

# Point defect concentrations in InGaAsP quaternary alloys

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Point defect concentrations in InGaAsP grown from liquid phases were calculated. Vacancies and antisites were taken to be dominant defects. The calculated antisite concentrations decrease with increasing band gap, while the vacancy concentrations are weakly dependent on composition. Although development of dislocations is known to be easier in InGaAsP lattice matched to GaAs than in those lattice matched to InP, the difference in the vacancy concentration between them is small when their growth temperatures are assumed to be the same. However, a high growth temperature usually adopted for InGaAsP on GaAs will result in larger vacancy concentrations.

In order to understand and control physical properties of semiconductors, it is necessary to know type of dominant defects and their concentrations. For materials grown under nearly thermal equilibrium conditions, we can use the method of the chemical thermodynamics of defects to calculate defect concentrations.<sup>1</sup> So far, defect concentrations in a few compound semiconductors have been calculated on the basis of thermodynamic models.<sup>2-4</sup> The analysis was extended to III-V ternary alloys by Blom,<sup>5</sup> but we recently presented an alternative formalism which seems simpler and more reasonable than his.<sup>6</sup> In this work, we extend the defect model further and apply it to  $\text{In}_{1-x}\text{Ga}_x\text{As}_{1-y}\text{P}_y$  quaternary alloy semiconductors.

InGaAsP is widely used in various optoelectronic devices. In most cases, InGaAsP alloy is grown by the liquid-phase epitaxy (LPE) on InP or GaAs substrates. It is known that very reliable optoelectronic devices for 1.3- $\mu\text{m}$  wavelength region can be fabricated using InGaAsP lattice matched to InP (InGaAsP/InP). In contrast, devices of the shorter wavelength region, fabricated using InGaAsP/GaAs, are in general less reliable because of dislocation development.<sup>7,8</sup> It is expected that such difference is attributed to a difference in character or concentration of native defects in them. Deep-level-transient-spectroscopy measurement has been applied to InGaAsP in order to clarify the character of the defects.<sup>9</sup> However, to our knowledge, thermodynamic calculation of defect concentrations has not been attempted for InGaAsP, yet.

Our model is based on the theory of Van Vechten:<sup>10</sup> vacancies and antisites are considered as dominant defects. For  $\text{In}_{1-x}\text{Ga}_x\text{As}_{1-y}\text{P}_y$  in equilibrium with a liquid phase, we consider the following reactions of the defect formations.

$$\text{In}_l = \text{In}_{\text{III}} + V_{\text{V}}^x, \quad (1)$$

$$\text{Ga}_l = \text{Ga}_{\text{III}} + V_{\text{V}}^x, \quad (2)$$

$$\text{As}_l = \text{As}_{\text{V}} + V_{\text{III}}^x, \quad (3)$$

$$\text{P}_l = \text{P}_{\text{V}} + V_{\text{III}}^x, \quad (4)$$

$$V_{\text{V}}^x = V_{\text{V}}^+ + e^-, \quad (5)$$

$$V_{\text{III}}^x = V_{\text{III}}^- + h^+, \quad (6)$$

$$\text{In}_l = V_{\text{III}}^x + \text{In}_{\text{V}}^{2-} + 2h^+, \quad (7)$$

$$\text{Ga}_l = V_{\text{III}}^x + \text{Ga}_{\text{V}}^{2-} + 2h^+, \quad (8)$$

$$\text{As}_l = V_{\text{V}}^x + \text{As}_{\text{III}}^{2+} + 2e^-, \quad (9)$$

$$\text{P}_l = V_{\text{V}}^x + \text{P}_{\text{III}}^{2+} + 2e^-. \quad (10)$$

Here, subscripts  $l$ , III, and V indicate a liquid phase, a group III lattice site, and a group V lattice site, respectively.  $V$  is a vacancy,  $e$  an electron, and  $h$  a hole. Superscripts represent charge states,  $x$  being for a neutral state. The equilibrium condition is written using  $K_i$  as the equilibrium constant for reaction (i). For example, the conditions for reactions (1) and (2) are as follows.

$$K_1 = \frac{[V_{\text{V}}^x](1-x)}{a_{\text{In}}}, \quad K_2 = \frac{[V_{\text{V}}^x]x}{a_{\text{Ga}}}. \quad (11)$$

Here  $a$  is an activity of the element in the liquid phase, and  $[V_{\text{V}}^x]$  is the relative concentration of  $V_{\text{V}}^x$ . As can be seen from the above equations, the relation  $K_1/K_2 = (1-x)a_{\text{Ga}}/xa_{\text{In}}$  must be satisfied. A similar relation must hold between  $K_3$  and  $K_4$ , too. As shown in the previous paper, those relations are necessarily satisfied, if we appropriately define the free energies of the reactions.<sup>6</sup>

Each  $K_i$  is written as  $\exp(-\Delta G_i/kT)$ , where  $k$  is the Boltzmann constant and  $T$  the temperature. The free energy  $\Delta G$  of reaction (1), for example, is given by

$$\Delta G_1 = \Delta G(V_{\text{V}}) + \Delta G_0(\text{In}), \quad (12)$$

where  $\Delta G(V_{\text{V}})$  is the formation energy of a group V vacancy and  $\Delta G_0(\text{In})$  is the energy of the incorporation of an In atom from the liquid phase to a proper lattice site. The enthalpy and entropy of formation of each defect are taken from Ref. 10. For  $\text{In}_{1-x}\text{Ga}_x\text{As}_{1-y}\text{P}_y$  alloys, we use averaged values weighted by the alloy composition. The free energy of incorporation of each element from the liquid phase is estimated by the procedure described in the previous paper.<sup>6</sup> It is assumed that the formation energy of the alloy is equally apportioned to  $\Delta G_0$ 's of group III atoms

and those of group V atoms. This assumption is an extension of that proposed in Ref. 10.

The defect concentrations are calculated using the equilibrium conditions (the mass action constraint) of reactions (1)–(10), the charge neutrality condition, and the relation  $np = n_i^2$ , where  $n$ ,  $p$ , and  $n_i$  are concentrations of electrons, holes, and intrinsic carriers, respectively. In order to calculate composition of the liquid phase, we apply the regular solution model to both liquid and solid phases.

Calculation results are shown in Figs. 1 and 2. Figure 1 shows contours of the defect concentrations in  $\text{In}_{1-x}\text{Ga}_x\text{As}_{1-y}\text{P}_y$  at 650 °C. The most dominant defect is the group III antisite or the group V vacancy, which implies that the solid is group III rich. This is due to the fact that the liquid phase is group III rich. The contours of the antisites are nearly parallel to those of the band gap, i.e., the antisite concentrations decrease with increasing band gap. This is because the energies of the antisite-formation reactions include the band-gap energy.<sup>10</sup> In the composition region of  $x \approx 1$ , all the defect concentrations change sharply. In this region, the liquid phase changes rather abruptly from In-rich to Ga-rich. Accordingly, the activity of Ga in the liquid drastically increases, and  $\text{Ga}_V$  and  $V_V$  increase through reactions (2) and (8). At the same time, the group V antisite and  $V_{\text{III}}$  decrease because of low solubility of group V elements in liquid Ga.

The composition dependence of the vacancy concentrations is relatively weak compared with those of the antisite concentrations. Thus, the vacancies become more dominant as the band gap of the alloy becomes wider.

Figure 2 shows composition dependence of the defect concentrations in (a)  $\text{InGaAsP}/\text{InP}$  and (b)  $\text{InGaAsP}/\text{GaAs}$ . The vacancy concentrations are not very different between (a) and (b). In both the cases, the group III-antisite concentrations decrease and the group V-vacancy concentrations increase with P composition, except near compositions of  $x = 1$ , where the drastic change occurs in the liquid composition.

It has been reported that climb motion of dislocations and formation of dislocation loops occur more easily in  $\text{InGaAsP}/\text{GaAs}$  than in  $\text{InGaAsP}/\text{InP}$ . Vacancies are at least partly responsible for the development of dislocations. As shown in Fig. 2, a large difference is not found in the calculated vacancy concentrations between  $\text{InGaAsP}/\text{InP}$  and  $\text{InGaAsP}/\text{GaAs}$ . However, in most cases, the growth temperature of  $\text{InGaAsP}/\text{GaAs}$  is about 800 °C, i.e., higher than that of  $\text{InGaAsP}/\text{InP}$  (about 650 °C), because of a large immiscible region and/or low solubility of group V elements. According to our calculation, the vacancy concentrations in  $\text{InGaAsP}/\text{GaAs}$  grown at 800 °C is one order of magnitude larger than those shown in Fig. 2. Thus development of dislocations is expected to be relatively easy in  $\text{InGaAsP}/\text{GaAs}$ .

Although we believe that the calculated composition dependence of the defect concentrations is qualitatively correct, the absolute values of them will not be accurate

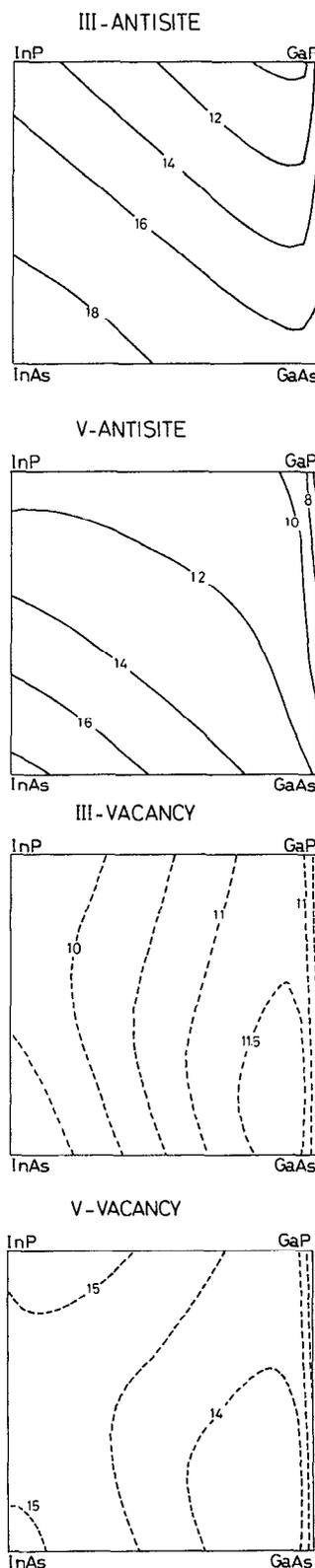


FIG. 1. Contour maps of common logarithms of the defect concentrations in  $\text{InGaAsP}$  grown at 650 °C.

because of uncertainty in the formation enthalpies of the defects. In particular, the enthalpy of the antisite formation seems too small: our results indicate that there are a large number of native acceptors (group III antisites) in

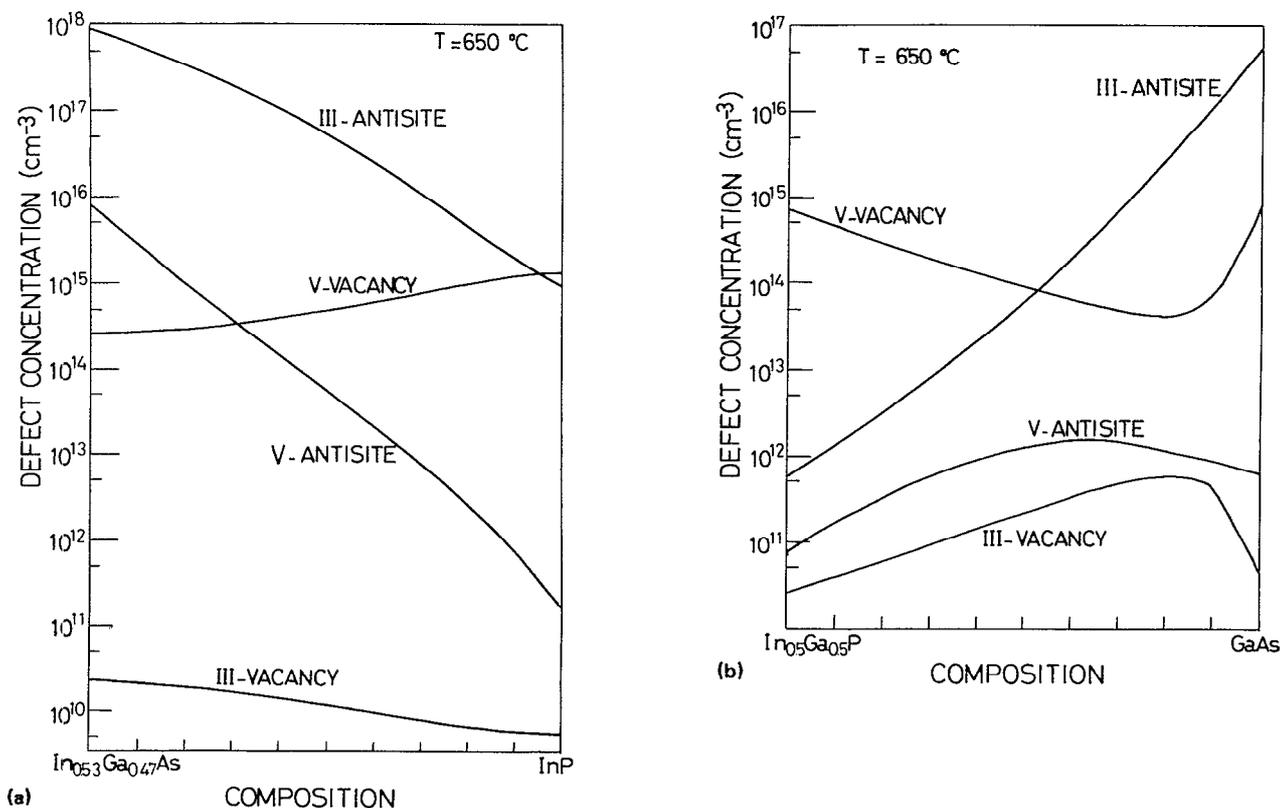


FIG. 2. Composition dependence of the defect concentrations in (a) InGaAsP/InP and (b) InGaAsP/GaAs.

$\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ , but this has not been experimentally confirmed.

Interstitials are neglected in the present model because their formation energy is expected to be large.<sup>10</sup> Although interstitial dislocation loops have also been observed in InGaAsP, existence of interstitial loops does not necessarily indicate abundance of interstitials.<sup>11</sup> However, further study is needed to accurately determine the formation energies of the defects including interstitials.

In conclusions, point defect concentrations in InGaAsP grown from liquid phases have been calculated. Vacancies and antisites were taken to be dominant defects. The calculated antisite concentrations decrease with increasing band gap, while the vacancy concentrations are weakly dependent on composition. At a certain temperature, the difference in the vacancy concentration between InGaAsP/InP and InGaAsP/GaAs is small. However, high growth temperature usually adopted for InGaAsP/

GaAs may result in large vacancy concentrations and formation of dislocations.

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