

Pyrolysis Effect of Group V Vapor Sources on the Composition Ranges for Metal-Organic Vapor Phase Epitaxy Growth of III-V Semiconductors

Changrong Li, Fuming Wang, and Weijing Zhang

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The pyrolysis effect of NH_3 and PH_3 vapor sources on the composition ranges necessary for growing single-phase semiconductors was studied with respect to the metal-organic vapor phase epitaxy (MOVPE) of GaN and $(\text{Ga}_{1-x}\text{In}_x)\text{P}$ semiconductors. The Ga-N-C-H system and the Ga-In-P-C-H system were thermodynamically analyzed respectively under the conditions of the equilibrium pyrolysis, the partial pyrolysis, and the non-pyrolysis of the vapor phase species, NH_3 and PH_3 . Both the complete equilibrium and the constraint equilibrium in these two systems were calculated with the aid of the specially designed database files and Thermo-Calc software. The experimental MOVPE data from the literature were compared with calculated results. The correspondence of the theoretical prediction with the experimental data indicates that the thermodynamic analysis for the MOVPE process of GaN and $(\text{Ga}_{1-x}\text{In}_x)\text{P}$ semiconductors needs to be considered in terms of the practical pyrolysis of NH_3 and PH_3 vapor sources. The approach of the complete thermodynamic equilibrium is applied only to some specific temperature region or certain epitaxy processes after typical pretreatment of vapor sources.

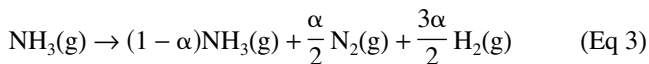
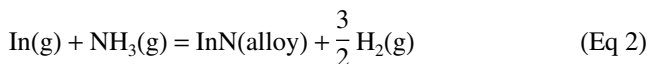
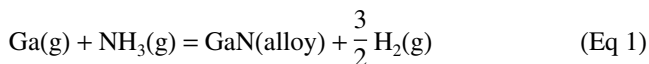
1. Introduction

For metal-organic vapor phase epitaxy (MOVPE) of III-V semiconductors, the requirements for group V sources are stringent.^[1] The liquid or solid sources with low vapor pressure are advantageous from a safety viewpoint. The precursor must be stable at room temperature without decomposition during storage or use. In addition, they must not participate in undesirable parasitic reactions with the group III source molecules, which deplete the source materials and contaminate the growth environment. However, a high room-temperature vapor pressure (>6666Pa, i.e., 50 torr) is preferable to avoid using extremely high carrier-gas flow rates. To be suitable for MOVPE growth of III-V semiconductors, the group V precursor must pyrolyze at the lowest desirable growth temperatures of 350–400 °C.

In practice, as for the group V sources for GaN and $(\text{Ga}_{1-x}\text{In}_x)\text{P}$ semiconductors, the pyrolysis of NH_3 and PH_3 depends on both the temperature and the environment of the related pyrolysis reactions. The decomposition rates of these group V sources affect the equilibrium thermodynamics and hence the compositional ranges and the deposition processes for the MOVPE growth of GaN and $(\text{Ga}_{1-x}\text{In}_x)\text{P}$ compound semiconductors.

Many contributions have been made toward understanding the thermodynamics of III-nitrides and III-phosphides.

The following chemical reactions occur at the substrate surface, and Eq 1 and 2 involve the mole fractions of the decomposed NH_3 (the α in Eq 3):



Koukitu et al. reported their chemical equilibrium model for predicting the growth condition of MOVPE and the composition of III-V nitrides.^[2–5] The phase diagrams showing three deposition modes (growth, etching, and droplet modes) were presented for the parameters of growth temperature and the extent of ammonia decomposition.

The present paper was undertaken to interrelate the decomposition rate of the group V sources with the compositional range for MOVPE growth as well as the compound composition of the III-V semiconductors. The CALPHAD (CALCulation of PHase Diagrams) technique is adopted in the way of minimizing the total Gibbs energy of the system. Through the creation of specialized database files, it is possible and convenient to calculate the constraint equilibrium under certain decomposition rates of the group V sources. With the comparison between the thermodynamic calculation and the experimental data, the pyrolysis effect of NH_3 and PH_3 on the MOVPE growth of GaN and $(\text{Ga}_{1-x}\text{In}_x)\text{P}$ compound semiconductors is illustrated.

Changrong Li and Weijing Zhang, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, People's Republic of China; and Fuming Wang, School of Metallurgical Engineering, University of Science and Technology, Beijing, Beijing 100083, People's Republic of China. Contact e-mail: fuming@public.fhnet.cn.net.

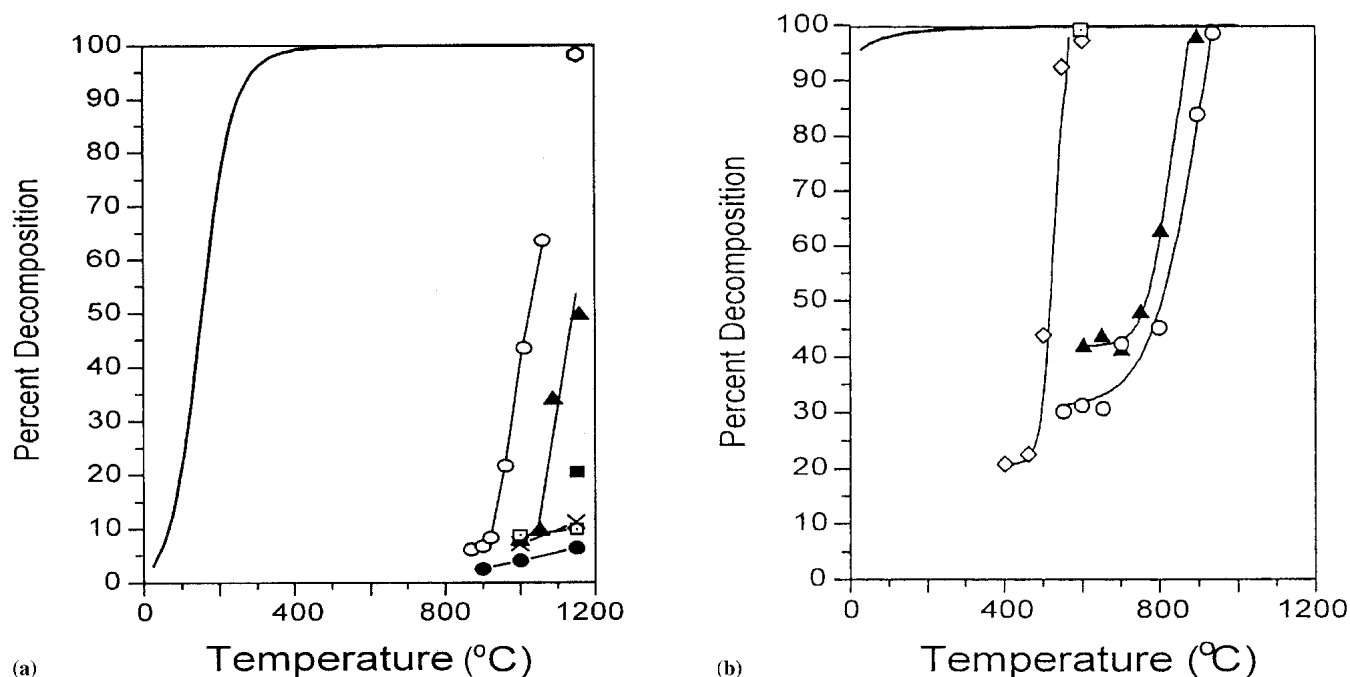


Fig. 1 Percent decomposition of NH_3 and PH_3 versus temperature in different catalytic environments: (a) experimental data from Ref 6, (●) quartz furnace only, graphite liner, graphite liner with GaN annealed in (N_2+NH_3) , (■) graphite liner with GaN annealed in N_2 , (▲) graphite liner with GaN annealed in H_2O , (Ga+GaN) in quartz boat n Graphite liner with Fe; (b) experimental data from Ref 7 (○) flow rate $100\text{cm}^3/\text{min}$, (△) flow rate $50\text{cm}^3/\text{min}$, (◇) packed with powdered GaP, (□) packed with powdered InP. (—) Equilibrium calculation in both (a) and (b).

2. Pyrolysis of NH_3 and PH_3

Ammonia and phosphine are most commonly used as the nitrogen and the phosphorus sources in MOVPE growth of GaN and $(\text{Ga}_{1-x}\text{In}_x)\text{P}$ semiconductors. A distinctive feature of this process is the use of NH_3 and PH_3 as active group V sources under conditions where NH_3 and PH_3 are thermodynamically unstable in practice, decompose incompletely. Thus the extent of pyrolysis of NH_3 and PH_3 is highly relevant to the semiconductor deposition process.

Figures 1(a) and 1(b) show the thermodynamic equilibrium results of the present calculation for NH_3 and PH_3 pyrolysis together with the experimental data from Ref 6 and 7, respectively. In the case of the NH_3 pyrolysis study, the extent of NH_3 decomposition was accomplished by an acid-base titration technique.^[6] The ammonia source, $\text{NH}_3\text{-H}_2$ gas mixture, after passing through the furnace [reaction chamber with different catalysts as listed in Fig. 1(a)], was passed through a series of traps containing HCl to ensure that there was complete trapping of the gas in question. The amount of NH_3 trapped was determined by titration of the remaining HCl in all traps using a standard 1N NaOH solution. The actual flow of NH_3 was checked by flowing the gases through a cold furnace under conditions such that no decomposition would occur. While in the case of the PH_3 pyrolysis study, the extent of PH_3 decomposition was accomplished by a redox reaction method.^[7] The phosphine source, $\text{PH}_3\text{-H}_2$ mixture, was passed through the furnace. After leaving the reaction zone [packed with different catalysts or using different flow rate as listed in Fig. 1(b)], the

reaction product (P_4) was deposited on the cool sections of the tubing. The unreacted PH_3 was then bubbled through a solution of AgNO_3 , and silver was precipitated according to the reaction: $8\text{AgNO}_3 + \text{PH}_3 + 4\text{H}_2\text{O} \rightarrow 8\text{Ag} + \text{H}_3\text{PO}_4 + 8\text{HNO}_3$. From the weight of the precipitate Ag and by comparison with the value for an unheated reactor, the amount of decomposed PH_3 was found.

As shown in Fig. 1, under the thermodynamic equilibrium condition, NH_3 and PH_3 pyrolyze almost completely in the high temperature range. For instance, the percent decomposition is greater than 99.5% when $T > 450^\circ\text{C}$ for NH_3 and $T > 300^\circ\text{C}$ for PH_3 . The main decomposition species are H_2 and N_2 for NH_3 and H_2 , P_4 , and P_2 for PH_3 . However, in practice the thermal decomposition of NH_3 or PH_3 is so much different that both temperature and catalysts play important roles. Therefore, in the thermodynamic simulation, the different pyrolysis conditions of NH_3 and PH_3 need to be considered to reach good correspondence between the calculation conditions and the experimental environment and to put the instructive significance of the thermodynamic analysis into effect.

3. Specialized Database and System Constituent

In the MOVPE process of GaN and $(\text{Ga}_{1-x}\text{In}_x)\text{P}$ semiconductor growth, the group III sources used are trimethylgallium (Ga_1Me_3 with $\text{Me} = \text{CH}_3$ or TMGa with $\text{TM} = \text{Me}_3$) for Ga and trimethyl-indium (In_1Me_3 or TMIIn) for In, and the group V sources are ammonia (NH_3) for N and phosphine (PH_3) for P. The carrier gas is hydrogen (H_2). Generally, the thermodynamic systems concerned are a four-

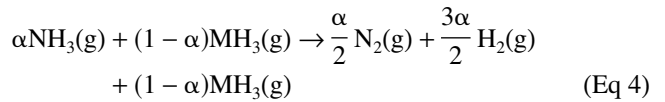
component system including Ga, N, C, and H for GaN growth and a five-component system including Ga, In, P, C, and H for $(\text{Ga}_{1-x}\text{In}_x)\text{P}$ growth, respectively. To study the effect of NH_3 or PH_3 pyrolysis on the MOVPE growth of nitrogen or phosphorus containing semiconductor, the hypothetical element M or Q needs to be introduced into the correspondent normal database to setup a specialized five-component system composed of Ga-N-M-C-H or a six-component system composed of Ga-In-P-Q-C-H. The hypothetical element M possesses all the same properties as the element N and stands for the nitrogen in the unpyrolyzed NH_3 (H_3M_1 in Table 1), while the original element N stands for all the other nitrogen-containing vapor species. The relative change of N and M composition, $X(\text{N})/[X(\text{N}) + X(\text{M})]$, determines the decomposition rate of NH_3 so does the element Q relate to the element P.

The phases and species included in the specialized databases as well as the sources of thermodynamic data are summarized in Table 1 for GaN and Table 2 for $(\text{Ga}_{1-x}\text{In}_x)\text{P}$. Other condensed substances were considered during the calculation, but due to their stability reason, they did not appear in diagrams and as a result were not listed in tables. The GaN is essentially a stoichiometric compound, and $(\text{Ga}_{1-x}\text{In}_x)\text{P}$ is a linear compound. The liquid phase is treated as one sublattice mixture, and the vapor phase as an ideal solution.

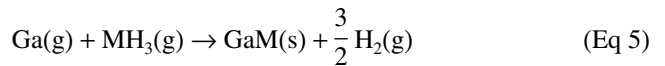
References 8 and 9 in Table 1 present the thermodynamics of the Ga-N binary system, while Ref 12 and 13 in Table 2 show the assessed data for the Ga-In-P ternary system. Since the elements C and H are introduced into the system by the input of the group III and V sources as well as the carrier gas, the thermodynamic data from Ref 10 and 11 are

also included in both of the specialized databases for MOVPE analysis.

The specialized database is helpful in calculating the equilibrium constrained by a fixed decomposition rate of the group V vapor source and studying the major group V element containing species contributing to the growth of III-V nitrides and phosphides, such as NH_3 or N_2 to GaN and PH_3 or P_4 to $(\text{Ga}_{1-x}\text{In}_x)\text{P}$. In the case of NH_3 pyrolysis study, the Ga-N-M-C-H database is used. The corresponding decomposition reaction of Eq 3 is changed to be the following:



When Ga(g) reacts with $\text{NH}_3(\text{g})$ to form GaN(s), which is the case of the present calculation, the species contained in the specialized database need to be $\text{H}_3\text{M}_1(\text{g})$, $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$, GaM(s), Since there is no $\text{M}_2(\text{g})$ included in the specialized database, the pyrolysis of $\text{H}_3\text{M}_1(\text{g})$ is constrained. The reaction mechanism will be



When Ga(g) reacts with $\text{N}_2(\text{g})$ to form GaN(s) with $\text{H}_3\text{M}_1(\text{g})$ kept unpyrolyzed, the species that need to be contained are $\text{H}_3\text{M}_1(\text{g})$, $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$, GaN(s), Then the reaction mechanism will be



Table 1 Phases and Species in the Specialized Database of the Ga-N(-M)-C-H System

Phase	Species	Reference
Semiconductor	GaN/GaM (Wurtzite)	[8, 9]
Liquid (L)	(Ga, N)	[8, 9]
Vapor (Gas)	$\text{C}_1, \text{C}_1\text{H}_1, \text{C}_1\text{H}_1\text{N}_1, \text{C}_1\text{H}_2, \text{C}_1\text{H}_3, \text{C}_1\text{H}_4, \text{C}_1\text{N}_1, \text{C}_1\text{N}_2\text{-CNN}, \text{C}_1\text{N}_2\text{-NCN}, \text{C}_2, \text{C}_2\text{H}_1, \text{C}_2\text{H}_2, \text{C}_2\text{H}_3, \text{C}_2\text{H}_4, \text{C}_2\text{H}_5, \text{C}_2\text{H}_6, \text{C}_2\text{N}_1, \text{C}_2\text{N}_2, \text{C}_3, \text{C}_3\text{H}_4\text{-1}, \text{C}_3\text{H}_4\text{-2}, \text{C}_3\text{H}_6\text{-1}, \text{C}_3\text{H}_6\text{-2}, \text{C}_3\text{H}_8, \text{C}_4, \text{C}_4\text{N}_2, \text{C}_5, \text{H}, \text{H}_1\text{N}_1, \text{H}_2, \text{H}_2\text{N}_1, \text{H}_2\text{N}_2, \text{H}_3\text{N}_1/\text{H}_3\text{M}_1, \text{H}_4\text{N}_2, \text{N}, \text{N}_2, \text{N}_3, \text{Ga}, \text{Ga}_2$ $\text{Ga}_1\text{Et}_1, \text{Ga}_1\text{Et}_2, \text{Ga}_1\text{Et}_3, \text{Ga}_1\text{Me}_1, \text{Ga}_1\text{Me}_2, \text{Ga}_1\text{Me}_3, \text{Ga}_1\text{H}_1, \text{Ga}_1\text{H}_2, \text{Ga}_1\text{H}_3, \text{Ga}_2\text{H}_6, \text{H}_1\text{Ga}_1\text{Et}_1, \text{H}_1\text{Ga}_1\text{Et}_2, \text{H}_1\text{Ga}_1\text{Me}_1, \text{H}_1\text{Ga}_1\text{Me}_2, \text{H}_2\text{Ga}_1\text{Et}_1, \text{Me}_1\text{Ga}_1\text{Et}_1, \text{Me}_2\text{Ga}_1\text{Et}_1$	[10] [11]

Note: Me, Methyl (C_1H_3); Et, Ethyl (C_2H_5)

Table 2 Phases and Species in the Specialized Database of the Ga-In-P(-Q)-C-H System

Phase	Species	Reference
Semiconductor	$(\text{Ga}_{1-x}\text{In}_x)\text{P}/(\text{Ga}_{1-x}\text{In}_x)\text{Q}$ (Zinc blend)	[12]
Liquid (L)	(Ga, In, P)	[12]
Vapor (Gas)	$\text{Ga}_1, \text{Ga}_2, \text{Ga}_1\text{P}_1, \text{In}_1, \text{In}_2, \text{In}_1\text{P}_1, \text{P}_1, \text{P}_2, \text{P}_3, \text{P}_4$ $\text{C}_1, \text{C}_1\text{H}_1, \text{C}_1\text{H}_2, \text{C}_1\text{H}_3, \text{C}_1\text{H}_4, \text{C}_2, \text{C}_2\text{H}_1, \text{C}_2\text{H}_2, \text{C}_2\text{H}_3, \text{C}_2\text{H}_4, \text{C}_2\text{H}_5, \text{C}_2\text{H}_6, \text{C}_3, \text{C}_3\text{H}_4\text{-1}, \text{C}_3\text{H}_4\text{-2}, \text{C}_3\text{H}_6\text{-1}, \text{C}_3\text{H}_6\text{-2}, \text{C}_3\text{H}_8, \text{C}_4, \text{C}_5, \text{C}_1\text{P}_1, \text{C}_1\text{P}_2, \text{C}_2\text{P}_1, \text{C}_2\text{P}_2, \text{H}_1, \text{H}_1\text{P}_1, \text{H}_2, \text{H}_2\text{P}_1, \text{H}_3\text{P}_1/\text{H}_3\text{Q}_1, \text{C}_1\text{H}_1\text{P}_1$ $\text{Ga}_1\text{H}_1, \text{Ga}_1\text{H}_2, \text{Ga}_1\text{H}_3, \text{Ga}_2\text{H}_6, \text{Ga}_1\text{Me}_1, \text{Ga}_1\text{Me}_2, \text{Ga}_1\text{Me}_3, \text{Ga}_1\text{Et}_1, \text{Ga}_1\text{Et}_2, \text{Ga}_1\text{Et}_3, \text{Me}_1\text{Ga}_1\text{Et}_1, \text{Me}_1\text{Ga}_1\text{Et}_2, \text{Me}_2\text{Ga}_1\text{Et}_1, \text{H}_1\text{Ga}_1\text{Et}_1, \text{H}_1\text{Ga}_1\text{Et}_2, \text{H}_1\text{Ga}_1\text{Me}_1, \text{H}_1\text{Ga}_1\text{Me}_2, \text{H}_1\text{Me}_1\text{Ga}_1\text{Et}_1, \text{H}_2\text{Ga}_1\text{Me}_1$	[13] [10] [11]

Note: Me, Methyl (C_1H_3); Et, Ethyl (C_2H_5)

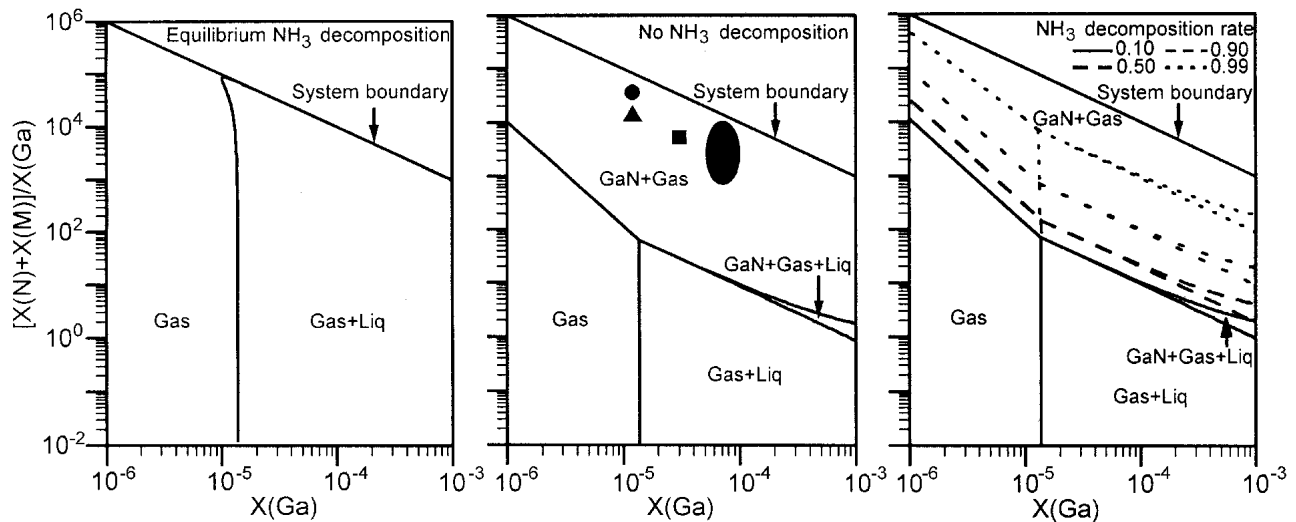


Fig. 2 Phase equilibria of Ga-N(-M)-C-H system under different NH₃ decomposition rate: (■) Detchprohm et al.^[14]; (▲) Akasaki et al.^[15]; (●) Nakamura et al.^[16]; (●) Lu et al.^[17]

The similar treatment applies to the Ga-In-P-Q-C-H database for the analysis of (Ga_{1-x}In_x)P growth.

4. Thermodynamic Calculation and Comparison With Experiments

The strategy adopted in the present paper for the equilibrium calculation is the minimization of the total Gibbs energy of the system. Based on the practical MOVPE process for semiconductor growth, the related parameters used in the present analysis were determined as follows.

4.1 Ga-N(-M)-C-H System

The mole fraction of Ga was changed between 10⁻⁶ and 10⁻³, and the ratio of the total group V elements to the total group III element, V/III = (X(N) + X(M))/X(Ga), between 10⁻² and 10⁶.

The carbon content was given by X(C) - 3 × X(Ga) = 0 since the use of metal-organic reagent of the group III source, Ga₁Me₃, and the hydrogen content adjusted by X(Ga) + X(N) + X(M) + X(C) + X(H) = 1 to meet the need of normalization. The relationship between the nitrogen content from the pyrolyzed NH₃ and the total nitrogen introduced by the NH₃ source was restricted by the decomposition rate,

$$\alpha = X(N)/(X(N) + X(M)).$$

The temperature was taken as 1050 °C and the pressure 101 325 Pa.

4.2 Ga-In-P(-Q)-C-H System

The total mole fraction of the group III elements, X(Ga) + X(In), was changed between 5 × 10⁻⁴ and 5 × 10⁻³, and the ratio of the total group V elements to the total group

III elements was set to V/III = (X(P) + X(Q))/(X(Ga) + X(In)) = 100.

The carbon content was given by X(C) - 3 × X(Ga) - 3 × X(In) = 0 since the use of metal-organic sources for the group III elements, Ga₁Me₃ and In₁Me₃, and the hydrogen content adjusted by X(Ga) + X(In) + X(P) + X(Q) + X(C) + X(H) = 1 to also meet the need of normalization. The relationship between the phosphorus content from the pyrolyzed PH₃ and the total phosphorus introduced by PH₃ source was restricted by the decomposition rate,

$$\alpha = X(P)/(X(P) + X(Q)).$$

The growth temperature was 550-750 °C and the pressure 101 325 Pa.

Figure 2 and 3 show the thermodynamic calculation under different decomposition conditions of NH₃ and PH₃; Fig. 2(a) and 3(a) with equilibrium pyrolysis, Fig. 2(b) and 3(b) with no-pyrolysis, and Fig. 2(c) and 3(c) with partial pyrolysis of different degrees. Figure 2 shows the phase diagram to determine the most favorable compositional range, GaN+Gas two-phase region, for the vapor phase epitaxy of GaN. While Fig. 3 shows the phase composition to predict the compositional change of (Ga_{1-x}In_x)P semiconductor with the input ratio of the group III vapor sources.

5. Conclusions and Discussion

The thermodynamic analysis for the MOVPE growth of GaN and (Ga_{1-x}In_x)P semiconductors was performed under conditions of the equilibrium pyrolysis, partial pyrolysis, and non-pyrolysis of the input species NH₃ and PH₃. The calculation results were compared with the experimental data from the practical processes. It is illustrated that in the material design and prediction for nitrogen or phosphorus containing semiconductors, the thermodynamic analysis

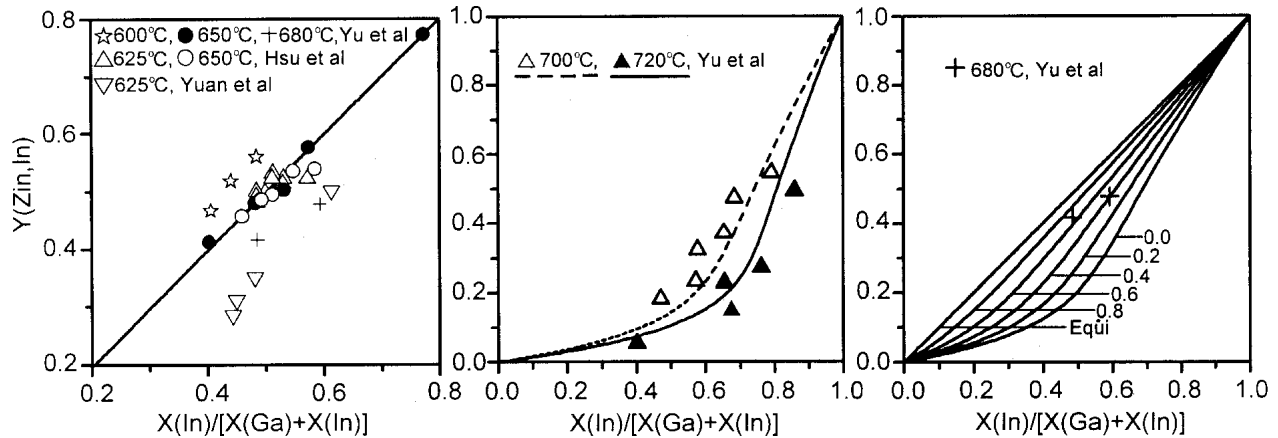


Fig. 3 The In mole fraction of semiconductor phase versus the input In_1Me_3 ratio of vapor phase under the conditions of $p = 101325\text{Pa}$, $X(\text{C}) - 3X(\text{Ga}) - 3X(\text{In}) = 0$, and (a) PH_3 equilibrium pyrolysis, $T = 550$ to 750 °C, $V/\text{III} = X(\text{P})/[X(\text{Ga}) + X(\text{In})] = 100$, ($\star, \circ, +$) Yu et al.^[18], (Δ, \circ) Hsu et al.^[19], (∇) Yuan et al.^[20]; (b) PH_3 no pyrolysis, $T = 700$ °C, 720 °C, $V/\text{III} = X(\text{Q})/[X(\text{Ga}) + X(\text{In})] = 100$ (Δ, Δ) Yu et al.^[18]; (c) PH_3 partial pyrolysis, $T = 680$ °C, $V/\text{III} = [X(\text{P}) + X(\text{Q})]/[X(\text{Ga}) + X(\text{In})] = 100$, (+) Yu et al.^[18]

needs to be taken into account through the complete equilibrium or the constraint equilibrium depending on the practical situation.

For the Ga-N(-M)-C-H system, the Gas + GaN two-phase region, which is necessary for the MOVPE growth of high quality single-phase GaN film, was paid special attention. With complete thermodynamic pyrolysis of NH_3 , the two-phase region does not exist (Fig. 2a), while without pyrolysis of NH_3 , the two-phase region exists only under high V/III ratio (Fig. 2b). Increasing the decomposition rate of NH_3 leads to narrowing of the two-phase region (Fig. 2c). All the practical parameters are situated in the upper part of the two-phase region (Fig. 2b), indicating indirectly the partial pyrolysis of NH_3 and explaining reasonably the high value of V/III ratio during the practical growth process. The present analysis indicates that a low decomposition rate of NH_3 is thermodynamically beneficial to the MOVPE growth of GaN semiconductors.

For the Ga-In-P(-Q)-C-H system, the temperature effect on the PH_3 pyrolysis in the MOVPE process of $\text{Ga}_{1-x}\text{In}_x\text{P}$ semiconductor was studied in detail. The relationship between the In_1Me_3 or Ga_1Me_3 fraction of the group III vapor sources, and the In composition of the epitaxial semiconductor was predicted. The temperature range was divided into two parts as illustrated in Ref 18. In the lower part, 550 - 650 °C, the growth rate increases with increasing temperature, and the epitaxial growth is controlled by the chemical reaction taking place near the vapor-semiconductor interface. Since the chemical reaction is the lowest step, the pyrolysis of PH_3 may reach equilibrium (Fig. 3a). In the higher part, 650 - 720 °C, the growth rate remains unchanged, and the mass transfer becomes the controlling process. Since the mass transfer controls the process, the chemical reaction near the surface is quick enough and the pyrolysis may hardly proceed (Fig. 3b). While in the intermediate part, the pyrolysis may be only partially complete. Considering the progress of PH_3 pyrolysis, the change of the semiconductor composition is gradual with reducing the pyrolysis of PH_3 . It becomes more and more difficult for In

atom to enter into the lattice of a $(\text{Ga}_{1-x}\text{In}_x)\text{P}$ semiconductor (Fig. 3c). It is concluded from the current study that in the viewpoint of thermodynamic analysis, the different pyrolysis model of the PH_3 vapor source applies to describing different control process. The decomposition rate distinctly affects the thermodynamic equilibrium as well as the semiconductor composition.

In the analysis of the MOVPE process of III-V semiconductor, the detailed insight into the decomposition of source reagents may help explain the investigation.

Acknowledgments

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References

1. G.B. Stringfellow, *Organometallic Vapor-Phase Epitaxy: Theory and Practice*, Academic Press Inc., London; San Diego, 1989, pp. 29-43.
2. A. Koukitu, N. Takahashi, T. Taki, and H. Seki: "Thermodynamic Analysis of $\text{In}_x/\text{Ga}_{1-x}\text{N}$ Alloy Composition Grown by Metalorganic Vapor Phase Epitaxy," *Jpn. J. Appl. Phys.*, 1996, 35, pp. L673-75.
3. A. Koukitu, N. Takahashi, and H. Seki: "Thermodynamic Study on Metalorganic Vapor-Phase Epitaxial Growth of Group III Nitrides," *Jpn. J. Appl. Phys.*, 1997, 36, pp. L1136-38.
4. A. Koukitu and H. Seki: "Thermodynamic Study on Phase Separation During MOVPE Growth of $\text{In}_x\text{Ga}_{1-x}\text{N}$," *J. Cryst. Growth*, 1998, 189/190, pp. 13-18.
5. A. Koukitu, T. Taki, N. Takahashi, and H. Seki: "Thermodynamic Study on the Role of Hydrogen During the MOVPE Growth of Group III Nitrides," *J. Cryst. Growth*, 1999, 197, pp. 99-105.
6. S.S. Liu and D.A. Stevenson: "Growth Kinetics and Catalytic Effects in the Vapor Phase Epitaxy of Gallium Nitride," *J.*

Section I: Basic and Applied Research

- Electrochem. Soc.: Solid-State Science and Technology*, 1978, 125, pp. 1161-69.
7. C.A. Larsen and G.B. Stringfellow: "Decomposition Kinetics of OMVPE Precursors," *J. Cryst. Growth*, 1986, 75, pp. 247-53.
 8. A.V. Davydov and T.J. Anderson: "Thermodynamic Analysis of the Ga-N System," *Calphad*, 1997, 21, p. 106.
 9. J. Unlanda, B. Onderkaa, A. Davydovb, and R. Schmid-Fetzer: "Thermodynamics and Phase Stability in the Ga-N System," *J. Cryst. Growth*, 2003, 256, pp. 33-51.
 10. SGTE, Substances Database distributed together with the Thermo-Calc AB, Stockholm, Sweden.
 11. M. Tirtowidjojo and R. Pollard: "Equilibrium Gas Phase Species for MOCVD of $\text{Al}_x\text{Ga}_{1-x}\text{As}$," *J. Cryst. Growth*, 1986, 77, pp. 200-09.
 12. Ch. Li, J-B. Li, Z. Du, and W. Zhang: "A Thermodynamic Assessment of the Ga-In-P System," *J. Phase Equilibria*, 2000, 21, pp. 357-63.
 13. I. Ansara, C. Chatillon, H.L. Lukas, T. Nishizawa, H. Ohtani, K. Ishida, M. Hillert, B. Sundman, B.B. Argent, A. Watson, T.G. Chart, and T. Anderson: "A Binary Database for III-V Compound Semiconductor Systems," *Calphad*, 1994, 18, pp. 177-222.
 14. T. Detchprohm, K. Hiramatsu, N. Sawaki, and I. Akasaki: "Metalorganic Vapor Phase Epitaxy Growth and Characteristics of Mg-Doped GaN Using GaN Substrates," *J. Cryst. Growth*, 1994, 145, pp. 192-96.
 15. I. Akasaki, H. Amano, Y. Koide, K. Hiramatsu, and N. Sawaki: "Effects of AlN Buffer Layer on Crystallographic Structure and on Electrical and Optical Properties of GaN and $\text{Ga}_{1-x}\text{Al}_x\text{N}$ ($0 < x < 0.4$) Films on Sapphire Substrate by MOVPE," *J. Cryst. Growth*, 1989, 98, pp. 209-19.
 16. S. Nakamura, T. Mukai, and M. Senoh: "Candela-Class High-Brightness InGaN/AlGaN Double-Heterostructure Blue-Light-Emitting Diodes," *Appl. Phys. Lett.* 1994, 64, pp. 1687-89.
 17. S. Duan and D-C. Lu: "Thermodynamic Modeling and Phase Diagram for the MOVPE Growth of GaN," *Chinese J. Semiconductors*, 1997, 18, pp. 385-90.
 18. Q. Yu, C. Li, and R. Peng: "Thermodynamics and Characterization of GaInP by MOCVD," *Chinese J. Semiconductors*, 1997, 18, pp. 253-57.
 19. C.C. Hsu, J.S. Yuan, R.M. Cohen, and G.B. Stringfellow: "Doping Studies of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ Organometallic Vapor-Phase Epitaxy," *J. Appl. Phys.*, 1986, 59, pp. 395-98.
 20. J.S. Yuan, C.H. Chen, R.M. Cohen, and G.B. Stringfellow: "High Quality $\text{Ga}_x\text{In}_{1-x}\text{P}$ ($x = 0.65, 0.69$) Growth by OMVPE," *J. Cryst. Growth*, 1986, 78, pp. 63-68.