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# REVUE DE PHYSIQUE APPLIQUÉE

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## Equilibrium calculations for VPE-InGaAsP (\*)

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**Résumé.** — L'équilibre hétérogène du système InGaAsP/HCl/H<sub>2</sub> a été étudié dans un domaine de température et de pression caractéristiques de l'épitaxie en phase vapeur (EPV) par la méthode des hydrures. Les prévisions théoriques sont comparées aux données expérimentales pour la croissance d'alliages GaInAsP ayant la même maille cristalline que le substrat InP. Les résultats présentés sont en bon accord avec quelques données expérimentales. Quelques cas de désaccord entre résultats thermodynamiques et résultats expérimentaux ou entre différentes valeurs expérimentales sont également discutés.

**Abstract.** — The heterogeneous equilibrium in the InGaAsP/HCl/H<sub>2</sub> system has been studied at pressure and temperature conditions pertaining to the hydride-VPE growth. The results have been compared with the available experimental data on the growth of the above quaternary alloys lattice-matched to InP. A remarkably good agreement has been achieved with some existing data. Possible causes of discrepancies both between equilibrium and experimental results and between different experimental findings have been briefly discussed.

**1. Introduction.** — The state-of-the-art fibers for lightwave communications can carry more information for longer distances when the light-carrier wavelength is within the 1.0-1.3  $\mu\text{m}$  and 1.5-1.6  $\mu\text{m}$  spectral regions [1, 2].

This accounts for the efforts which have been spent in preparing double heterostructure lasers, light emitting diodes and photodiodes operating within the above windows.

Structures such as GaAsSb/GaAlAsSb on GaAs [3], InGaAs/InGaP on GaAs [4] and InGaAsP/InP on InP [5, 6] have been considered to date for the continuous laser operating at room temperature (CW-RT) at wavelengths beyond 1  $\mu\text{m}$ ; however the last is thought of as being the most promising one, since it does not require lattice matching layers between the substrate and the double heterojunction itself.

Until now, most of the work on InGaAsP/InP heterostructures has been done using Liquid Phase Epitaxy (LPE); however Vapour Phase Epitaxy (VPE) appears to be very interesting, since it seems to be more suitable for multi-slice growth.

This interest is confirmed by the works of Sugiyama *et al.* [7], Hyder *et al.* [8] and Enda [9], dealing with

the vapour phase deposition of InGaAsP on GaAs [7] and InP [7, 8, 9] substrates and especially by the results of Olsen *et al.* who succeeded in obtaining CW-RT operation in VPE InGaAsP/InP double heterostructure lasers at 1.25  $\mu\text{m}$  [6].

In this paper the thermodynamical equilibrium in the InGaAsP/HCl/H<sub>2</sub> heterogeneous system is considered at temperature and pressure conditions pertaining to the hydride VPE growth; as a result, the vapour Ga- and P-molar fractions in equilibrium with solids of given composition have been calculated.

This is of interest for establishing the growth conditions of layers having definite compositions, since the vapour molar fractions may be related to the input gas flows.

**2. Alloy and equilibrium thermodynamics.** — To describe the thermodynamics of a quaternary alloy with substitution on both sublattices, a semiempirical [10] and a regular solution [11] model have been proposed; the former gives the binary compounds activities as functions of their lattice constants.

This approach has been used for calculating the heterogeneous equilibrium in the InGaAsP/HCl/H<sub>2</sub> system by Seki *et al.* [12] and by Pelosi *et al.* [13].

The regular solution model uses three interaction parameters ( $\Omega_{\text{III}}$ ,  $\Omega_{\text{V}}$ ,  $\Omega_{\text{III-V}}$ ) which take into account the bonding energy between atoms both on the same ( $\Omega_{\text{III}}$ ,  $\Omega_{\text{V}}$ ) and on different fcc sublattices ( $\Omega_{\text{III-V}}$ ).

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Following Jordan and Ilegems [11]  $\Omega_{III}$  and  $\Omega_V$  are given by

$$\Omega_{III} = \Omega_{InGaP} Y + \Omega_{InGaAs}(1 - Y)$$

$$\Omega_V = \Omega_{GaAsP} X + \Omega_{InAsP}(1 - X)$$

where  $X$  and  $Y$  are the Ga- and P-molar fractions in the InGaAsP solid solution and  $\Omega_{InGaP}$ ,  $\Omega_{InGaAs}$ ,  $\Omega_{GaAsP}$  and  $\Omega_{InAsP}$  are the experimental interaction coefficients of the ternary alloy specified in the subscripts; their values are 3 250 [14], 2 000 [15], 1 000 [16] and 400 [10] cal., respectively.

$\Omega_{III-V}$  is obtained by algebraically adding either the four binary compound formation energies, or, if convenient, their reaction energies. Then :

$$\Omega_{III-V} = -RT \ln (K_{GaAs} K_{InP} / (K_{GaP} K_{InAs}))$$

where  $K_{GaAs}$ ,  $K_{InP}$ ,  $K_{GaP}$  and  $K_{InAs}$  are the heterogeneous dissociation reaction constants of the binary compounds.

An important result of the regular solution treatment is that all the thermodynamical properties of the above quaternary solid solutions are completely and exactly described by the following three equations :

$$\ln \gamma_{GaP} = \Omega_{III}(1 - X)^2 + \Omega_V(1 - Y)^2 - \Omega_{III-V}(1 - X)(1 - Y)$$

$$\ln \gamma_{InP} = \Omega_{III} X^2 + \Omega_V(1 - Y)^2 + \Omega_{III-V} X(1 - Y)$$

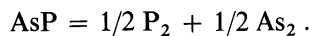
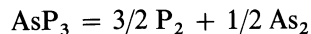
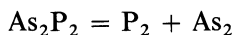
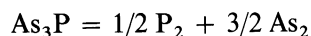
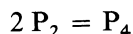
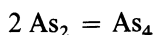
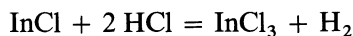
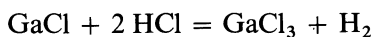
$$\ln \gamma_{GaAs} = \Omega_{III}(1 - X)^2 + \Omega_V Y^2 + \Omega_{III-V}(1 - X) Y$$

where  $\gamma_{GaP}$ ,  $\gamma_{InP}$  and  $\gamma_{GaAs}$  are the binary compound activity coefficients.

The reaction constants of the binary compounds in the alloy ( $K_{GaAs}(ss)$ , etc.) are related to those of the pure compounds by equations such as :

$$K_{GaAs}(ss) = K_{GaAs} \gamma_{GaAs} X(1 - Y).$$

The description of the heterogeneous system is given considering the following reactions :



The system is completely defined when the following external constraints are met : stoichiometry of the

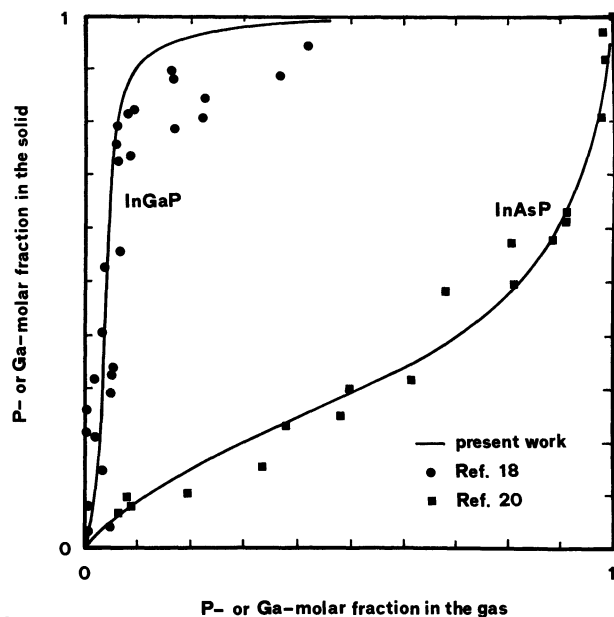


Fig. 1. — Comparison of the theoretical dependence (full line) of the solid Ga- or P-molar fractions on the vapour Ga- or P-molar fractions with the experimental points for InGaP or InAsP ternary alloys, respectively.

vapour phase and constancy of both the HCl/H<sub>2</sub> ratio and the total pressure. The above parameters and the temperature have been set as 10<sup>-3</sup>, 1 atm. and 1 000 K respectively. The system of 15 equations has been solved by numerical methods.

The homogeneous-reaction constants used in this work are those previously selected [13]. The values of the heterogeneous-reaction constants are subject to considerable fluctuations. Since a critical analysis of

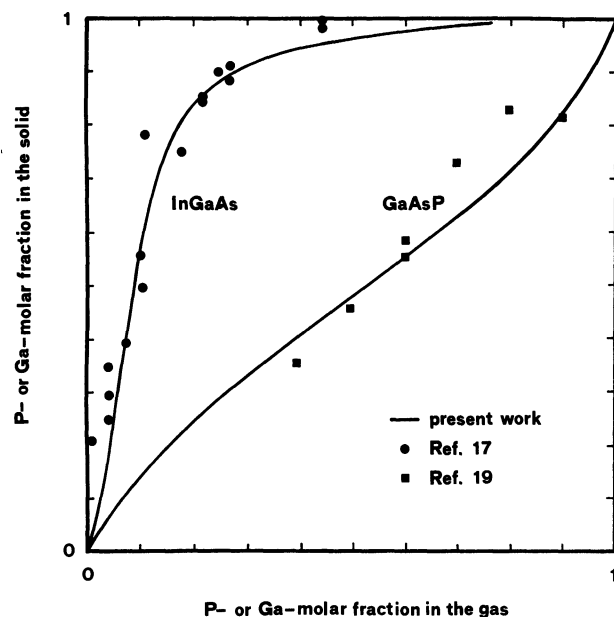


Fig. 2. — Comparison of the theoretical dependence (full line) of the solid Ga- or P-molar fractions on the vapour Ga- or P-molar fractions with the experimental points for InGaAs or GaAsP ternary alloys, respectively.

the existing thermochemical data is beyond the scope of this work, we have used the values which allow for a fairly good agreement with the well-established experimental data relative to InGaAs [17], InGaP [18], GaAsP [19] and InAsP [20], used simultaneously. The comparison between these data and those obtained by solving the above system is shown in figures 1 and 2. On the basis of the fitting procedure the following values (at  $T = 1000$  K) have been chosen for the heterogeneous reaction constants :  $K_{\text{GaP}} = 0.1$ ,  $K_{\text{InP}} = 2.2$ ,  $K_{\text{GaAs}} = 0.103$  and  $K_{\text{InAs}} = 1.034$ .

**3. Results and discussion.** — Figure 3 is a plot of the Ga- and P-molar fraction in the vapour phase ( $x$  and  $y$  respectively) in equilibrium with a solid of given composition ( $X, Y$ ) : in particular each point in the figure gives ( $x, y$ ) or ( $X, Y$ ) depending on whether the rectangular or the curvilinear coordinates are referred to, respectively.

The interesting feature of figure 3 is that In in the vapour phase is converted into the quaternary solid phase to a much lesser extent than Ga. This has already been observed for InGaP [21] and InGaAs [22] and is related to the large difference in the free energy of reaction of the In- and Ga-containing III-V compounds.

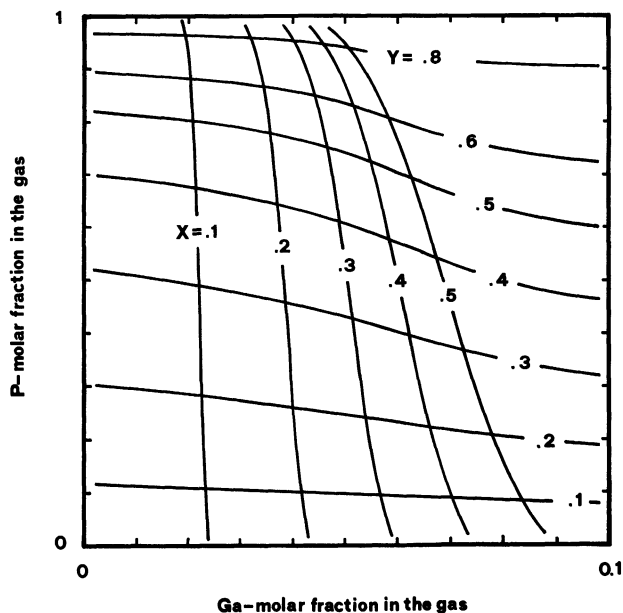


Fig. 3. — Equilibrium gas-phase composition versus the  $\text{In}_{(1-x)}\text{Ga}_x\text{As}_{(1-y)}\text{P}_y$  alloy composition.

In figure 4 the lattice constant of the quaternary solid solution is plotted as a function of the equilibrium Ga- and P-molar fraction in the vapour phase; the lines on the quaternary surface represent the intersections with constant lattice-parameter planes. It should be noted that the alloys which are lattice matched to InP (dashed line) lie in the steep part of

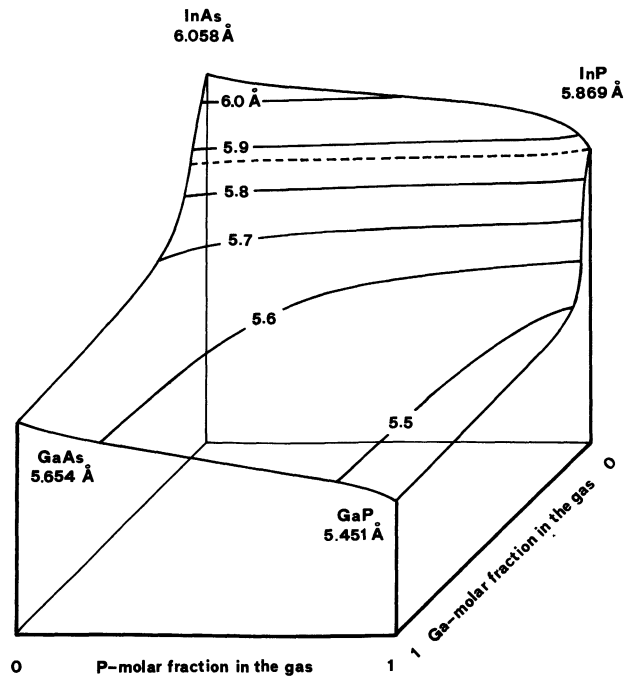


Fig. 4. — Dependence of the InGaAsP lattice parameter on the equilibrium Ga- and P-molar fractions in the vapour phase. The dashed line gives the vapour composition in equilibrium with alloys lattice-matched to InP.

the surface. As a consequence, it is very important to maintain an accurate control of the vapour Ga-molar fraction in growing InGaAsP/InP lattice-matched heterostructures, since reliable continuous laser operation at room temperature is likely to be obtained when the lattice-mismatch within the InP/InGaAsP/InP double heterojunction is less than  $10^{-3}$ . This can be pointed out on the analogy with heterostructures based on ternary compounds, where, because of misfit dislocations, the surface recombination velocity  $S$  at the heterointerfaces is linearly related to the lattice-mismatch [23, 24], and by recalling that the lasing threshold current density is approximately proportional to  $S$  [25]. Figure 5 shows in more detail the relationship which should exist between the Ga- and P-molar fractions in the vapour phase for growing quaternary alloys lattice-matched to InP; the open circles represent the vapour phase composition which is in equilibrium with alloys which emit light at the wavelengths shown. An exhaustive description of the experimental growth conditions of InGaAsP on InP substrates has been given by Hyder *et al.* [8] and Sugiyama *et al.* [7].

The data of reference [8] and those which can be extrapolated from figure 2 in reference [7] are reported in figure 5 as closed triangles and circles respectively.

The agreement between the results of the present work and the data derived from Sugiyama *et al.* [7] is remarkably good when the set of thermodynamical constants which have been singled out by the simultaneous fitting of the ternary alloy data (Figs. 1 and 2) is used.

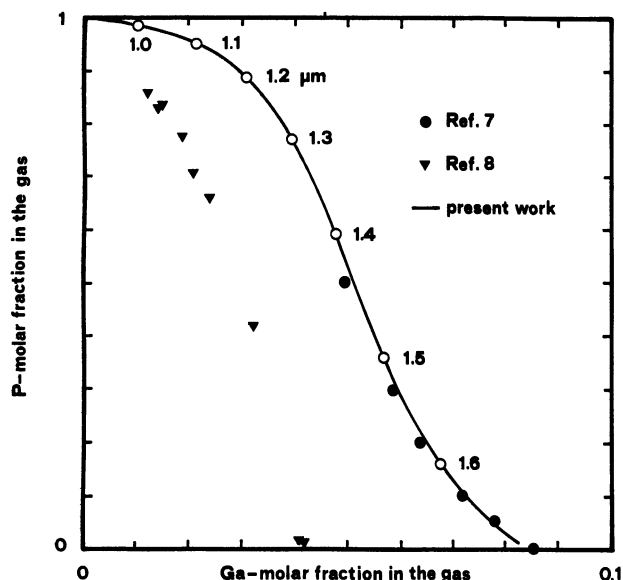


Fig. 5. — Gas phase composition in equilibrium with InGaAsP alloys lattice-matched to InP (full line). Experimental data taken from references [7] and [8] are reported for comparison. Alloy light-emission wavelengths are reported as parameters.

The difference between the data obtained by Hyder *et al.* [8] and by Sugiyama *et al.* [7] and the difference

between the Hyder's and the present equilibrium results suggest that care should be taken in interpreting the equilibrium findings in terms of experimental growth parameters.

Infact the thermodynamical equilibrium may not be complete within the epitaxial reactor and this may depend on the actual experimental geometry, gas flow velocities and temperature profiles. The above may also explain differences between experimental results obtained using different set-ups. For instance, it is generally agreed that the conversion of HCl into metal chlorides is dependent upon metal source areas and upon the gas velocities.

Furthermore, because of the different reactivity of the InCl with AsH<sub>3</sub> and PH<sub>3</sub> or with the As- and P-dimers and tetramers, the percentage of the hydride cracking may influence the solid phase composition [26]. In conclusion it has been shown that a judicious analysis based on the thermodynamical equilibrium can be useful in selecting the growth parameters of InGaAsP quaternary alloys of definite compositions. This result stems from the accurate choice of the thermodynamical constants and from the use of the regular solution model for the description of the quaternary solid solutions.

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