AN UNIFIED GSMBE GROWTH MODEL FOR GaInAsP ON InP AND GaAs

Jin-Shung Liu, Tsuen-Lin Lee, and Hao-Hsiung Lin
Room 419, Department of Electrical Engineering,
National Taiwan University,
Taipei, Taiwan, R. O. C.

Abstract

A GaInAsP GSMBE growth model considering an intermediate state is presented. This model is very simple and needs only two fitting parameters, k_{In} and k_{Ga}, which are determined from the experimental results of $In_{1-x}Ga_xAs_yP_{1-y}$ on InP ($0 < x < 0.47$ and $0 < y < 1$) and $In_{1-x}Ga_xAs_yP_{1-y}$ on GaAs ($0.51 < x < 1$ and $0 < y < 1$). At a growth temperature of 480°C, they are 27.5 and 2.75, respectively. Their temperature dependancy, i. e., activation energies are -27.5 and -457 meV, respectively. The average lattice mismatch difference between the theoretical and experimental results of grown epilayers is less than 7×10^{-4}.

I. Introduction

On the gas source molecular beam epitaxial growth of the mixed group V compound semiconductor $In_{1-x}Ga_xAs_yP_{1-y}$, to control the composition y is crucial. In previous studies[1-10], it is found that the AsH_3 to PH_3 flow rate ratio can not solely decide the composition y. V to III flux ratio, composition x, substrate temperature, As_2 and P_2 fluxes all play important roles on the composition control of the group V elements. A simple but efficient method is needed for growing this important optoelectronic material. In this study, we propose a simple unified GSMBE growth model for this quarternary alloy. This model considers an intermediate state for the atoms. In this state, group V elements may be either desorbed or incorporated into the epilayer, and the group III atoms can only be incorporated. Rate equations considering the incident flux rates, desorption rates and incorporation rates of these elements are solved to determine their intermediate state densities and the solid compositon of y. This model is very simple and needs only two fitting parameters, k_{In} and k_{Ga}, whose physical meanings are the product of As to P desorption time constant ratio and incorporation rate constant ratio for $InAs_yP_{1-y}$ and $GaAs_yP_{1-y}$, respectively. A series of $In_{1-x}Ga_xAs_yP_{1-y}$ epilayers grown on InP with $0 < x < 0.47$ and $0 < y < 1$ and on GaAs with $0.51 < x < 1$ and $0 < y < 1$ were used to fit the parameters. The experimental and theoretical lattice mismatch of the grown epilayers are all within 2×10^{-3}. These good fitting results indicate that this model can cover the whole composition range of GaInAsP.

II. Growth Model

In this model, an intermediate state in which the incident group V atoms can be adsorbed is considered. These absorbed group V atoms can either incorporate into the crystal or desorb away from the growing surface. The rate equations of the group V atoms on the intermediate state can be expressed as follows:

$$\frac{\partial N_{As}}{\partial t} = f_{As} - e_{As} - d_{As} \quad (1)$$

$$\frac{\partial N_P}{\partial t} = f_P - e_P - d_P \quad (2)$$

where N_{As} and N_P are the As and P atom concentrations in the intermediate state, respectively, f_{As} and f_P are the incident flux rates of gas sources As and P, respectively, e_{As} and d_{As} and e_P and d_P are the incorporation and desorption rates of gas sources As and P, respectively. In our GSMBE, a conversion factor which has been determined to be 0.496[1,2] is used to convert the gas source flow rate to incident flux rate. The units of the flux rates, desorption rates and the flow rates are ML/sec, ML/sec and SCCM, respectively.

Next, consider the chemical reactions on the growing surface:

$$1/2As_{2(g)} = As_{(ms)} \quad (3)$$

$$1/2P_{2(g)} = P_{(ms)} \quad (4)$$

$$As_{(ms)} + In_{(ms)} = InAs_{(s)} \quad (5)$$

$$P_{(ms)} + In_{(ms)} = InP_{(s)} \quad (6)$$

$$As_{(ms)} + Ga_{(ms)} = GaAs_{(s)} \quad (7)$$

$$P_{(ms)} + Ga_{(ms)} = GaP_{(s)} \quad (8)$$

where ms represents the intermediate state. The As and P incorporation rates for the chemical reactions are:

$$e_{As} = k_{InAs} N_{As} N_{In} + k_{GaAs} N_{As} N_{Ga} \quad (9)$$

$$e_P = k_{InP} N_P N_{In} + k_{GaP} N_P N_{Ga} \quad (10)$$

where N_{In}, N_{Ga}, N_{As}, and N_P are the atom concentrations of In, Ga , As, and P atoms on the intermediate state, respectively, and k_{InAs}, k_{InP}, k_{GaAs}, k_{GaP}, are the rate constants for the reactions (5) to (8), respectively.

If the growth temperature is not too high and $V/III > 1$, the desorption of group III can be ignored. We can obtain the following equations:

$$f_{In} = (k_{InAs} N_{As} + k_{InP} N_P) \times N_{In} \quad (11)$$

$$f_{Ga} = (k_{GaAs} N_{As} + k_{GaP} N_P) \times N_{Ga} \quad (12)$$

where f_{In} and f_{Ga} are the incident flux rates of In and Ga beams, respectively. Therefore, the incorporation rate of As and P can be formulated as:

$$e_{As} = \frac{k_{InAs} N_{As}}{k_{InAs} N_{As} + k_{InP} N_P} \times f_{In} + \frac{k_{GaAs} N_{As}}{k_{GaAs} N_{As} + k_{GaP} N_P} \times f_{Ga} \quad (13)$$

$$e_P = \frac{k_{InP} N_P}{k_{InAs} N_{As} + k_{InP} N_P} \times f_{In} + \frac{k_{GaP} N_P}{k_{GaAs} N_{As} + k_{GaP} N_P} \times f_{Ga} \quad (14)$$

The desorption rate can be written as the intermediate state concentration divided by the desorption time constant:

$$d_{As} = \frac{N_{As}}{\tau_{As}} \quad (15)$$

$$d_P = \frac{N_P}{\tau_P} \quad (16)$$

where τ_{As} and τ_P are the desorption time constants of As and P, respectively.

Under steady state conditions, the rate equations (1) and (2) become:

$$f_{As} - \frac{k_{In} d_{As}}{k_{In} d_{As} + d_P} \times f_{In} - \frac{k_{Ga} d_{As}}{k_{Ga} d_{As} + d_P} \times f_{Ga} - d_{As} = 0 \quad (17)$$

$$f_P - \frac{d_P}{k_{In} d_{As} + d_P} \times f_{In} - \frac{d_P}{k_{Ga} d_{As} + d_P} \times f_{Ga} - d_P = 0 \quad (18)$$

with

$$k_{In} = \frac{k_{InAs}}{k_{InP}} \times \frac{\tau_{As}}{\tau_P} = k^0_{In} exp(-\Delta E_{In}/k_B T_s) \quad (19)$$

$$k_{Ga} = \frac{k_{GaAs}}{k_{GaP}} \times \frac{\tau_{As}}{\tau_P} = k^0_{Ga} exp(-\Delta E_{Ga}/k_B T_s) \quad (20)$$

where ΔE_{In} and k^0_{In} and ΔE_{Ga} and k^0_{Ga} are the activation energies and the zero temperature intercepts of k_{In} and k_{Ga}, respectively, T_s is the substrate temperature (K), and k_B is Boltzmann's constant.

The solid group V composition ratio of $Ga_x In_{1-x} As_y P_{1-y}$ is,

$$\frac{y}{1-y} = \frac{e_{As}}{e_P} = \frac{f_{As} - d_{As}}{f_P - d_P} \quad (21)$$

With f_{In}, f_{Ga}, f_{As}, f_P, k_{In} and k_{Ga} as input parameters, d_{As} and d_P can be solved numerically from Eq. (17) and (18). And then, the solid composition y can be determined from Eq. (21). Among the input parameters, the incorporation parameters, i. e., k_{In} and k_{Ga}, have to be determined experimentally.

III. Experiments

In order to determine the incorporation parameters, a series of $Ga_x In_{1-x} As_y P_{1-y}$ quaternary alloys on (100) InP and GaAs were grown by VG V80H GSMBE. High purity hydrides (PH_3 and AsH_3) and elemental group III sources (In and Ga) were used. By using the Baratron capacitance manometer, the gas flow rate can be controlled accurately within $0.01 SCCM$. After growth, room temperature pholoIuminescence (PL), electron probe micro-analysis (EPMA) ,single crystal x-ray (400) plane diffraction (XRD) and conventional beam equivalent pressure (BEP) ratio method were adopted for the determination of the solid composition of these $Ga_x In_{1-x} As_y P_{1-y}$ layers.

IV. Results and Discussion

Least square fitting method were used to extract the incorporation parameters. For samples grown at $480°C$, the best fitting values of k_{In} and k_{Ga} are 27.5 and 2.75. Based on these two parameters, the growth conditions of GaInAsP on InP and GaAs are calculated. Figure 1 shows the diagram of arsenic solid composition in $Ga_x In_{1-x} As_y P_{1-y}$ versus Ga composition for different AsH_3 flow rate ratio ($xfAs = AsH_3/(AsH_3 + PH_3)$) at $480°C$, while the group V to group III flux ratio is kept at 5. The two dashed lines represent the alloy compositions lattice matched to InP and $GaAs$, respectively. This calculation agrees with the thermodynamic analysis by H. Seki and A. Koukitu.[4]

To determine the temperature dependency of k_{In} and k_{Ga}, the compositions of quaterary GaInAsP layers grown at temperatures from 420 to $520°C$ were used to fit the four parameters of Eq. (19) and (20). The best fitting values of ΔE_{In} and k^0_{In} and ΔE_{Ga} and k^0_{Ga} are 18 and -27.5 meV and 0.0024 and -457 meV, respectively.

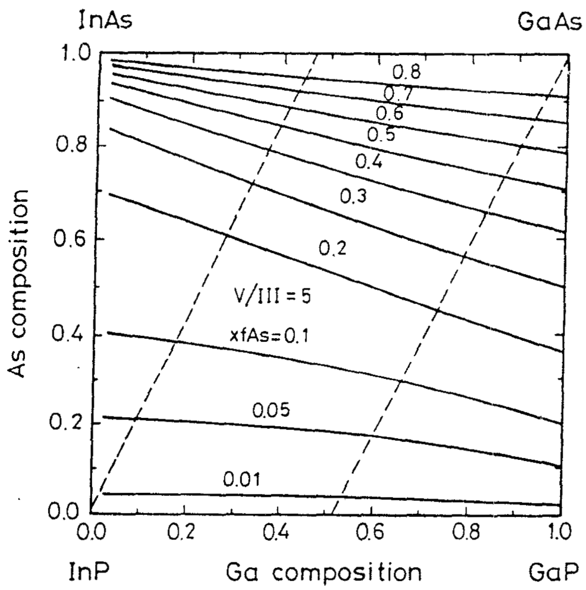

Fig. 1 The diagram of arsenic solid composition in $Ga_xIn_{1-x}As_yP_{1-y}$ versus Ga composition for different AsH_3 flow rate ratio ($xfAs = (AsH_3/AsH_3 + PH_3)$), while the group V to group III flux ratio is kept at 5 and the substrate temperature is $480°C$. The two dashed lines represent the alloy compositions lattice-matched to InP and $GaAs$, respectively.

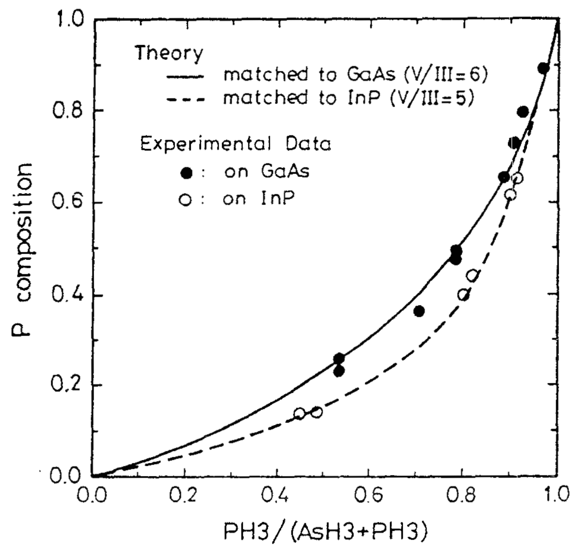

Fig. 2 The experimental results and theoretical curves for the phosphous solid composition of lattice-matched $Ga_xIn_{1-x}As_yP_{1-y}$ as a function of the PH_3 flow rate ratio. The growth temperature is 450°C. V/III ratios are 6 and 5 for those grown on GaAs and InP, respectively.

Fig. 2 shows the phosphous mole fraction (1-y) for lattice-matched $Ga_xIn_{1-x}As_yP_{1-y}$ as a function of the PH_3 flow rate ratio. Data of GaInAsP grown on GaAs and InP are both plotted in the figure. The GaInAsP on GaAs layers were grown at $\sim$ 450°C and with a V/III ratio of 6, while those GaInAsP on InP were grown at the same temperature but with a smaller V/III ratio of 5. As can be seen, both the curves are in excellent agreement with the experimental results.

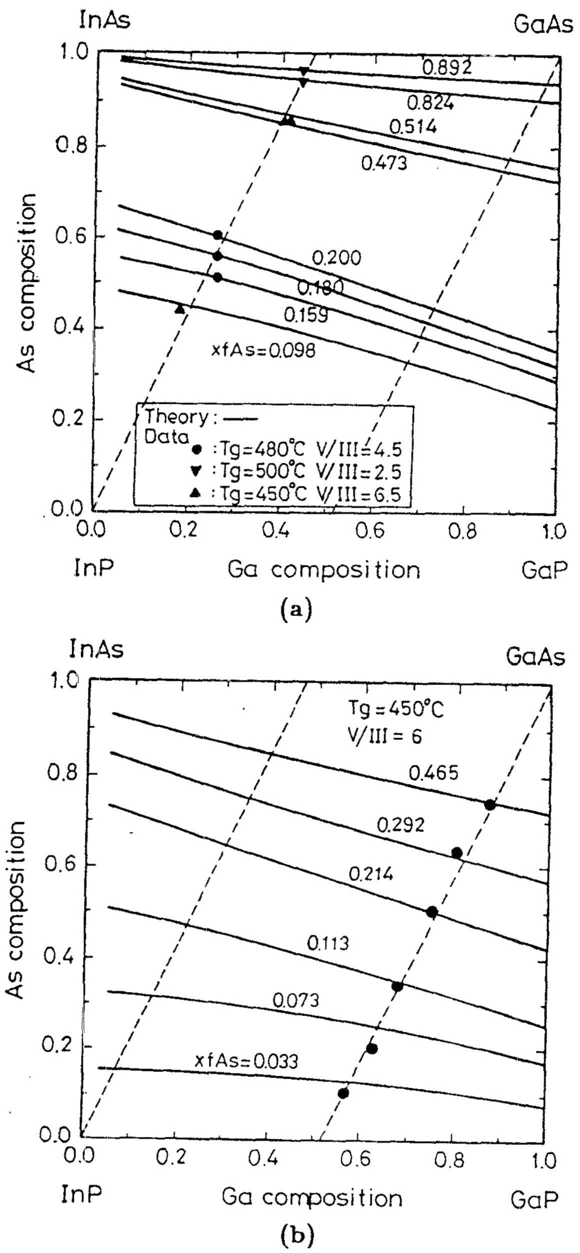

Fig. 3 The diagram of arsenic solid composition in $Ga_xIn_{1-x}As_yP_{1-y}$ versus Ga composition for different AsH_3 flow rate ratio ($xfAs = (AsH_3/AsH_3 + PH_3)$). The two dashed lines represent the alloy compositions lattice-matched to InP and $GaAs$, respectively. The experimental results and theoretical curves of GaInAsP on InP and GaInAsP on GaAs are shown in (a) and (b), respectively.

Fig. 3(a) and (b) show the diagrams of arsenic mole fraction in $Ga_xIn_{1-x}As_yP_{1-y}$ versus gallium mole fraction for different AsH_3 flow rate ratio ($xfAs = AsH_3/(AsH_3 + PH_3)$). The two dashed lines represent the alloy compositions lattice matched to InP and $GaAs$. The results of GaInAsP on InP and GaInAsP on GaAs with their theoretical curves are plotted in Fig. 3(a) and (b), respectively. The solid symbols represent the experimental results, while the solid curves represent the theoretical values calculated for the entire Ga composition range. It is clear that the experimental results of GaInAsP on GaAs and InP both agree with the theoretical results predicted by the model in spite of different growth conditions. The error on composition y is less than 0.03, which means a lattice mismatch smaller than 1×10^{-3}.

To give a overview on the precsion of our growth model, Fig. 4 shows the lattice mismatch difference between the experimental and theoretical results as a function of growth temperature. Solid and open circles represent the data of quaternary layers grown on GaAs and InP, respectively. From the figure, it can be seen that the error is all within 2×10^{-3} and most within 1×10^{-3} for both. This finding indicates that this model can be used to predict the growth conditions of GaInAsP on InP and GaAs.

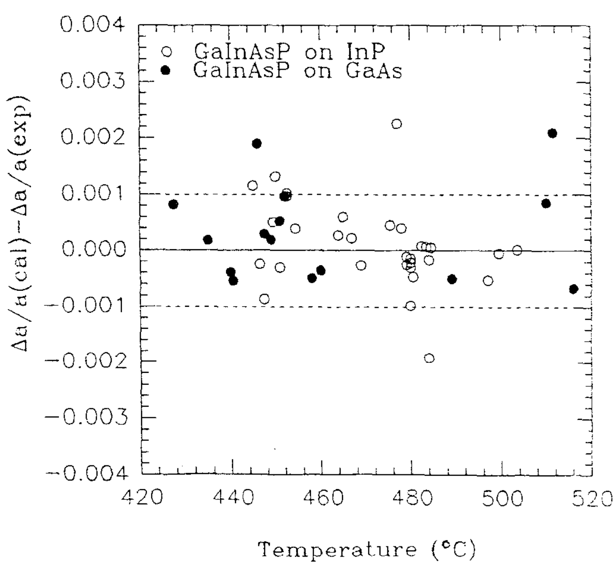

Fig. 4 The lattice mismatch difference between experimental and theoretical results as a function of growth temperature. Solid and open circles represent the data of quaternary layers grown on GaAs and InP, respectively.

IV. Conclusion

In this study, we propose an unified GSMBE growth model for GaInAsP on GaAs and InP. This model is very simple and needs only two fitting parameters, k_{In} and k_{Ga}, whose physical meanings are the product of As to P desorption time constant ratio and incorporation rate constant ratio for $InAs_yP_{1-y}$ and $GaAs_yP_{1-y}$, respectively. The parameters k_{In} and k_{Ga} are determined from the experimental results of $In_{1-x}Ga_xAs_yP_{1-y}$ on InP ($0 < x < 0.47$ and $0 < y < 1$) and $In_{1-x}Ga_xAs_yP_{1-y}$ on GaAs ($0.51 < x < 1$ and $0 < y < 1$). At a growth temperature of 480°C, they are 27.5 and 2.75, respectively. Their activation energies were also studied and are -27.5 and -457 meV, respectively. The average error of this model in terms of lattice mismatch is less than 7×10^{-4}.

Acknowledgment

This study was supported by the Telecommunication laboratory of the Ministry of Communication, Republic of China under contract number TL-85-5101.

References

1. T. L. Lee, J. S. Liu and H. H. Lin, Proc. of Seventh International Conference on Indium Phosphide and Related Materials, Sapporo, Hokkaido, Japan, 179 (1995).
2. T. L. Lee, J. S. Liu and H. H. Lin, J. Crystal Growth 155, 16 (1995).
3. T. L. Lee, J. S. Liu and H. H. Lin, J. Electron. Mater., (1995), in progress.
4. H. Seki and A. Koukitu, J. Crystal Growth 78, 342 (1986).
5. G. Zhang, M. Pessa, K.Hjelt, H. Collan and T. Tuomi, J. Crystal Growth 150, 607 (1995).
6. J. E. Cunningham, M. D. Williams, R. N. Pathak and W. Jan, J. Crystal Growth 150, 492 (1995).
7. J. N. Baillargeon, A. Y. Cho, F. A. Thiel, R. J. Fischer, P. J. Pearah and K. Y. Cheng, Appl. Phys. Lett. 65, 207 (1994).
8. C. W. Tu, B. W. Liang and H. Q. Hou, J. Crystal Growth 127, 251 (1993).
9. B. W. Liang and C. W. Tu, J. Appl. Phys. 74, 255 (1993).
10. H. Q. Hou and C. W. Tu, J. Crystal Growth 120, 167 (1992).