The incorporation behavior of As and P in GaInAsP ($\lambda \approx 1.3 \mu\text{m}$) on InP grown by gas source molecular beam epitaxy

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Abstract

A simple model has been successfully developed to explain the incorporation behavior of As and P in growing $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ quaternary alloys on (100) InP using gas source molecular beam epitaxy (GSMBE). In this model there is only one incorporation parameter, i.e. the As to P incorporation ratio, which was determined by fitting the calculated solid composition ratio of P/As to the experimental results. It is found that when x is fixed at 0.263 the incorporation ratio is about 16 at a growth temperature of 490°C and slightly increases when the growth temperature decreases. Additionally, the RHEED pattern observations and the growth temperature dependence are also discussed. This model can be expanded to the whole range of compositions by adjusting only one fitting parameter, k , and can provide a very useful guide for the epitaxial growth of $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ quaternary alloys on InP substrate by GSMBE.

1. Introduction

$\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ quaternary alloys on InP are very important for optoelectronic device applications, and have been investigated by molecular beam epitaxy (MBE) techniques, including solid source, MO source, and gas source machines [1–7]. The use of gas sources can eliminate the frequent replenishment of the toxic group V elements. Moreover, precise control and quick change of the group V fluxes can readily be achieved by tuning the gas flow rate controller. However, because of the complicated sticking behavior of As and P, understanding the incorporation behavior of these two group V elements is a necessary step to precise composition control. Several

groups have studied the incorporation behavior of the group V atoms in (Ga)InAsP alloys [8–16]. Although there exist some discrepancies between these results, the basic agreement is that As is more effective in adsorption than P. Several models [17–20] have been proposed to explain this complicated phenomenon. Most considered the chemical reactions on the growing surface, and thus introduced many reaction parameters such as the activation energies for chemisorption and desorption, thermo-equilibrium constants, etc. These parameters should be determined either by other experiments or by curve fitting to the experimental results, mathematically.

In this report, a series of $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ quaternary alloys ($\lambda \approx 1.3 \mu\text{m}$) were grown on (100) InP by gas source MBE (GSMBE) with different gas flow rate ratios ($\text{PH}_3/(\text{PH}_3+\text{AsH}_3)$). A simple growth

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model was proposed to describe the group V incorporation behavior quantitatively. Without the complicated chemical reaction parameters, the incorporation probability is controlled by the effective concentrations of the group V atoms on the migration state. Only two parameters, the As to P incorporation ratio and the conversion factor between the gas flux rate and the gas flow rate, exist in this model. Furthermore, this model can be expanded to the whole range of alloy compositions by adjusting the incorporation ratio only. RHEED pattern observations for the different surface reconstructions and the growth temperature dependence of the incorporation ratio are also discussed.

2. Growth model

In MBE growth, the sticking coefficient of group III atoms is approximately unity if the growth temperature is less than the desorption temperature. Consequently, the growth rate is always controlled by the group III flux, and the solid compositions can be more easily controlled in III–III–V systems such as $\text{Ga}_x\text{In}_{1-x}\text{As}$ and $\text{Ga}_x\text{In}_{1-x}\text{P}$. However, this is not the case for III–III–V–V systems because of the smaller and different sticking coefficient of group V atoms. Therefore, the composition control of $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ is more complicated and difficult. Here, we propose a simple growth model to interpret the incorporation behavior of As and P in the GSMBE growth of $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ alloys on InP substrate. Considering the group V monolayer, the incident group V atoms can adsorb on the growing surface to form a migration state. Then, these group V atoms can either incorporate into the crystal or desorb from the growing surface. Consider the chemical reactions on the growing surface

where ms represents the atoms on the migration state and III is a group III atom on the migration state, either

In or Ga. The reaction rates for the chemical reactions, Eqs. (3) and (4), are

$$e_{\text{As}} = k_{\text{As}}N_{\text{As}}N_3, \quad (5)$$

$$e_{\text{P}} = k_{\text{P}}N_{\text{P}}N_3, \quad (6)$$

where N_3 , N_{As} and N_{P} are the concentrations of group III, As and P atoms on the migration state, respectively, and k_i is the rate constant of gas source i on the migration state; $i = \text{As}$ or P .

In addition, mathematically, the rate equations of the atoms on the migration state can be expressed as:

$$\frac{\partial N_{\text{As}}}{\partial t} = \frac{f_{\text{As}}}{m} - e_{\text{As}} - d_{\text{As}}, \quad (7)$$

$$\frac{\partial N_{\text{P}}}{\partial t} = \frac{f_{\text{P}}}{m} - e_{\text{P}} - d_{\text{P}}, \quad (8)$$

$$\frac{\partial N_3}{\partial t} = f_3 - e_{\text{As}} - e_{\text{P}}, \quad (9)$$

where f_i is the flow rate of gas source i , $i = \text{As}$ or P ; d_i is the desorption rate of gas source i , $i = \text{As}$ or P , on the migration state; f_3 is the total flux rate of group III atoms; and m is the flux rate to flow rate conversion factor. The units of the flux rates, desorption rates and the flow rates are ML/s, ML/s and SCCM, respectively. The conversion factor is a function of the cracking efficiency and the flux angular density distribution of the gas cell. In our system, PH_3 and AsH_3 share a gas cell. Both the cracking efficiencies measured using a residual gas analyzer are very close to 0.99. Therefore, we believe that the conversion factors of AsH_3 and PH_3 should be very close, and only one m is used in the model.

In the group-V-stabilized regions ($V/\text{III} > 1$), under steady-state conditions the rate equations are equal to zero. From Eqs. (9), (5) and (6), we obtain

$$N_3 = \frac{f_3}{k_{\text{As}}N_{\text{As}} + k_{\text{P}}N_{\text{P}}}, \quad (10)$$

therefore the reaction rate of e_i can be formulated as:

$$e_{\text{As}} = \frac{k_{\text{As}}N_{\text{As}}}{k_{\text{As}}N_{\text{As}} + k_{\text{P}}N_{\text{P}}} \times f_3, \quad (11)$$

$$e_{\text{P}} = \frac{k_{\text{P}}N_{\text{P}}}{k_{\text{As}}N_{\text{As}} + k_{\text{P}}N_{\text{P}}} \times f_3, \quad (12)$$

The desorption rate can be written as the migration state density divided by the lifetime:

$$d_{As} = \frac{N_{As}}{\tau_{As}}, \quad (13)$$

$$d_P = \frac{N_P}{\tau_P}, \quad (14)$$

where τ_i is the lifetime of gas source i . Substituting Eqs. (11), (12), (13) and (14) into Eqs. (7) and (8), we obtain

$$\frac{\partial N_{As}}{\partial t} = \frac{f_{As}}{m} - \frac{k_{As}N_{As}}{k_{As}N_{As} + k_P N_P} \times f_3 - \frac{N_{As}}{\tau_{As}}, \quad (15)$$

$$\frac{\partial N_P}{\partial t} = \frac{f_P}{m} - \frac{k_P N_P}{k_{As}N_{As} + k_P N_P} \times f_3 - \frac{N_P}{\tau_P}. \quad (16)$$

If we assume $k_{As}/k_P = k_1$ and $\tau_{As}/\tau_P = k_2$, and let $k = k_1 \times k_2$, under steady-state conditions, Eqs. (15) and (16) can be simplified as:

$$\frac{f_{As}}{m} - \frac{k d_{As}}{k d_{As} + d_P} \times f_3 - d_{As} = 0, \quad (17)$$

$$\frac{f_P}{m} - \frac{d_P}{k d_{As} + d_P} \times f_3 - d_P = 0. \quad (18)$$

Combining Eqs. (17) and (18), the solid composition ratio of P/As in $Ga_xIn_{1-x}As_yP_{1-y}$ can be solved analytically:

$$(1-y)/y = 2f_P \left[k f_{As} - f_P - (k-1)f_3 m \right. \\ \left. + \sqrt{(k f_{As} - f_P - (k-1)f_3 m)^2 + 4k f_{As} f_P} \right]^{-1}. \quad (19)$$

It should be emphasized that there are only two parameters to be fitted: m and k . Once the m and k factors are determined, the solid compositions of $Ga_xIn_{1-x}As_yP_{1-y}$ can be accurately controlled by adjusting the gas flow rate. Furthermore, this model can be extended to the whole range of $Ga_xIn_{1-x}As_yP_{1-y}$ quaternary alloys on InP substrate by only changing the value of k . Remember that the factor k describes the influences of the lifetime and the chemical rate constants of As to P. Therefore, k can be a good indicator for the incorporation ability of As to P. Moreover, because of the different activation energies of the group V atoms for desorption from InAs, GaAs, InP and GaP surfaces [21], it is expected that the value of k will depend on the group III compositions in $Ga_xIn_{1-x}As_yP_{1-y}$ as well as the growth temperature.

3. Experiments

$Ga_xIn_{1-x}As_yP_{1-y}$ quaternary alloys on (100) InP for wavelengths near $1.3 \mu m$ were prepared by VG V80H gas source molecular beam epitaxy (GSMBE). High-purity PH_3 and AsH_3 was introduced through a high-temperature cracking cell maintained at $1000^\circ C$. By using a Baratron capacitance manometer, the gas flow rate can be controlled accurately to within 0.01 SCCM. As for the group III flux, a conventional beam equivalent pressure (BEP) ratio method was used to determine the In and Ga flux ratio. In order to study the gas incorporation behavior, the In and Ga flux ratio was fixed and a series of gas flow rate ratios ($PH_3/(PH_3 + AsH_3)$) were used to grow the $Ga_xIn_{1-x}As_yP_{1-y}$ layers on (100) InP. The growth temperature, monitored by an IRCON v-series pyrometer, was about $490^\circ C$. The growth rate was kept at 0.98 ML/s, measured by cross-section scanning electron microscopy (SEM). After growth, electron probe micro-analysis (EPMA) and single crystal X-ray (400) plane diffraction (XRD) were adopted for the determination of the solid compositions of the $Ga_xIn_{1-x}As_yP_{1-y}$ layers.

To double check the composition of the standard sample, a SEM structure was designed. As shown in Fig. 1, it consists of $Ga_xIn_{1-x}As_yP_{1-y}$, InP and $Ga_xIn_{1-x}As_yP_{1-y}$ layers. During growth, the In and Ga fluxes were fixed, and the growth times for these three layers were 60, 60 and 15 min, respectively. The In mole fraction in $Ga_xIn_{1-x}As_yP_{1-y}$ can be calculated from the thickness ratio:

$$1-x = \frac{d_1 a_q}{d_2 a_{InP}}, \quad (20)$$

where d_1 and d_2 represent the thickness of InP and $Ga_xIn_{1-x}As_yP_{1-y}$, respectively; a_q is the lattice constant of $Ga_xIn_{1-x}As_yP_{1-y}$ obtained by X-ray measurement; and a_{InP} is the lattice constant of InP. According to Vegard's law, the lattice constant of $Ga_xIn_{1-x}As_yP_{1-y}$ layers can be expressed by

$$a = y(0.0124x + 0.1896) - 0.4175x + 5.8687. \quad (21)$$

Therefore, the group V composition can be extracted from the lattice mismatch data. The result shows that $x = 0.268$ and $y = 0.58$, which is consistent with the room PL measurement results.

Fig. 1. SEM cross section of the standard sample. The thicknesses of the InP and GaInAsP layers are d_1 and d_2 , respectively.

4. Results and discussion

In this study, four groups of $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ layers for wavelength near $1.3\ \mu\text{m}$ were grown by changing the gas flow ratios. In Fig. 2, the solid composition P/As ratio, measured by EPMA and XRD, is plotted

Fig. 2. The solid composition ratio of P/As as a function of the PH_3 flow rate at two different AsH_3 flow rates. Open and closed symbols correspond to AsH_3 flow rates of 0.43 and 0.35 SCCM, respectively. Square and circle symbols represent the results from EPMA and X-ray diffraction measurements, respectively.

as a function of the PH_3 flow rate at two different AsH_3 flow rates. These two methods show good agreement with each other. As expected, the solid composition ratio P/As in $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ increases as PH_3 flow rate increases, and the larger the AsH_3 flow rate, the smaller the solid composition ratio, P/As. Similar results can be seen in Fig. 3. This figure shows the solid

Fig. 3. The solid composition ratio of As/P in $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ as a function of the AsH_3 flow rate at two different PH_3 flow rates. The PH_3 flow rates were 1.13 and 1.87 SCCM for closed and open symbols, respectively.

composition ratio of As/P in $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ as a function of AsH_3 flow rate at two different PH_3 flow rates. As can be seen, there exists a larger discrepancy at the largest As/P point for both PH_3 flow rates. The difference between these two characterization methods may be due to the partial relaxation of the strained $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ layers, which would result in an error in the calculation of the free lattice constant.

As for the model calculations, the unknown parameters, k and m , in Eq. (19) are determined by fitting the calculated composition ratios to the experimental results. As can be seen, the calculation curves in Figs. 2 and 3 show excellent agreement with the experimental results. The two fitting parameters m and k are 0.496 and 16, respectively. This means that, in this GSMBE system, it requires a 0.496 SCCM gas flow rate to support a 5.8×10^{14} atoms/cm²·s flux, corresponding to a 1 ML/s growth rate on a (100) InP substrate. Additionally, the k value of 16 implies that the incorporation ability of As atoms on the migration state is 16 times larger than that of P atoms.

Fig. 4 shows the RHEED pattern observations along the [110] azimuth for the epitaxial growth of $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ at different AsH_3 and PH_3 flow rates. The growth rate and substrate temperature are 490°C and 0.98 ML/s, respectively. As for the

growth on (100) GaAs, the surface reconstruction of $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ changes from 2×4 for the group-V-stabilized condition to 4×2 for the group-III-stabilized condition. In this figure, open and closed circles represent the upper and lower flow rate limits for the 4×2 (group-III-stabilized) and 2×4 (group-V-stabilized) conditions, respectively. Between these two surface RHEED patterns, there is a transition region. As can be seen, the x (AsH_3) and y (PH_3) intersections of the 4×2 line are 0.52 and 0.97 SCCM, respectively. Remember that, in the model calculation, the best fitting result for m is 0.496 SCCM, which means that a 0.496 SCCM hydride flow rate can support a 1 ML/s flux on the (100) InP growing surface. However, the RHEED pattern observations show that the lowest flow rate to remain in the group-V-stabilized condition is a little bit larger for AsH_3 and almost two times larger for PH_3 . It is believed that there exists a critical surface density, N_{3c} , for the group III atoms on the migration state, beyond which the RHEED pattern changes from the 2×4 (group-V-stabilized) to the 4×2 (group-III-stabilized) region. Therefore, from Eq. (10), we have

$$\frac{f_3}{k_{\text{As}}N_{\text{As}} + k_{\text{P}}N_{\text{P}}} = N_{3c}. \quad (22)$$

After simplification, this equation can be formulated as:

$$kd_{\text{As}} + d_{\text{P}} = f_3/r, \quad (23)$$

where $r = N_{3c}k_{\text{P}}\tau_{\text{P}}$. Substituting Eq. (23) into Eqs. (17) and (18), we have

$$d_{\text{As}} = \frac{f_{\text{As}}}{m(1 + kr)}, \quad (24)$$

$$d_{\text{P}} = \frac{f_{\text{P}}}{m(1 + r)}. \quad (25)$$

Again, substituting Eqs. (24) and (25) into Eq. (23), the RHEED pattern change conditions can be solved as:

$$\frac{f_{\text{As}}}{f_3m((1 + kr)/kr)} + \frac{f_{\text{P}}}{f_3m((1 + r)/r)} = 1. \quad (26)$$

The result, Eq. (26), which is a straight line with different x and y intersections, is consistent with the experimental data. The difference between the intersections is due to k , the incorporation ratio. By fitting

Fig. 4. RHEED pattern observations for the growth of $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ with different AsH_3 and PH_3 flow rates. The growth temperature and growth rate were 490°C and 0.98 ML/s, respectively.

this line to the experimental RHEED results with the same fitting parameters, k and m , as mentioned above, the r value is found to be about 1. Notice that

$$r = N_{3c} k_p \tau_p = \frac{k_p N_{3c} N_p}{N_p / \tau_p} = \frac{e_p}{d_p}. \quad (27)$$

This implies that the reaction rate and the desorption rate of P atoms are very close on the 4×2 boundary. Therefore, there needs to be a two times larger PH_3 flow rate to maintain the growth in the group-V-stabilized regions. The above equation can be further modified as follows

$$\begin{aligned} r = N_{3c} k_p \tau_p &= N_{3c} (k_{As} / k_1) (\tau_{As} / k_2) \\ &= \frac{1}{k} \frac{k_{As} N_{3c} N_{As}}{N_{As} / \tau_{As}} = \frac{1}{k} \frac{e_{As}}{d_{As}}. \end{aligned} \quad (28)$$

Since k is about 16, this result indicates that, for As atom, the reaction rate is about 16 times larger than the desorption rate. Therefore, the lowest flow rate to remain in the group-V-stabilized region is only slightly larger than $f_3 m$, the flow rate that allows the fluxes of group III and group V be equal.

In order to investigate the growth temperature dependence of the k value, three samples were grown at 400, 490 and 530°C, respectively, with the same group III flux and group V flow rate. Fig. 5 shows the k factor versus the reciprocal growth temperature. As

Fig. 5. The k factor as a function of the reciprocal growth temperature. The activation energy of k is 61 meV.

we can see, the activation energy of the k factor is only 61 meV. This activation energy comes from the different temperature dependence of the lifetime and chemical reaction constant for As and P. The small activation energy means that the relative incorporation behavior of As to P is almost insensitive to the growth temperature in the range from 400 to 530°C. Because group-V-stabilized growth conditions were used, an abrupt phosphorus composition change in $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ ($\lambda \approx 1.3 \mu\text{m}$) was not observed, which may be due to the different incorporation behaviors of As and P in the group-III-rich conditions [8,10].

Finally, Fig. 6 shows the mole fraction of P in $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ as a function of the gas flow rate ratio ($\text{PH}_3/(\text{PH}_3 + \text{AsH}_3)$). As we can see, it shows good agreement with the experimental results. The P composition in $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ depends on the gas flow rate ratio and the V/III flux ratio, especially in the high gas flow rate ratio regions. This calculation and experimental results also agree with the thermodynamic calculations proposed by Seki and Koukitsu [19]. It should be emphasized that the constraint of a lattice matched to InP in Ref. [19] is removed in our calculations. This implies that the lattice mismatch has only a small influence on the incorporation behavior of As and P on (100) InP. Similar results

Fig. 6. The mole fraction of P in $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ as a function of the gas flow rate ratio ($\text{PH}_3/(\text{PH}_3 + \text{AsH}_3)$). Solid and broken lines represent calculations with V/III ratios of 3 and 5, respectively, using the model.

have been reported using the chemical beam epitaxy (CBE) technique [13].

5. Conclusion

A simple model has been proposed to explain the incorporation behavior of As and P in $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ quaternary alloys on InP for wavelength near $1.3\ \mu\text{m}$. According to this model, it was found that the incorporation ability of As is about 16 times larger than that of P at a growth temperature of 490°C . Additionally, the incorporation behavior of As and P on (100) InP mainly depends on the gas flow rate ratio as well as the V/III flux ratio, especially in the high gas flow rate ratio regions; the influence of growth temperature and lattice mismatch is negligible in the temperature range from 400 to 530°C . Furthermore, this model can be expanded to the whole range of compositions by adjusting only one fitting parameters, k , and can provide a very useful guide for the epitaxial growth of $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ quaternary alloys on InP substrate by GSMBE.

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