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Calculation of the In/Ga/P Ternary Phase Diagram and its Relation to Liquid Phase Epitaxy

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The Ga/In/P ternary phase diagram is calculated. A regular solution is assumed for binary solubility and the derived interaction parameters are used to calculate the deviation from ideality of the ternary system using a quasi-regular solution model. Comparison is made between theoretical and experimental results on liquid epitaxial layers. It is suggested that a solid/solid miscibility gap in the Ga/In/P system is a distinct possibility.

1. Introduction

Direct transition electroluminescence with photon energies of 2.17 eV at 300° K has been observed by Hakki [1] in $In_{1-x}Ga_xP$ alloys with $x = 0.6$. As this photon energy is near to the maximum visual sensitivity of the human eye and the material has a direct band gap, then $In_{1-x}Ga_xP$ appears to be attractive from an electroluminescent device standpoint.

A ternary phase diagram for the In/Ga/P system would be very useful in the growth of mixed crystals from the liquid phase. The complete investigation of a ternary phase diagram is a lengthy, time consuming process with the added complication, in this case, of a high phosphorus pressure over the melt at elevated temperatures. A method of calculation is therefore desirable. Ilegems and Pearson [2] have derived the Ga/Al/As ternary phase diagram, a similar method is employed here where the phase diagram for the In/Ga/P system is calculated from binary data.

2. Binary Liquidus Data

Using a regular solution treatment, a regular solution being defined as one in which the excess enthalpy of mixing is non-zero, while the excess entropy of mixing is zero, Vieland [3] has analysed the liquidus curves for a number of III-V compounds. He has shown that the liquidus curve for a compound AB in equilibrium with a regular solution is given by:

$$\alpha = -\frac{RT}{2(0.5-x)^2}\left[\ln 4x(1-x) + \frac{\Delta S^F}{R}\left(\frac{T_M}{T} - 1\right)\right] \qquad (1)$$

where α = interaction parameter characterising the departure from ideality of the system, T = absolute temperature, T_M = melting point of AB in °K, R = gas constant, ΔS^F = entropy of fusion of AB, and x = mole fraction of B. Using the solubility data of Hall [4] and Rubenstein [5] for GaP, and Hall [4] and van den Boomgaard and Schol [6] for InP, α as a function of T can be calculated. Fig. 1 shows the results obtained using values of T_M and ΔS^F ($\Delta H^F/T$) from table I, after Willardson [7].

The ΔH^F values are obtained from direct arithmetic averages of values obtained from the left A^{III} and right B^V branches of experimental liquidus curves for the binary $A^{III}B^V$. The shape of an ideal liquidus curve is given by Raoults law:

$$\ln x = -\frac{\Delta H^F}{RT_M}\left(\frac{T_M}{T} - 1\right) \qquad (2)$$

This can be approximated by:

$$\ln x = -\frac{C}{T} + D \qquad (3)$$

TABLE I

	InP	GaP
Melting point, °K	1333	1813
ΔH^F = enthalpy of fusion (average of liquidus curves) kcal/gm/mole	19.7	23.3
$\Delta S^F = \Delta H^F/T_M$ eu.	14.76	12.85

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where C and D are constants. Plots of experimental $\ln x$ and $\ln(1\text{-}x)$ against $1/T$ yield C and D from the linear parts of the curves obtained. Equating equations 2 and 3 yields ΔH^F.

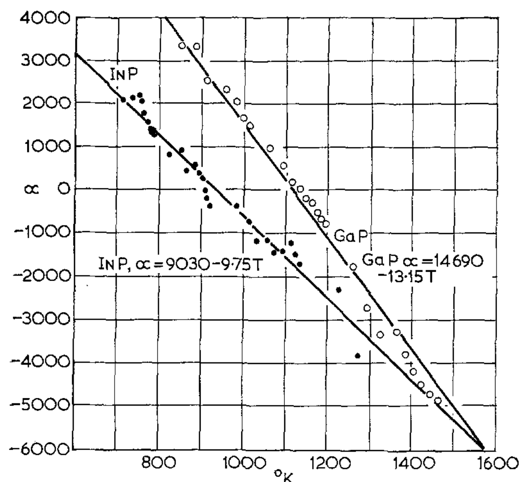

Figure 1 Interaction parameter α as a function of temperature.

From fig. 1 we have:

$$\alpha\text{GaP} = 14{,}690 - 13.15T \qquad (4)$$

$$\alpha\text{InP} = 9030 - 9.75T \qquad (5)$$

For a strictly regular solution α is independent of T, but as α is found to be a linear function of T these solutions are called quasi-regular. A value of $\alpha = 1066$ cal/mole is assumed for the In/Ga interaction parameter after Stringfellow [8]. The InP/GaP equilibrium will be assumed to exhibit an ideal pseudo-binary phase diagram.

3. Ternary Phase Diagram Calculation

Following the analysis of Ilegems [2] we have:

$$RT \ln\gamma_{\text{Ga}} = \alpha_{\text{GaP}} N^2_{\text{P}} + \alpha_{\text{InGa}} N_{\text{In}}^2 + (\alpha_{\text{GaP}} - \alpha_{\text{InP}} + \alpha_{\text{InGa}}) N_{\text{P}} N_{\text{In}} \qquad (6)$$

where γ_i = activity coefficient, N_i = mole fraction of the ith constituent. Formulae for γ_{In} and γ_{p} are obtained by cyclic substitution of the indices.

The chemical potentials in the liquid phase are given by equations of the form:

$$\mu_{\text{Ga}}^{1}(T) = \mu_{\text{Ga}}^{01}(T) + RT \ln \gamma_{\text{Ga}} N_{\text{Ga}}$$

and in the solid by:

$$\mu_{\text{GaP}}^{\text{c}}(T) = \mu_{\text{GaP}}^{0\text{c}}(T) + RT \ln x\ .$$

Where 0, 1 and c refer to the pure state, liquid phase and crystalline state respectively. A relation between the chemical potential of a pure compound to the chemical potentials of liquid phase constituents is given by Vieland [3]. Using this relation, equating chemical potentials in the liquid and solid phase and neglecting specific head terms yields:

$$x = 4N_{\text{Ga}}\, N_{\text{P}} \frac{\gamma_{\text{Ga}}\gamma_{\text{P}}}{\gamma_{\text{Ga}}SL\gamma_{\text{P}}SL} \exp\left[\Delta S^{\text{F}}{}_{\text{GaP}}(T_{\text{MGaP}} - T)/RT\right] \qquad (7)$$

$$1 - x = 4N_{\text{In}}\, N_{\text{P}} \frac{\gamma_{\text{In}}\gamma_{\text{P}}}{\gamma_{\text{In}}SL\gamma_{\text{P}}SL} \exp\left[\Delta S^{\text{F}}{}_{\text{InP}}(T_{\text{MInP}} - T)/RT\right] \qquad (8)$$

where x = mole fraction GaP in $\text{Ga}_x\text{In}_{1-x}\text{P}$ and the superscript SL refers to activities in stoichiometric liquid, i.e. at T_{M}. Adding equations 7 and 8 and substituting activities from equation 6 together with α from equations 4 and 5, gives the liquidus surface for any given set of values of N_{Ga} and T. These liquidus values at temperature T substituted back in equation 7 give the corresponding solidus. The resulting equations cannot be solved analytically and a numerical solution using a computer is required. Isothermal liquidus curves are shown in fig. 2.

To be of immediate practical use to liquid phase epitaxy the liquidus curves, calculated as mole fractions *v*. T, need to be changed to physically measurable units *v*. T. Experimentally $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloys can be grown by slowly cooling a solution of InP in a mixed In/Ga solvent. Accordingly the following isothermal curves have been calculated:

fig. 3 x *v*. wt % Ga expressed as a fraction of the total metal solvent weight.
fig. 4 Solubility of InP in 100 g of mixed metal solvent *v*. wt % Ga in solution.

4. Comparison with Experimental Results

Epitaxial layers of indium gallium phosphide have been grown on gallium phosphide substrates using a modification of the vertical liquid epitaxial technique of Rupprecht [9]. Compositional analyses of the grown layers were effected with an electron probe microanalyser, atomic number, absorption and fluorescence corrections are applied to the emitted X-ray intensity ratios. It was found that for growth cycles over the temperature range *ca*. 690 to 590° C alloys with

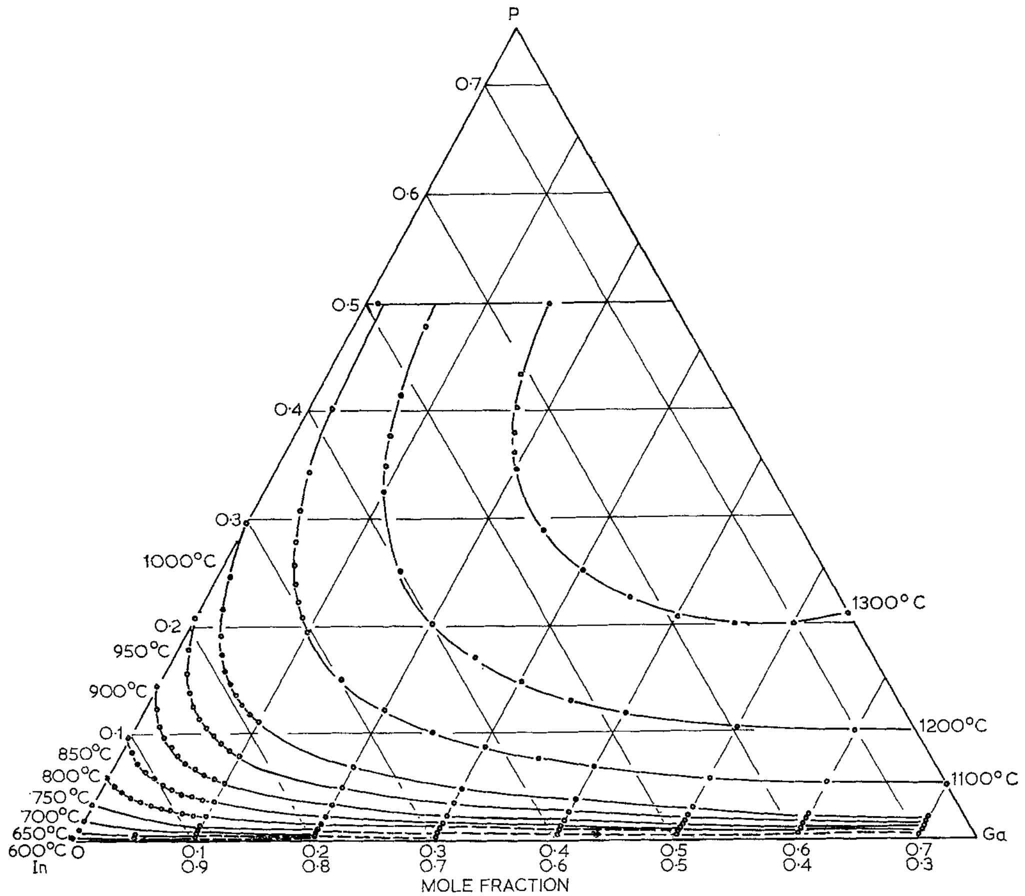

Figure 2 Liquidus curves for isothermal sections of the In/Ga/P phase diagram.

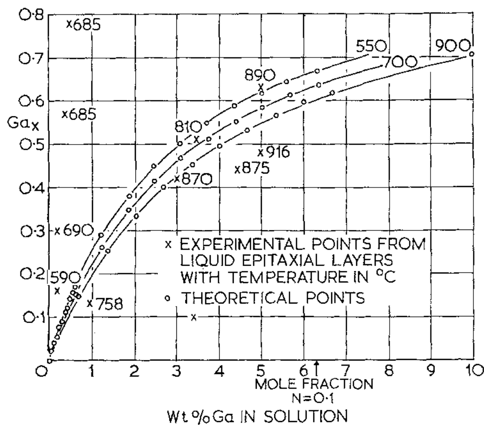

Figure 3 Alloy composition x as a function of solution wt % gallium.

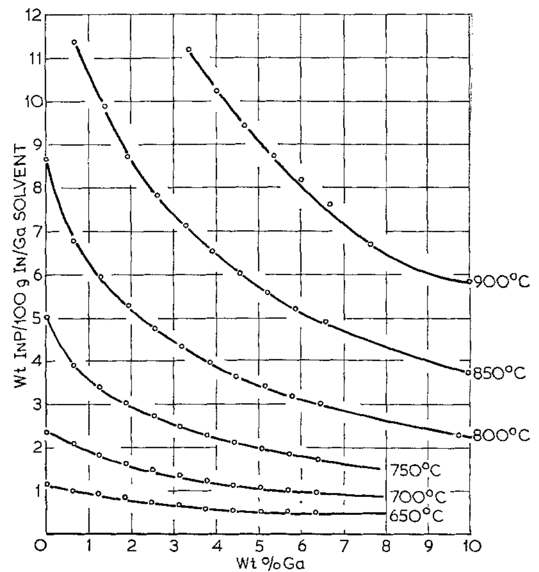

Figure 4 Solubility of InP in 100 g of In/Ga solvent

$0.35 < x < 0.55$ could not be grown and that for growth from *ca.* 900 to 800° C, depending on the solution gallium concentration, two distinct alloy phases tended to separate out in the same epitaxial layer. This phase segregation showed

itself as two different composition layers, each of which were of approximately constant composition, in the same epilayer. Fig. 3 shows theoretical, isothermal, solidus curves together with experimental, initial growth, solid compositions obtained by microprobe analyses of cleaved epitaxial layers.

As epitaxial growth does not take place under equilibrium conditions, and considering the assumptions made in the calculation, agreement between theory and experiment is quite good for alloys grown at temperatures above *ca.* 750° C. However, there is no correlation between theoretical and experimental results for alloys grown below 700° C, implying a marked deviation from regularity. The difficulty in growing alloys with $0.35 < x < 0.55$ from 690° C and the fact that two phases tend to separate when growth is attempted from below 900° C suggest that a solid-solid miscibility gap is a distinct possibility. A pseudo-binary cross-section of the complete ternary phase diagram would then be expected to exhibit a "pseudo-peritectic" reaction at some temperature below 900° C. This being the case then depending on compositional separation between the α and β phases produced in the reaction, it would be expected that either a sharp compositional change would be seen in an epitaxial layer or that an epitaxial layer would not form at all. Both of these possibilities have been observed.

5. Conclusions

It would seem that growth of $Ga_xIn_{1-x}P$ from the liquid phase is more difficult than it would at first sight seem. However, by increasing the growth temperature and growing over a limited temperature range the two phase segregation should be controllable. Alternatively a constant temperature, temperature gradient growth technique could be used to advantage.

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