$, substrate and binaries AC and BC.

RESULTS AND DISCUSSION

The model outlined above has been demonstrated for the growth of $In_{1-x}Ga_xAs$ on (100) and (111)B-oriented InP substrates. Equation (10) has been solved to determine surface composition from bulk compositions. Values of L and M mentioned earlier have been used. Liquid-phase compositions were then determined from these surface compositions by using eqn (9). The parameters used in the analysis are listed in Table 1. The solidus isotherms, relating surface- and liquid-phase compositions for growth along the (100) and (111) directions, are thus obtained.

Figure 2 shows the calculated solidus isotherm for growth of $In_{1-x}Ga_xAs$ on (111)InP substrate at $650^\circ C$ along with the experimental data of Nakajima *et al.* [11] obtained under identical conditions. The good agreement between calculated and observed data, within the limits of experimental error, is very encouraging. A similar solidus isotherm calculated for growth on (111)B substrates at $621^\circ C$ is shown in Fig. 3, alongside the data of Pearsall *et al.* [12] obtained for the same growth conditions. The effect of not including the surface phase is also shown in the figure, and it is evident that the present model provides a better agreement with experimental data for (111)-oriented growth of $In_{1-x}Ga_xAs/InP$. The calculated solidus isotherm for growth on (100) substrates is shown by the solid curve in Fig. 4, along with the data of Nakajima *et al.* [11].

It should be mentioned that the calculated solidus for (100)-oriented growth, using the present model, agrees well with the data, as shown in Fig. 4, only after a slight adjustment of the parameters. Such adjustments are not necessary at all for the (111) orientation. It is not easy to justify this, but any one or more of the following reasons could be responsible. The surface energies for the (100) and (111) orienta-

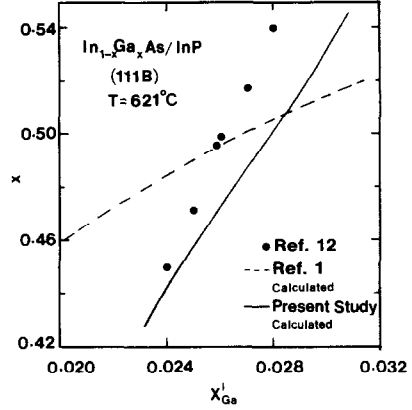


Fig. 3. Calculated solidus isotherms at $621^\circ C$ compared with the experimental data of Pearsall *et al.* [12] for growth on (111)B InP substrates.

tions used in our model are theoretical estimates [8]. No experimental values of the parameter exist, to our knowledge. Therefore, the values quoted for the [100] planes, as a matter of pure coincidence, may be slightly inaccurate. Good agreement with the experimental solidus data for growth on (100) substrates can be obtained by a slight adjustment of the thermodynamic input parameters. Many authors have done this in the past but we prefer to use the parameters established by us and other authors [1]. Again, there may be a change in the number of effective neighbors, thereby producing corresponding changes in the surface energy. Finally, the experimental data for growth on (100) substrates, with which an agreement is being sought, extend over a very small range of liquid compositions and the spread in data is considerable. It can be seen that the (111)B solidus data extend over a larger liquid composition range. In our case, as a matter of convenience, we have adjusted the surface energy difference to obtain an agreement with the data of Fig. 4. However, the near-perfect agreement in the case of growth along the (111) direction is extremely encouraging.

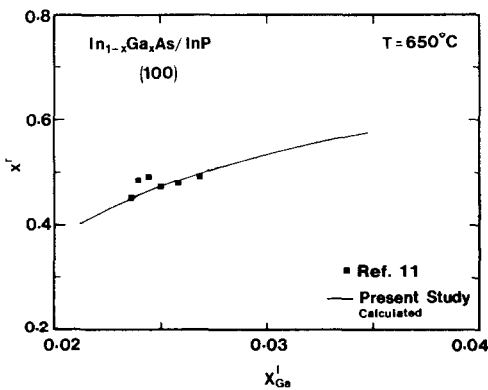


Fig. 2. Calculated solidus isotherms at $650^\circ C$ in the Ga-In-As system compared with the experimental data of Nakajima *et al.* [11] for growth on (111)B InP substrate.

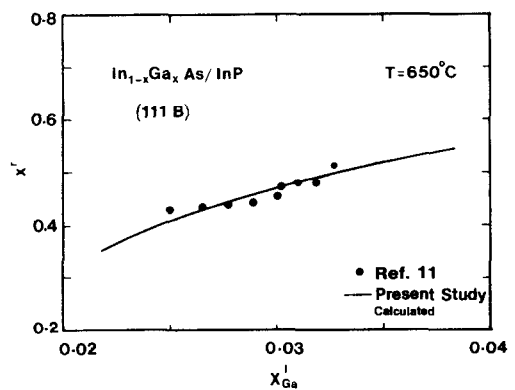


Fig. 4. Calculated solidus isotherms at $650^\circ C$ compared with the experimental data of Nakajima *et al.* [11] for growth on (100) InP substrates.

The model used in this study can be extended to other ternary and quaternary systems, where similar orientation dependence has been observed.

Acknowledgments—P. K. Bhattacharya acknowledges fruitful discussions with Professor M. Ilegems (Lausanne). This work was partly supported by the National Science Foundation under Grant ECS-801197.

REFERENCES

1. Bhattacharya P. K. and Srinivasa S., *J. Appl. Phys.* **54**, 5090 (1983).
2. de Cremoux, B., *J. de Physique* **12**, 19 (1982).
3. Quillec M., Launois H. and Joncour M. C., *J. Vac. Sci. Technol.* **B1**, 238 (1983).
4. Ilegems M. and Panish M. B., *J. Phys. Chem. Solids* **35**, 409 (1974).
5. Defay R. and Prigogine I., *Surface Tension and Adsorption*, pp. 171–176. John Wiley, New York (1966).
6. Williams F. L. and Nason D., *Surface Sci.* **45**, 377 (1974).
7. Neuberger, M., *Handbook of Electronic Materials*, Vol. 2: *III–V Semiconducting Compounds*. IFI/Plenum, New York (1971).
8. Blakely, J. M., *International Series on Materials Science and Technology*, Vol. 12, p. 116. Pergamon Press, New York (1973).
9. de Cremoux B., *IEEE J. Quantum Electron.* **QE-17**, 123 (1981).
10. Overbury S. H., Bertrand P. A. and Somorjai G. A., *Chem. Rev.* **75**, 549 (1975).
11. Nakajima K., Tanahashi T., Akita K. and Yamaoka T., *J. Appl. Phys.* **50**, 4976 (1979).
12. Pearsall T. P., Bisaro R., Ansel R. and Merenda P., *Appl. Phys. Lett.* **32**, 497 (1978).