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$_x$P 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$_x$P 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:

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

(1)

where $\alpha$ = interaction parameter characterising the departure from ideality of the system, $T =$ absolute temperature, $T_M =$ melting point of AB in °K, $R =$ gas constant, $\Delta S^F =$ 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, $\alpha$ as a function of $T$ can be calculated. Fig. 1 shows the results obtained using values of $T_M$ and $\Delta S^F (\Delta H^F/T)$ from table I, after Willardson [7].

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

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

(2)

This can be approximated by:

$$\ln x = - \frac{C}{T} + D$$

(3)

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

\[
\mu_{\text{GaP}}(T) = \mu_{\text{GaP}}^0(T) + RT \ln x \quad \text{\( \mu_{\text{GaP}}^0(T) \) refers to the pure state.}
\]

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:

\[
x = 4N_{\text{Ga}} N_{\text{P}} \frac{\gamma_{\text{GaP}}}{\gamma_{\text{GaSL}} \gamma_{\text{P,SL}}} \exp \left[ \frac{\Delta S^F_{\text{GaP}}(T_{\text{NGaP}} - T)/RT}{\gamma_{\text{GaP}} \gamma_{\text{P,SL}}} \right]
\]

\[
1 - x = 4N_{\text{In}} N_{\text{P}} \frac{\gamma_{\text{InP}}}{\gamma_{\text{InSL}} \gamma_{\text{P,SL}}} \exp \left[ \frac{\Delta S^F_{\text{InP}}(T_{\text{MinP}} - T)/RT}{\gamma_{\text{InP}} \gamma_{\text{P,SL}}} \right]
\]

where \( x \) = mole fraction GaP in Ga\(_x\)In\(_{1-x}\)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 \( \alpha \) from equations 4 and 5, gives the liquidus surface for any given set of values of \( N_{\text{Ga}} \) 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 \( v \cdot T \), need to be changed to physically measurable units \( v \cdot T \). Experimentally In\(_{1-x}\)Ga\(_x\)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 microanalyzer, 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 \( \text{ca.} 690 \) to \( 590 \, ^\circ \text{C} \) alloys with...