The Incorporation Behavior of As and P in GaInAsP($\lambda \approx 1.3\mu m$) on InP Grown by Gas Source Molecular Beam Epitaxy

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Introduction

$Ga_xIn_{1-x}As_yP_{1-y}$ quaternary alloys on InP are very important for optoelectronic device applications, and have been investigated by molecular beam epitaxy (MBE) techniques (1-7). Because of the complicated sticking behavior of As and P, to understand the incorporation behavior of these two group V elements is a necessary step to precise composition control. Several groups (8-16) have studied this complicated phenomenon. Most of them 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 $Ga_xIn_{1-x}As_yP_{1-y}$ quaternary alloys ($\lambda \approx 1.3\mu m$) on (100) InP were grown by gas source MBE (GSMBE) with different gas flow rate ratios ($PH_3/(PH_3 + AsH_3)$). A simple growth 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, 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. It is found that the incorporation ratio strongly depends on the Ga-compositions in $Ga_xIn_{1-x}As_yP_{1-y}$ alloys.

Growth Model

Figure 1 is the schematic representation of the growth model for the interaction of group III atoms and group V atoms on the growing surface. Consider the group V monolayer, the incident group V atoms can adsorb on the growing surface to form a migration state. And then, these group V atoms can either incorporate into the crystal or desorb away from the growing surface. Consider the chemical reactions on the growing surface:

where ms represents the atoms on the migration state; III is group III atom on the migration state, either In or Ga. The reaction rates for the chemical reactions, Eq.(3) and (4), are:

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

$$e_P = k_P N_P N_3 \quad (6)$$

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 reaction constant of gas source i on the migration state; $i = As$, or P .

Growth Model

Fig. 1 The schematic representation of the growth model for the interaction of group III atoms and group V atoms on the growing surface.

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

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

$$\frac{\partial N_P}{\partial t} = \frac{f_P}{m} - e_P - d_P \quad (8)$$

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

where f_i is the flow rate of gas source i , $i = As$ or P ; d_i is the desorption rate of gas source i , $i = As$ 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/sec, ML/sec and SCCM, respectively.

Under steady state conditions, the rate equations are equal to zero. We obtain

$$N_3 = \frac{f_3}{k_{As}N_{As} + k_P N_P} \quad (10)$$

$$e_{As} = \frac{k_{As}N_{As}}{k_{As}N_{As} + k_P N_P} \times f_3 \quad (11)$$

$$e_P = \frac{k_P N_P}{k_{As}N_{As} + k_P N_P} \times f_3 \quad (12)$$

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

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

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

where τ_i is the life time of gas source i . Substituting Eqs.(11), (12), (13) and (14) to 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 Equations (17) and (18), the solid composition ratio of P/As in $Ga_xIn_{1-x}As_yP_{1-y}$ can be solved, analytically:

$$\frac{1-y}{y} = \frac{2f_P}{kf_{As} - f_P - (k-1)f_3m + \sqrt{4(kf_{As} - f_P - (k-1)f_3m)^2 + 16kf_{As}f_P}} \quad (19)$$

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 $GaInAsP$ 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 . Remind that k factor describe the influences of the life time and the chemical reaction constant of As to P . So, k can be a good indicator for the incorporation ability of As to P . Moreover, because of the different activation energy for the group V atoms to desorb from $InAs$, $GaAs$, InP , and GaP surfaces (11), it is expected that the value of k will depend on the group III compositions in $Ga_xIn_{1-x}As_yP_{1-y}$.

Experiment

The $Ga_xIn_{1-x}As_yP_{1-y}$ quaternary alloys on (100) InP for the wavelength near $1.3\mu m$ were prepared by VG V80H gas source molecular beam epitaxy (GSMBE) machine equipped with a 400l/s diffusion pump. High purity AsH_3 and PH_3 , controlled by the pressure set-point of a Baratron capacitance manometer, was introduced through a high temperature cracking cell kept at $1000^\circ C$. As for the group III flux, a conventional beam equivalent pressure (BEP) ratio method was used to determine the In and Ga flux ratio. The growth rate was kept at $0.98 ML/sec$, which was measured by cross-section scanning electron microscopy (SEM). After growth, room temperature photoluminescence (PL), electron probe micro-analysis (EPMA) and single crystal x-ray (400) plane diffraction (XRD) were adopted for the determination of the solid compositions of these $Ga_xIn_{1-x}As_yP_{1-y}$ layers.

Results and Discussions

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 rate of 0.43 and 0.35 SCCM, respectively. Square and circle symbols represent the results from EPMA and x-ray diffraction measurement, respectively.

Figure 2 shows the solid composition ratio of P/As as a function of the PH_3 flow rate at two different AsH_3 flow rates. Square and circle symbols represent the results obtained by EPMA and x-ray diffraction measurement, respectively. These two methods shows a good agreement with each other. As expected, the solid composition ratio P/As in $Ga_xIn_{1-x}As_yP_{1-y}$ 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 figure 3.

Fig. 3 The solid composition ratio of As/P in $GaInAsP$ as a function of AsH_3 flow rate at two different PH_3 flow rate. The PH_3 flow rates were 1.13 and 1.87 SCCM for closed and open symbols, respectively.

As for the model calculations, the unknown parameters, k and m , in Eq.(19) are determined by fitting the calculation composition ratios to the experimental results. It can be seen, the calculation curves in figure 2 and figure 3 show an excellent agreement with the experimental results. Fitting parameters m and k are 0.496 and 16, respectively. This means that in this GSMBE system, there needs 0.496 SCCM gas flow rate to support 1ML/sec growth rate on (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.

Figure 4 shows the mole fraction of P in $Ga_xIn_{1-x}As_yP_{1-y}$ as a function of the gas flow rate ratio ($PH_3/(PH_3 + AsH_3)$). As we can see, it shows a good agreement with the experimental results. The P composition in $Ga_xIn_{1-x}As_yP_{1-y}$ depends on the gas flow rate ratio and V/III flux ratio, especially in the high gas flow rate ratio regions. It should be emphasized that the constraint of lattice matched to InP in ref. (16) is removed in our calculations. This implies that the lattice mismatch has only a little influence on the incorporation behavior of As and P on (100) InP.

Similar results has been reported by chemical beam epitaxy (CBE) technique (13).

Fig. 4 The mole fraction of P in $Ga_xIn_{1-x}As_yP_{1-y}$ as a function of the gas flow rate ratio ($PH_3/(PH_3 + AsH_3)$). Solid and broken lines represent the calculations with V/III ratios of 3 and 5, respectively, by using the model.

Fig. 5 The k factor as a function of group III compositions in $Ga_xIn_{1-x}As_yP_{1-y}$ at a growth temperature of 490°C.

Because of the different bonding energies of $InAs$, InP , $GaAs$, and GaP , it is expected that the k factor in this growth model will depend on the group III compositions. Figure 5 shows the Ga composition dependence of k factor in $Ga_xIn_{1-x}As_yP_{1-y}$ at a growth temperature of 490°C. As can be seen, the k value strongly depends on the Ga compositions. Using the

linearly approximative line, we can see that the k value can be as large as 33.5 in the near InP regions. This explains why the fast replacement of phosphorus by arsenic occurs at the InP surface when PH_3 is switched off and AsH_3 is switched on, and thus the $InAs_xP_{1-x}$ quantum well can be formed (17). B. W. Liang et al. (11) also observed that for the In -contamination compounds, phosphorus desorption rate constant is always much higher than that of arsenic. In addition, this result also implies that the mixed-group-V composition control in the low Ga composition regions becomes more and more difficult. A small AsH_3 flow rate variation would result in a large As composition change.

Conclusions

A growth model has been proposed to explain the incorporation behavior of As and P in $GaInAsP$ quaternary alloys on (100) InP . According to this model, it is found that the incorporation ability indicator, k , depends on the Ga -compositions in $Ga_xIn_{1-x}As_yP_{1-y}$ alloys. For the $\lambda \approx 1.3 \mu m$ materials the k value is about 16 at the growth temperature of $490^\circ C$. Additionally, the incorporation behavior of As and P on (100) InP mainly depends on the gas flow rate ratio as well as V/III flux ratio, especially in the high gas flow rate ratio regions; the influence of lattice mismatch is negligible at the growth temperature of $490^\circ C$. This model can provide a very useful guide for the epitaxial growth of $Ga_xIn_{1-x}As_yP_{1-y}$ quaternary alloys on InP substrate by GSMBE.

Acknowledgement

This study was supported by the National Science Council of the Republic of China under contract No. NSC-84-2215-E002-008, CSIST under contract No. CS84-0210-D002-028, and the Telecommunication laboratory of the Republic of China under contract No. TL-NSC-83-5104.

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