

Improvement of Composition Uniformity of InGaAsP Crystals Grown by MOVPE Using AsH₃ and tBPH₂

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There is a large inhomogeneity of the group V compositions of InGaAsP crystals in 2-inch wafer grown by MOVPE. We attribute the inhomogeneity to the difference in the decomposition rates of AsH₃ and PH₃. Using AsH₃ and tBPH₂, which have nearly the same decomposition rate, we improved the group V composition uniformity. The inhomogeneity was 1/6 that obtained by using AsH₃ and PH₃.

Introduction

InGaAsP crystals are widely used as the basic materials for optical semiconductor devices. For high yield, uniformity in thickness, composition, and carrier concentration is very important. Metal organic vapor phase epitaxy (MOVPE) produces quite uniform InP and InGaAs crystals, where gas-flow patterns are controlled and the susceptor is rotated.¹⁾ However, there have been few reports on the composition distribution of InGaAsP quaternary alloys, but it is not good enough yet.

Our purpose is to clarify the origin of the InGaAsP composition inhomogeneity and to find a way to grow InGaAsP with highly uniform composition. We show that the composition inhomogeneity is attributed to the difference in the decomposition rates of arsine (AsH₃) and phosphine (PH₃). To improve the composition uniformity, we use MOVPE growth with various combination of source gases including tertiarybutylarsine (tBAsH₂) and tertiarybutylphosphine (tBPH₂) which have faster decomposition rates than AsH₃ or PH₃.

We improved the composition uniformity using the combination of AsH₃ and tBPH₂, which have nearly the same decomposition rate.

Experiments

InGaAsP crystals were grown in low pressure vertical reactor with a total pressure of 76 torr, and a flow rate of 6.5 l/min. Growth temperature was 600°C. Substrates were (100) oriented 2-inch InP. Source gases were injected perpendicularly to the substrate from four injectors and passed from the center to the edge of the wafer (Fig. 1). The composition distributions were investigated parallel to the flow (the dashed line in Fig. 1). Susceptor rotation was stopped for the sake of simplicity. Trimethylindium (TMI) and triethylgallium (TEG) were used as the group III sources. Three combinations of group V sources were used: AsH₃ + PH₃, AsH₃ + tBPH₂, and tBAsH₂ + tBPH₂. Total flow of group III sources was 22.3 μmol/min, and growth rate was 2.4 μm/hr. Total flow of group V sources was 4460 μmol/min for AsH₃ + PH₃ and 1780 μmol/min for

AsH₃ + tBPH₂ and tBPH₂ + tBAsH₂, corresponding to a V/III ratio of 200 and 80, respectively.

X-ray measurements were performed using the K_{α1} line of a Cu target. The rocking curves around the (400) peak were measured to determine the lattice constant perpendicular to the growth plane. Photoluminescence (PL) measurements were performed at 300 K using the Kr⁺ laser with an excitation intensity of 1220 W/cm².

Results and Discussion

1. Origin of the composition inhomogeneity

To determine the origin of the composition inhomogeneity in InGaAsP crystals grown using AsH₃ and PH₃, we estimated the group III and group V composition distributions in the wafer (Fig. 2). Compositions were calculated from the lattice constants perpendicular to the substrate and the PL peak wavelength.²⁾ There is only a small inhomogeneity for the group III composition (less than 1%), while there is fairly a large inhomogeneity for the group V composition (about 6%). The P concentration increases from the center to the edge along the gas flow.

As the origin of the group V composition inhomogeneity, we noticed the change in the effective vapor composition, which is the ratio of decomposition products from AsH₃ and

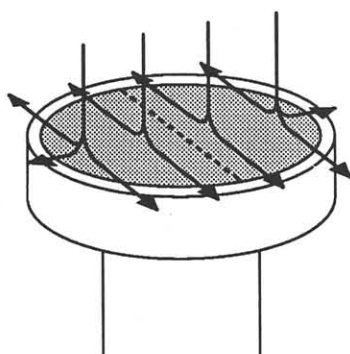


Fig. 1 Flow of the source gases. The dashed line shows the direction in which the composition distribution was investigated.

PH₃, along the flow. When the source gases reach near the substrate, they start to decompose. The decomposition is incomplete at the wafer center and proceeds as the source gases pass on the heated substrate from the center to the edge along the flow. Since the decomposition rates of AsH₃ and PH₃ are different, the effective vapor composition varies with position along the flow.

Supposing that the decompositions of AsH₃ and PH₃ are first order reactions and the decomposition products are AsH and PH, the effective vapor composition, $c_{\text{eff}}(t)$, can be written as follows:

$$\begin{aligned} c_{\text{eff}}(t) &= [\text{PH}] / [\text{AsH}] \\ &= [\text{PH}_3]_0 (1 - \exp(-k_p t)) / \\ &\quad [\text{AsH}_3]_0 (1 - \exp(-k_{\text{As}} t)) \\ &= c_0 f(t) \end{aligned}$$

where t is the time, k_{As} and k_p are decomposition rate constants, $[\text{AsH}_3]_0$ and $[\text{PH}_3]_0$ are the initial partial pressures, c_0 is the initial source gas composition, and $f(t)$ is the ratio of the degree of the decomposition. Figure 3 shows how $c_{\text{eff}}(t)$ varies with the time. In Fig. 3, t_c and t_e correspond to the center and the edge of a wafer. The value of $c_{\text{eff}}(t)$ varies from $c_0 k_p / k_{\text{As}}$ to c_0 . For the source gas combination of AsH₃ and PH₃, the P concentration increases from center to edge

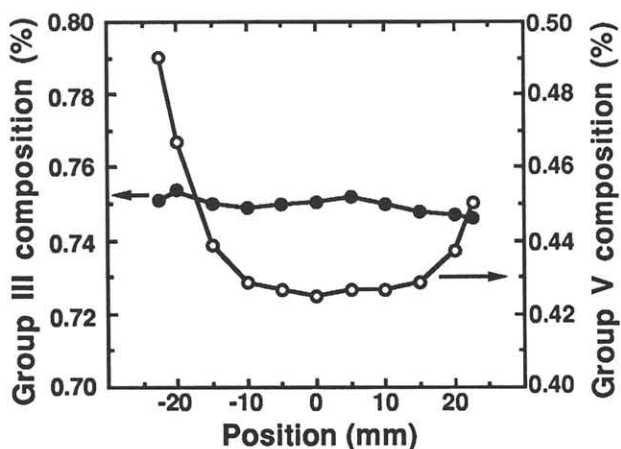


Fig. 2 Composition distributions of InGaAsP crystal on a 2-inch wafer. Source gas flow was from center to edge.

(Fig. 2). This is because the decomposition rate of PH_3 is smaller than that of AsH_3 ($k_P/k_{As} < 1$) and the decomposition at the wafer center is incomplete (Fig. 3 (a)).

2. Improvement of the composition uniformity

To improve composition uniformity, the difference between $c_{\text{eff}}(t_c)$ and $c_{\text{eff}}(t_e)$ should be reduced. When $c_{\text{eff}}(t_c)$ is close to c_0 , the difference between $c_{\text{eff}}(t_c)$ and $c_{\text{eff}}(t_e)$ becomes small because $c_{\text{eff}}(t_e)$ is always between $c_{\text{eff}}(t_c)$ and c_0 . We can predict whether the composition distribution will be uniform by looking at $c_{\text{eff}}(t_c)$.

There are two methods to move $c_{\text{eff}}(t_c)$ closer to c_0 . The first method is to use the P source with the same decomposition rate as that the As source. When both As and P source have same decomposition rate, $c_{\text{eff}}(t)$ is always c_0 (Fig. 3 (b)). We selected $\text{AsH}_3 + \text{tBPH}_2$ as the source gas combination because

tBPH_2 seems to have nearly same decomposition rate as AsH_3 .^{3),5)} The second method is to use gases that decompose quickly for both As and P sources. Since decomposition at the center is complete, $c_{\text{eff}}(t_c)$ is equal to c_0 (Fig. 3 (c)). We selected $\text{tBAsH}_2 + \text{tBPH}_2$ as the source gases for this method because they have faster decomposition rates than AsH_3 and PH_3 , respectively.^{5),6)}

To estimate $c_{\text{eff}}(t_c)$ at the wafer center, we compared the measured vapor-solid composition relationships between $(\text{P/As})_{\text{solid}}$ and c_0 with the calculated relationship (Fig. 4). Solid composition at the wafer center can be written as follows:

$$\begin{aligned} \log(\text{P/As})_{\text{solid,center}} &= A \log(c_{\text{eff}}(t_c)) + B \\ &= A \log(c_0) + A \log(f(t_c)) + B. \end{aligned}$$

Constants A and B were calculated assuming equilibrium between AsH , As_2 , PH , P_2 , H_2 and the crystal. Calculated values of A and B are

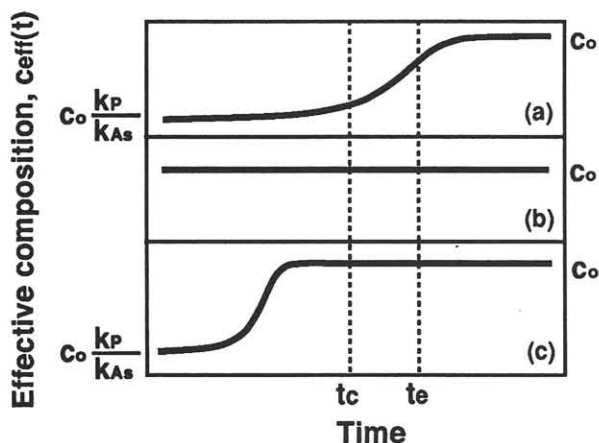


Fig. 3 Variation of the effective composition with time; (a) k_P and k_{As} are small and $k_P \neq k_{As}$, (b) $k_P = k_{As}$, (c) k_P and k_{As} are large and $k_P \neq k_{As}$.

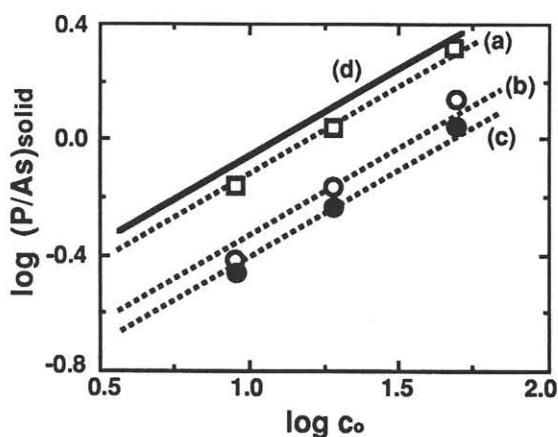


Fig. 4 Vapor-solid composition relationships; (a) $\text{AsH}_3 + \text{tBPH}_2$, (b) $\text{tBAsH}_2 + \text{tBPH}_2$, (c) $\text{AsH}_3 + \text{PH}_3$, (d) calculated relationship for $c_{\text{eff}} = c_0$.

Table 1. Equilibrium constants used in the calculation.

Reaction	Equilibrium constant
$\text{In(g)} + 1/2 \text{P}_2(\text{g}) = \text{InP(s)}$	$\ln K = -26.82 + 46770 / T$
$\text{Ga(g)} + 1/2 \text{As}_2(\text{g}) = \text{GaAs(s)}$	$\ln K = -26.99 + 54760 / T$
$\text{In(g)} + 1/2 \text{As}_2(\text{g}) = \text{InAs(s)}$	$\ln K = -25.71 + 47740 / T$
$1/2 \text{As}_2(\text{g}) + 1/2 \text{H}_2(\text{g}) = \text{AsH(g)}$	$\ln K = 1.908 - 17630 / T$
$1/2 \text{P}_2(\text{g}) + 1/2 \text{H}_2(\text{g}) = \text{PH(g)}$	$\ln K = 2.652 - 19760 / T$

0.604 and -0.658. The equilibrium constants used in the calculation are listed in Table 1.⁷⁻¹¹) We can estimate $c_{\text{eff}}(t_c)$ by fitting the calculated relationship to the measured relationships between $(P/As)_{\text{solid,center}}$ and c_0 . Estimated values of $c_{\text{eff}}(t_c)$ are $0.74c_0$ for $\text{AsH}_3 + \text{tBPH}_2$, $0.32c_0$ for $\text{tBAsH}_2 + \text{tBPH}_2$, and $0.25c_0$ for $\text{AsH}_3 + \text{PH}_3$.

Since $c_{\text{eff}}(t_c)$ is closest to c_0 with $\text{AsH}_3 + \text{tBPH}_2$, composition uniformity should be improved. The reason $c_{\text{eff}}(t_c)$ is closest to c_0 with this combination is that the decomposition rates of AsH_3 and tBPH_2 are nearly the same. However, with $\text{tBAsH}_2 + \text{tBPH}_2$, $c_{\text{eff}}(t_c)$ is not close to c_0 . The reason is probably due to the incomplete decomposition of the source gases, especially tBPH_2 . It is considered that the decomposition rate of tBPH_2 is not as fast as we expected.

Figure 5 shows the distributions of the PL peak wavelength. The change of PL peak wavelength is 9 nm with $\text{AsH}_3 + \text{tBPH}_2$, 82 nm with $\text{tBAsH}_2 + \text{tBPH}_2$, and 66 nm with $\text{AsH}_3 + \text{PH}_3$. Uniformity is excellent with $\text{AsH}_3 + \text{tBPH}_2$. The composition inhomogeneity is reduced to 1/6 that grown from $\text{AsH}_3 + \text{PH}_3$.

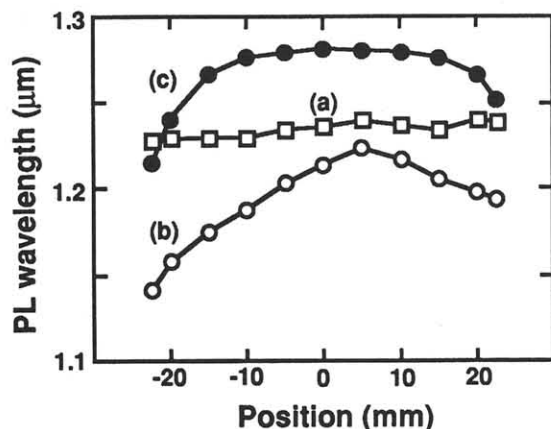


Fig. 5 Distributions of the PL peak wavelength on a 2-inch wafer; (a) $\text{AsH}_3 + \text{tBPH}_2$, (b) $\text{tBAsH}_2 + \text{tBPH}_2$, (c) $\text{AsH}_3 + \text{PH}_3$.

Summary

We investigated the origin of the InGaAsP composition inhomogeneity and found that there was a large inhomogeneity only in group V composition due to the difference in decomposition rates between AsH_3 and PH_3 . We used MOVPE growth with various combinations of group V source gases including tBAsH_2 and tBPH_2 which have faster decomposition rates than AsH_3 or PH_3 . We found that the most uniform composition distribution could be obtained using the combination of AsH_3 and tBPH_2 , which have nearly the same decomposition rate. The composition inhomogeneity could be reduced to 1/6 that using AsH_3 and PH_3 .

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