because of the preferential incorporation of InAs for the growth of InAsP [5]. On the other hand, the area of the InGaAsSb alloys is very narrow because of the preferential incorporation of InAs and GaAs for the growth of InAsSb and GaAsSb, respectively [5]. Therefore, we can predict a similar preferential incorporation of arsenic as that of InAsSb and GaAsSb ternaries for the growth of InGaAsSb alloys (see fig. 7).

For practical applications, the growth of InGaAsP lattice-matched to InP and GaAs substrates is of considerable importance. Figs. 9 and 10 show the calculated input mole ratios necessary to deposit the lattice-matched alloys. In these figures the variation of the composition with the V/III ratio and the total pressure of the system are also indicated. The gallium content increases linearly with the increase of the input Ga/(Ga + In) ratio, while the P/(P + As) ratio in the solid changes in a complex way for the increase of the input P/(P + As) ratio, depending on the V/III ratio and on the total pressure. Consequently, precise control of the input P/(P + As) ratio is essential for the reproducible preparation of these

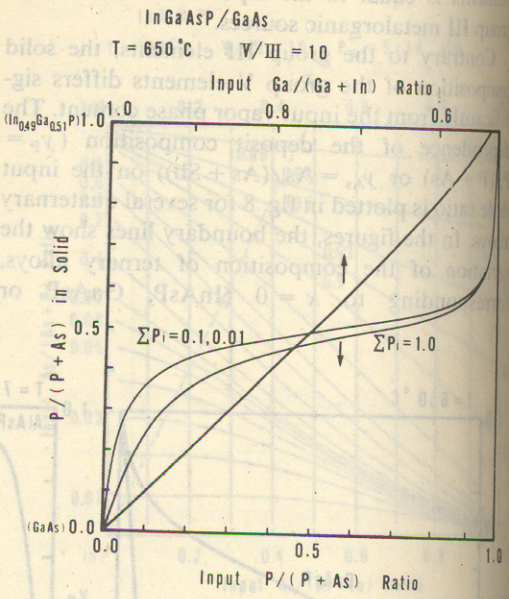

Fig. 10. The input mole ratios necessary to deposit InGaAsP lattice matched to GaAs.

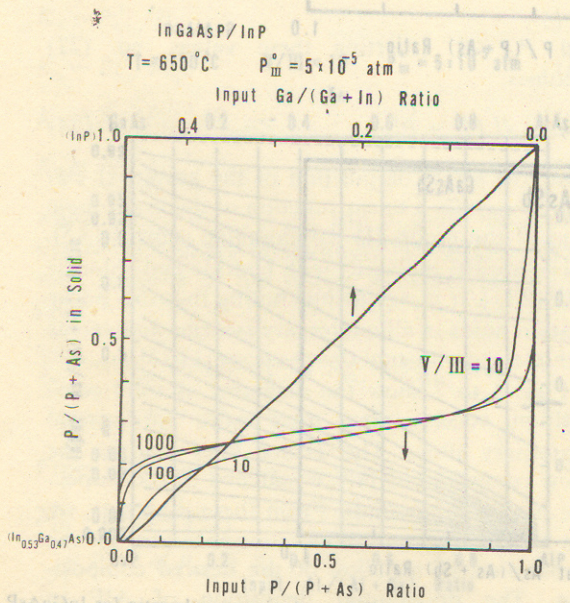

Fig. 9. The input mole ratios necessary to deposit InGaAsP lattice matched to InP.

alloys. Another interesting feature of these figures is that a preferential incorporation of arsenic is expected at large input P/(P + As) ratios.

In fig. 11 the theoretically-predicted compositions of the alloys are compared with the experimental data of Razeghi et al. [14]. Although some deviation is observed in the long wavelength range for the input P/(P + As) ratio, the agreement between the experimental and calculated compositions is reasonable. The deviation is probably due to the slow pyrolysis rate of PH_3, because the growth temperature used in the experiment is low.

3.2. III–III–III–V systems

AlGaInP and AlGaInAs alloys are very attractive materials for practical applications. Figs. 12 and 13 show the equilibrium partial pressures of the gaseous species for these alloys. Again, the partial pressures of the group III elements are very small when the V/III ratio is larger than unity. The difference of the partial pressures of the group III elements is due to the values of the equilibrium

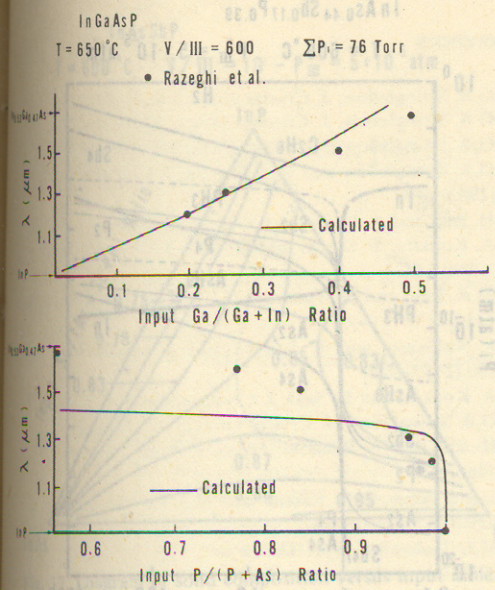

Fig. 11. Comparison between the experimental and calculated compositions of $In_{1-x}Ga_xAs_yP_{1-y}$. The data are from the work of Razeghi et al. [14].

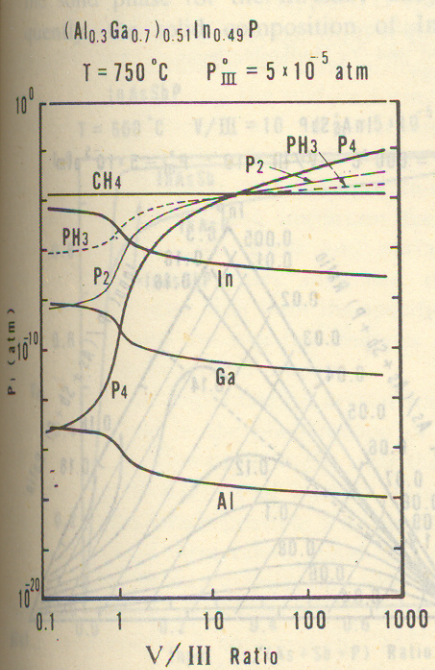

Fig. 12. The equilibrium partial pressures over AlGaInP as a function of the V/III ratio.

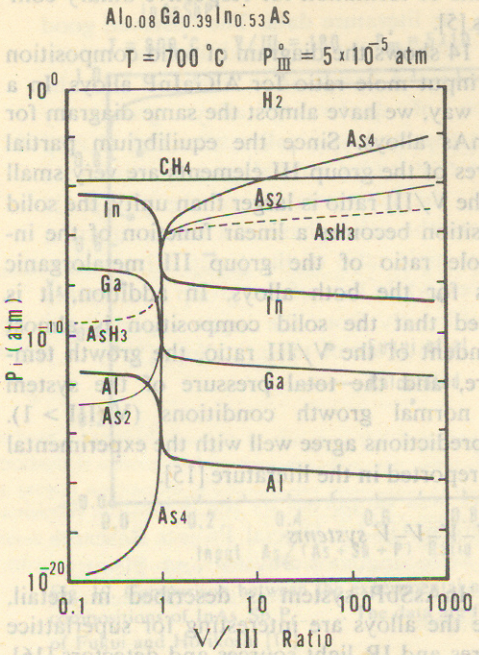

Fig. 13. The equilibrium partial pressures over AlGaInAs as a function of the V/III ratio.

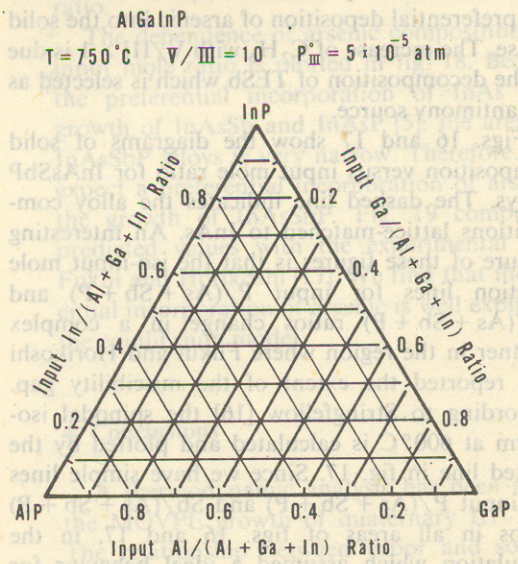

Fig. 14. Diagram of solid composition versus input mole ratio for AlGaInP alloys.

constants of formation for respective binary compounds [5].

Fig. 14 shows the diagram of solid composition versus input mole ratio for AlGaInP alloys. In a similar way, we have almost the same diagram for AlGaInAs alloys. Since the equilibrium partial pressures of the group III elements are very small when the V/III ratio is larger than unity, the solid composition becomes a linear function of the input mole ratio of the group III metalorganic sources for the both alloys. In addition, it is predicted that the solid composition is almost independent of the V/III ratio, the growth temperature, and the total pressure of the system under normal growth conditions (V/III > 1). These predictions agree well with the experimental results reported in the literature [15].

3.3. III–V–V–V systems

The InAsSbP system is described in detail, because the alloys are interesting for superlattice structures and IR light sources and detectors [16]. Fig. 15 shows the equilibrium partial pressures of gaseous species over $InAs_{0.44}Sb_{0.17}P_{0.39}$. In the calculation, TEIn, AsH_3, PH_3 and TESb are selected as source materials. The low partial pressures of arsenic species with V/III > 1 indicate the preferential deposition of arsenic into the solid phase. The increase of C_2H_6 with V/III > 1 is due to the decomposition of TESb which is selected as the antimony source.

Figs. 16 and 17 show the diagrams of solid composition versus input mole ratio for InAsSbP alloys. The dashed line indicates the alloy compositions lattice-matched to InAs. An interesting feature of these figures is that the iso-input mole fraction lines for input P/(As + Sb + P) and Sb/(As + Sb + P) ratios change in a complex manner in the region where Fukui and Horikoshi [17] reported the extent of the miscibility gap. According to Stringfellow [16] the spinodal isotherm at 600°C is calculated and plotted by the dotted line in fig. 17. Since we have simple lines for input P/(As + Sb + P) and Sb/(As + Sb + P) ratios in all areas of figs. 16 and 17, in the calculation which assumed a ideal behavior for InP and InSb in the InAsSbP solid solution, the

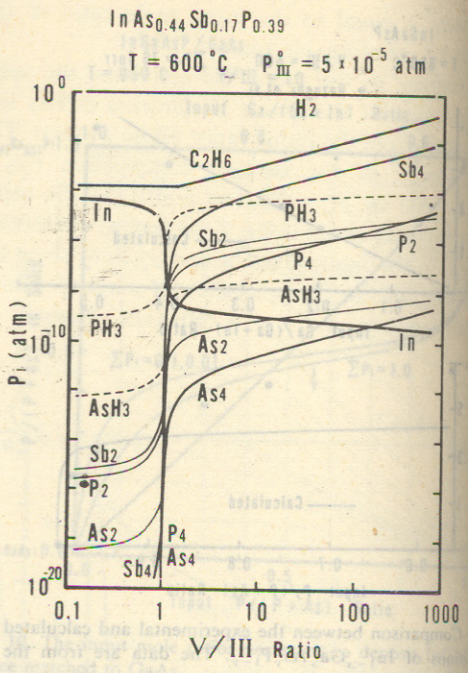

Fig. 15. The equilibrium partial pressures over InAsSbP as a function of the V/III ratio.

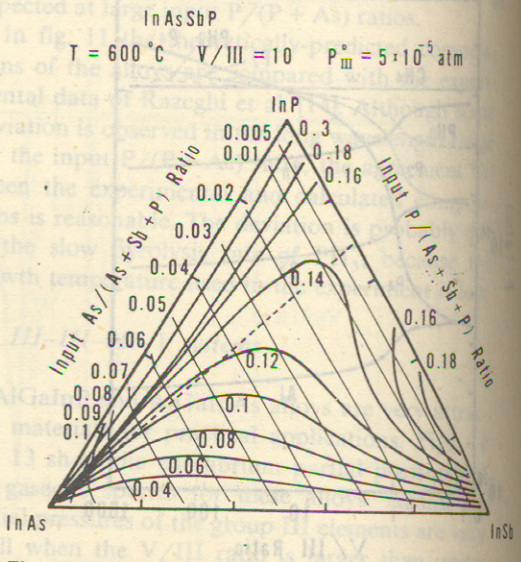

Fig. 16. Diagram of solid composition versus input mole ratio for InAsSbP alloys.

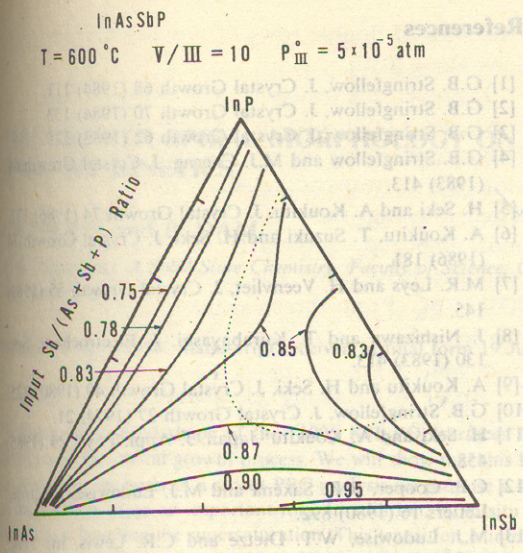

Fig. 17. Diagram of solid composition versus input mole ratio for InAsSbP alloys.

complicated variation is due to the non-ideality of the solid phase for the InAsSbP alloys. Consequently, the solid composition of InAsSbP is

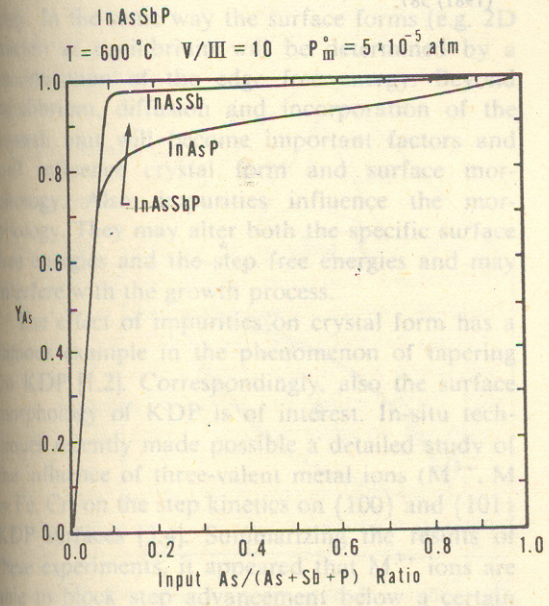

Fig. 18. The dependence of arsenic composition on the input mole ratio for InAsSbP alloys.

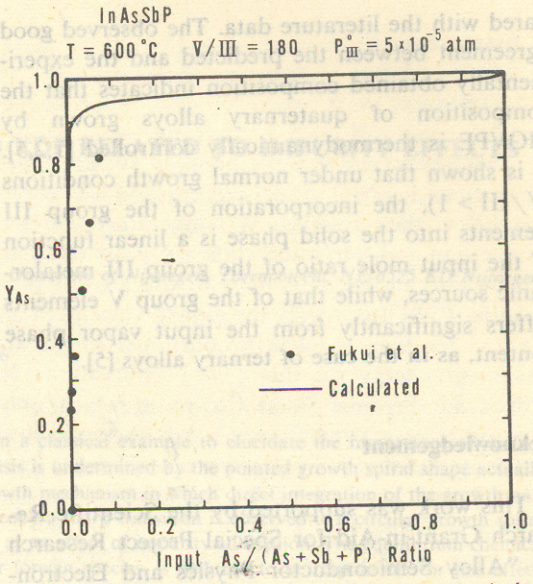

Fig. 19. Comparison between the experimental and calculated compositions of $InAs_xSb_yP_{1-x-y}$. The data are from the work of Fukui and Horikoshi [17].

governed largely by the non-ideality of the solid, in addition to the Gibbs free energy of formation of the binary compounds and the input V/III ratio.

The dependence of arsenic composition on the input mole ratio is plotted in fig. 18. Because of the preferential incorporation of InAs for the growth of InAsSb and InAsP [5], the area of the InAsSbP alloys is very narrow. Therefore, we can expect a preferential incorporation of arsenic for the growth of InAsSbP. Fig. 19 compares the predicted values with the experimental data of Fukui and Horikoshi [17]. We find that the preferential incorporation of arsenic is well explained by the equilibrium model.

4. Conclusions

A thermodynamic analysis has been made for the MOVPE growth of quaternary III–V alloys. The relationship between vapor and solid composition has been calculated for the III–III–V–V, III–III–III–V, and III–V–V–V systems and com-

pared with the literature data. The observed good agreement between the predicted and the experimentally obtained composition indicates that the composition of quaternary alloys grown by MOVPE is thermodynamically controlled [1,2,5]. It is shown that under normal growth conditions ($V/III > 1$), the incorporation of the group III elements into the solid phase is a linear function of the input mole ratio of the group III metalorganic sources, while that of the group V elements differs significantly from the input vapor phase content, as in the case of ternary alloys [5].

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