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Analysis for Relationship between Vapor and Solid Phase Composition in MOVPE −InGaAsP Case−

Takuya FUJII, Susumu YAMAZAKI, and Kazuo NAKAJIMA

Fujitsu Laboratories, Atsugi

10-1, Morinosato-Wakamiya, Atsugi, 243-01, Japan

The relationship between the vapor and solid phase composition in InGaAsP grown by low pressure metalorganic vapor phase epitaxy has been investigated. Each group solid composition is determined only by the same group vapor composition in a certain V/III ratio. The vapor and solid relationship of each group species is written in a simple equation including a term that is invariable for V/III ratio changes.

1. Introduction

Experimental determination of the exact relationship between the vapor and solid phase composition in metalorganic vapor phase epitaxy (MOVPE) is indispensable from the viewpoint of investigating the growth mechanism and the practical point of view.

We investigated the composition relationship for $III_xIII'_{1-x}V_yV'_{1-y}$ quaternary system. In this quaternary system, mixing of group III (III, III') and group V (V, V') species occurs in two sublattices, and we can see the dependence of the group III solid composition on both the group III and group V vapor species and see the dependence of the group V solid composition on both the group the vapor phase compositions.

There are three independent vapor phase parameters, $(III/III')_{gas}$, $(V/V')_{gas}$, and V/III ratio to determine the solid compositions, $(III/III')_{solid}$ and $(V/V')_{solid}$, in this system. In general, the relationship between $(III/III')_{gas}$ and $(III/III')_{solid}$ is influenced by the $(V/V')_{gas}$ and V/III ratio, and the relationship between $(V/V')_{gas}$ and $(V/V')_{solid}$ is also influenced by the $(III/III')_{gas}$ and V/III ratio. However, no systematic and quantitative investigation of these influences for the relationships has been reported yet. Untill now, only $(III/III')_{gas}$ dependece of $(III/III')_{solid}$, and only $(V/V')_{gas}$ dependence of $(V/V')_{solid}$ have been reported[1)-4)]. Our purpose is to find out the relationships between $(III/III')_{solid}$ and the three vapor phase parameters, and between $(V/V')_{solid}$ and the three vapor phase parameters.

In this work, we studied these relationships for the quaternary InGaAsP system systematically. This paper describes the relationships between the vapor and solid compositions in a certain V/III ratio, and also in various V/III ratios.

2. Experimental

Both lattice matched and mismatched samples were grown by the horizontal low pressure MOVPE system on InP (100) exact substrates over the entire composition range. Growth tempetature, operating pressure, and total gas flux were fixed at 620 °C, 50 torr, and 10 slm, respectively. Trimethylindium (TMIn) and triethylgalium (TEGa) were used as the group III metalorganic sourses. PH_3 and AsH_3 were used as the group V hydride sources. Hydrogen was used as a carrier gas. Total metalorganic gas flux was kept constant at 0.3 sccm. Growth rates were about 0.7 um/hour in this condition. V/III ratio was changed in the range of 60-220.

Solid phase compositions were caluculated from lattice constants and energy gaps of the epitaxial layers. Lattice constants and energy gaps were determined by the double crystal X-ray diffraction technique and photoluminescense (PL) measurements at room temperature, respectively. The dependence of elastic constant on solid composition and PL energy shift due to elastic strain were considered in the caluculation of those for lattice mismatched epitaxial layers. These formulas can be written as follows;

$$
\begin{aligned}
(da/a)_e &= (1 + C_{11}/C_{12})\,(da/a)_b\,, \\
E_e &= E_b + D\,(da/a)_e\,, \\
(da/a)_b &= a_0 + a_1 x + a_2 y + a_3 x y\,, \\
E_b &= e_0 + e_1 x + e_2 y + e_3 x^2 \\
&\quad + e_4 x y + e_5 y^2\,, \\
C_{11}/C_{12} &= c_0 + c_1 x + c_2 y\,,
\end{aligned}
$$

where $(da/a)_e$ and E_e are the lattice mismatch and PL energy of the epitaxial layers,respectively. da is equal to the lattice constant of InGaAsP minus the lattice constant of InP, a. $(da/a)_b$ and E_b are these of bulk crystals with the composition x and y, respectively. C_{11} and C_{12} are elastic constants. Coefficients a_i, e_i, c_i (i=0-5) were determined using values of bulk crystals. Energy shift correction factor, D was assumed to be constant. The D factor for $In_xGa_{1-x}As$ was determined by X-ray diffraction and PL data as 3.4 meV.

3. Results and discussion

We studied the dependences of the solid compositions for the group III and group V species on the vapor phase compositions $(In/Ga)_{gas}$ and $(P/As)_{gas}$, in a certain V/III ratio. Figure 1 shows solid compositions, $(In/Ga)_{solid}$ and $(P/As)_{solid}$, as a function of $(In/Ga)_{gas}$ at a constant $(P/As)_{gas}$ of 1.77 and a constant V/III

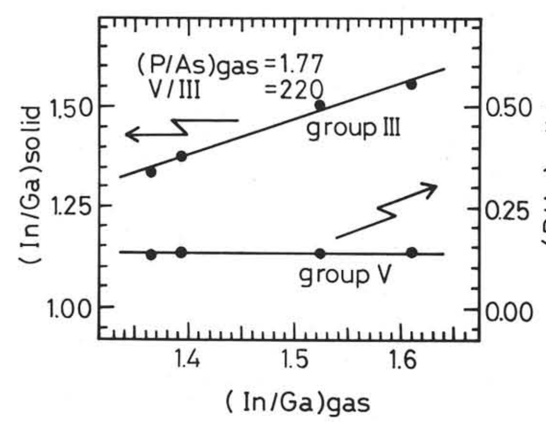

Fig. 1 $(In/Ga)_{solid}$ and $(P/As)_{solid}$ versus $(In/Ga)_{gas}$ under the condition of constant $(P/As)_{gas}$.

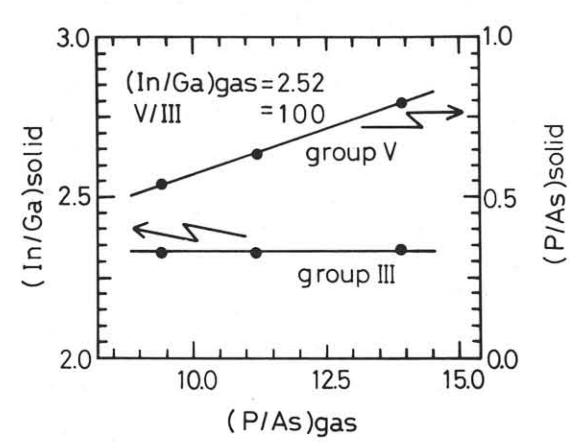

Fig. 2 $(In/Ga)_{solid}$ and $(P/As)_{solid}$ versus $(P/As)_{gas}$ under the condition of constant $(In/Ga)_{gas}$.

ratio of 220. Figure 2 shows $(In/Ga)_{solid}$ and $(P/As)_{solid}$ as a function of $(P/As)_{gas}$ at a constant $(In/Ga)_{gas}$ of 2.52 and a constant V/III ratio of 100. $(P/As)_{solid}$ are constant for $(In/Ga)_{gas}$ (fig.1), and $(In/Ga)_{solid}$ are also constant for $(P/As)_{gas}$ (fig.2). These results indicate that the solid composition of each group sublattice is independent of another group vapor phase composition. Figures 3 and 4 show the relationships between vapor and solid compositions for group III and group V species at V/III of 220. In these figures, the subscript numeral of each data point shows the lattice mismatch. These lattice mismatched data points were certainly on the lattice matched lines. These results show that the solid composition, $(In/Ga)_{solid}$, is determined only by the same group vapor composition, $(In/Ga)_{gas}$, over the entire composition range, and that $(P/As)_{solid}$ is also determined only by $(P/As)_{gas}$ over the entire composition range. Each vapor and solid relationship can be approximately written as follows;

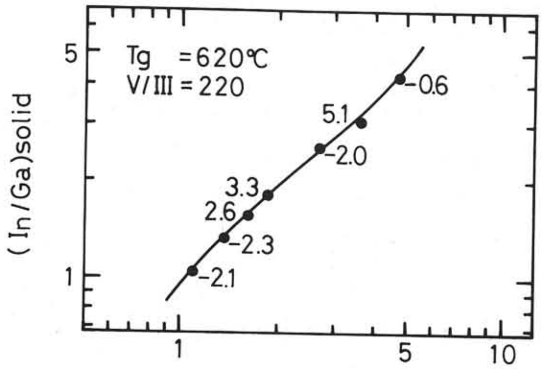

Fig. 3 Relationship between vapor and solid composition for group III species. Solid line indicates the relationship in lattice matched case. Numbers show values of lattice mismatch multiplied by 10^3.

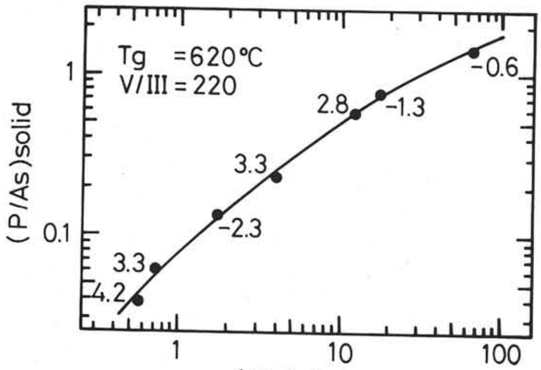

Fig. 4 Relationship between vapor and solid composition for group V spesies. Solid line indicates the relationship in lattice matched case. Numbers show values of lattice mismatch multiplied by 10^3.

$$\log_{10}(In/Ga)_{solid} = A \log_{10}(In/Ga)_{gas} + B ,$$
$$\log_{10}(P/As)_{solid} = A' \log_{10}(P/As)_{gas} + B'.$$

The V/III ratio affects above composition relationships in general. Therefore, we studied whether above equations depend on the V/III ratio or not in this quaternary system. From our experiments, B is 0, and B' is around -1 as shown in figure 5. The result that B is constantly 0 means the source supply limited step, and B' is considered to be determined mainly by the ratio of thermal decomposition efficiencies of two gas species PH_3 and AsH_3. B' depens on the V/III ratio, and B' increases as the V/III ratio decreases. B' depends on the specific design of the MOVPE system, because effective V/III ratio in a stagnant layer strongly depends on the MOVPE system. Figure 6 shows V/III ratio dependences of A and A'. A and A' are constant for various V/III ratios. A and A' are 0.9 and 0.7, respectively. A and A' must be invariables in any MOVPE systems, because effective V/III ratio is the most sensitive vapor phase parameter to the design of the MOVPE system. These values are considered fundamental parameters of MOVPE.

4. Conclusion

We investigated the relationship between vapor and solid phase composition in the InGaAsP qurternary system grown by low pressure MOVPE. We found out that group III solid composition is independent of group V vapor composition, and that group V solid composition is independent of group III vapor composition. Each group solid composition is determined only by the same group vapor composition in a certain V/III ratio. The composition relationship of each group species is written in a simple straight equation in logarithmic scale. This equation includes a term that is independent of V/III ratio.

1) J.S.Whiteley et al.; J.Electrochem. Soc. 129(1982) 383.
2) L.Samuelson et al.; J.Cryst. Growth 61(1983) 425.
3) T.Iwamoto et al.; Jpn.J.Appl. Phys. 22(1983) 191.
4) M.Ogura et al.; J.Cryst. Growth 68(1984) 32.

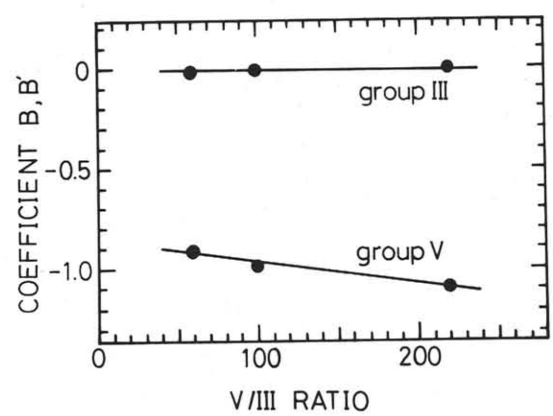

Fig. 5 V/III ratio dependences of B and B' in the composition relationship expressions.

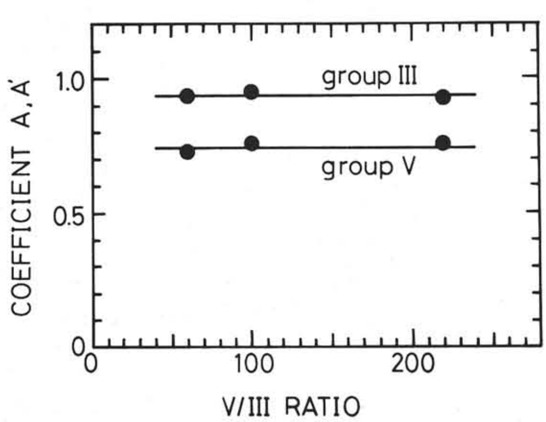

Fig. 6 V/III ratio dependences of A and A' in the composition relationship expressions.