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Quasi-Thermodynamic Model of MOVPE Growth of $Ga_xAl_yIn_{1-x-y}N$*

LU Da-cheng[1] and DUAN Shu-kun[2]

(1 *Laboratory of Semiconductor Materials Science, Institute of Semiconductors, The Chinese Academy of Sciences, Beijing* 100083, *China*)

(2 *Institute of Semiconductors, The Chinese Academy of Sciences, Beijing* 100083, *China*)

Abstract: A quasi-thermodynamic model of MOVPE growth of $Ga_xAl_yIn_{1-x-y}N$ alloys has been proposed with TMGa, TMAl, TMIn and ammonia as sources. In this model, the effect of decomposition of ammonia has been con-sidered and the number of moles is used to express the mass conservation constraints of element N, H, Ga, Al and In. It is assumed that the alloy is synthesized by the reactions between ammonia and group Ⅲ elements. The influence of growth conditions on the relationship between $Ga_xAl_yIn_{1-x-y}N$ lattice matched to GaN and input group Ⅲ metalorganic compounds has been calculated. Almost all the aluminum and gallium reaching the growing surface are incorporated in the alloy. In order to enhance the incorporation of indium into $Ga_xAl_yIn_{1-x-y}N$, lower growth temperature and higher input Ⅴ/Ⅲ ratio should be used and the decomposed fraction of ammonia should be reduced.

Key words: GaAlInN; MOVPE; thermodynamic; group Ⅲ nitrides
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1 Introduction

Group Ⅲ-nitrides and their alloys as very important semiconductor materials, are suitable for the fabrication of green, blue and ultraviolet light emitting diodes (LEDs) and laser diodes (LDs)[1,2]. In these devices, quantum well (QW) structures are widely used. InN of a fairly high percentage exists in the QWs in GaInN ternary alloy active layers. To avoid the lattice mismatch between the InGaN well and the AlGaN barriers, a well with thickness about 20nm has been used. The high-strained and extremely thin well will shift the emission to the higher energy and limit the InN content in the well. Thus, for In of high values, the AlGaN barrier layers will cause several limitations, which can be avoided by using a more versatile $Ga_xAl_yIn_{1-x-y}N$ quaternary alloy. By varying the composition of quaternary alloys, the band gap and the lattice constant can be adjusted individually so that the GaAlInN lattice-matched to the closely lattice-matched structures is obtained. Therefore, $Ga_xAl_yIn_{1-x-y}N$ can be adopted as a cladding layer to reduce the defects, without any strains on the laser structure. It can also be used as an ultraviolet photodetector. Compared with binary and ternary nitrides, however, little attention has

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LU Da-cheng male, was born in 1937, professor. His research interests are in the areas of semiconductor materials science and optoelectronic devices.

DUAN Shu-kun female, was born in 1938, professor. Her research interests are in the areas of semiconductor materials and optoelectronic devices.

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been paid to the $Ga_xAl_yIn_{1-x-y}N$ alloy experimentally[3—5] and theoretically[6].

For better investigation of the quaternary alloy, it is necessary to find out the favorable growth conditions for the epitaxial growth of GaAlInN. A quasi-thermodynamic model has been proposed to analysis the MOVPE growth of AlGaN, InGaN and InAlN[7—9]. The calculated and experimental composition of AlGaN and InGaN systems are in good agreement. The goal of this paper is to establish a quasi-thermodynamic model for MOVPE growth of $Ga_xAl_yIn_{1-x-y}N$, with TMGa, TMAl, TMIn and NH_3 as source materials so as to find out the favorable growth conditions, especially for the alloy which is lattice-matched to GaN. The following points have been improved in our model. Firstly, the number of moles is used to express the mass conservation constraints on element N, H, Al, In and Ga, because the variation in the total number of molecules cannot be neglected, which is caused by the reactions, especially by the decomposition of ammonia. Secondly, since the low-pressure process has advantages over atmospheric pressure one, the effect of reactor pressure has to be taken into consideration.

2 Model

The analysis of $Ga_xAl_yIn_{1-x-y}N$ is on the assumption as below, as what we did for AlGaN, InGaN and InAlN in References[7—9].

(1) Ignoring the pre-reactions between group Ⅲ and group Ⅴ precursors. TMGa, TMAl and TMIn are decomposed irreversibly near the vapor-solid interface at a usual growth temperature.

(2) In order to calculate the influence of decomposition of ammonia, we introduce a decomposed fraction of NH_3, η.

$$NH_3(g) = (1-\eta)NH_3(g) + \eta/2N_2(g) + 3\eta/2H_2(g) \quad (1)$$

(3) Ignoring the reactions between N_2 and the group Ⅲ elements in the temperature range of 500—900℃ since the N_2 molecule is inert.

Assumption (2) and (3) make this model a quasi-equilibrium model.

(4) Quaternary alloys are formed by the reactions between NH_3 and the group Ⅲ elements and the thermodynamic equilibrium established at the solid-vapor interface. Notice that $Ga_xAl_yIn_{1-x-y}N$ alloy is a quasi-quaternary system and can be written as $(GaN)_x(AlN)_y(InN)_{1-x-y}$.

Ga, Al, In, NH_3, H_2, N_2, inert gas (IG) and CH_4 are the chosen necessary vapor species. The equations of mass action for synthesizing GaAlInN are as follows:

$$\gamma_{GaN}P_{H_2}^{1/2}/(P_{Ga}P_{NH_3}P_{tot}^{1/2}) = K_1 \quad (2)$$

$$\gamma_{AlN}P_{H_2}^{1/2}/(P_{Al}P_{NH_3}P_{tot}^{1/2}) = K_2 \quad (3)$$

$$\gamma_{InN}P_{H_2}^{1/2}/(P_{In}P_{NH_3}P_{tot}^{1/2}) = K_3 \quad (4)$$

where P_i is the equilibrium partial pressure of i, P_{tot} is the total pressure, and K_i is the equilibrium constant. γ_{GaN}, γ_{AlN} and γ_{InN} are the activity coefficients of the solid GaN, AlN and InN in $Ga_xAl_yIn_{1-x-y}N$ alloy, respectively. They are determined from the regular solution model and expressed as follows:

$$RTLn(\gamma_{GaN}) = (\Omega_{GaN-AlN}Y_{AlN} + \Omega_{GaN-InN}Z_{InN})(1-X_{GaN}) - (\Omega_{AlN-InN}Y_{AlN}Z_{InN}) \quad (5)$$

$$RTLn(\gamma_{AlN}) = (\Omega_{AlN-GaN}X_{GaN} + \Omega_{AlN-InN}Z_{InN})(1-Y_{AlN}) - (\Omega_{GaN-AlN}X_{GaN}Z_{InN}) \quad (6)$$

$$RTLn(\gamma_{InN}) = (\Omega_{InN-GaN}X_{GaN} + \Omega_{InN-AlN}Y_{AlN})(1-Z_{InN}) - (\Omega_{GaN-AlN}X_{GaN}Y_{AlN}) \quad (7)$$

$$Z_{InN} = 1 - X_{GaN} - Y_{AlN} \quad (8)$$

where Ω is the interaction parameter of group Ⅲ-nitrides binary, and X, Y and Z are the mole fraction of GaN, AlN and InN in $Ga_xAl_yIn_{1-x-y}N$ alloys, respectively[10].

The variation in the total number of molecules, caused by the reactions, especially by the decomposition of ammonia, cannot be neglected. In this case, instead of partial pressure, we use number of moles to express the mass conservation constraints on element N, H, Ga, Al and In.

$$n_{NH_3}^0 + n_{N_2}^0 = n_{GaN}^{Alloy} + n_{AlN}^{Alloy} + n_{InN}^{Alloy} + n_{NH_3} + 2n_{N_2} \quad (9)$$

where n_i^0 is the input number of moles of species i; n_{Ga}^{alloy}, n_{Al}^{alloy} and n_{In}^{alloy} are the number of moles of GaN, AlN and InN in the alloy, respectively.

$$2n_{H_2}^0 + 3n_{NH_3}^0 = 3n_{NH_3} + 2n_{H_2} + 3n_{CH_4} \quad (10)$$

$$n_{TMGa}^0 = n_{GaN}^{Alloy} + n_{Ga} \quad (11)$$

$$n_{TMAl}^0 = n_{AlN}^{Alloy} + n_{Al} \quad (12)$$

$$n_{TMIn}^0 = n_{InN}^{Alloy} + n_{In} \quad (13)$$

where n_{Ga}, n_{Al} and n_{In} are the number of moles of Ga, Al and In in the gas phase, respectively.

The partial pressure of species i can be obtained by:

$$P_i = n_i(P_{tot}/n_{tot}) \quad (14)$$

where n_{tot} is the total number of moles in the gas phase.

The total pressure of the reactor is expressed as follows:

$$P_{tot} = P_{NH_3} + P_{N_2} + P_{H_2} + P_{Ga} + P_{Al} + P_{In} + P_{CH_4} + P_{IG} \quad (15)$$

where P_{IG} is the partial pressure of the inert gas, $P_{CH_4} = 3(n_{TMGa}^0 + n_{TMAl}^0 + n_{TMIn}^0)P_{tot}$.

In order to describe the effect of carrier composition, a parameter f is introduced:

$$f = n_{H_2}^0/(n_{H_2}^0 + n_{IG}^0 + n_{N_2}^0) \quad (16)$$

where f is the mole fraction of H_2 in the mixed carrier gas, relative to the inert gas and nitrogen in the carrier gas.

The values of x and y can be expressed as (on stoichiometry conservation constrains):

$$x = n_{Ga}^{alloy}/(n_{Ga}^{alloy} + n_{Al}^{alloy} + n_{In}^{alloy}) \quad (17)$$

$$y = n_{Al}^{alloy}/(n_{Ga}^{alloy} + n_{Al}^{alloy} + n_{In}^{alloy}) \quad (18)$$

In addition, the input Ⅴ/Ⅲ ratio, R, is introduced:

$$R = n_{NH_3}^0/(n_{TMGa}^0 + n_{TMAl}^0 + n_{TMIn}^0) \quad (19)$$

Solving Eqs. (2)—(19), we can obtain the equilibrium partial pressures in the gas phase, and the relationship between the input molar ratio of metal organic compounds of group Ⅲ and the deposited composition of GaAlInN at given growth temperature, reactor pressure, R, f, x, y and n_i^0.

3 Results and Discussions

Figure 1 (a) shows the effect of temperature on the equilibrium partial pressure of gaseous species over the $Ga_{0.8}Al_{0.15}In_{0.05}N$ alloys. The equilibrium partial pressures of gallium, aluminum and indium increase with the temperature. For comparison, the dotted lines denote the vapor pressures of pure In metal (P_{In}^0)[11]. The equilibrium partial pressures of Al and Ga are pretty low, which means that almost all the input aluminum and gallium reaching the growing surface are incorporated into the alloy. Therefore, it is unnecessary to take the formation of liquid gallium or aluminum droplets into consideration. However, the equilibrium partial pressure of In is much higher than that of Al and Ga, due to the different equilibrium constants (seen Eqs. 8, 9 and 10), as influences the deviation of vapor-solid distribution relationship. The equilibrium partial pressure of In is very close to P_{In}^0 (in Fig. 1(a)). Indium droplets will deposit if the growth conditions are not selected properly. Figure. 1(b) shows the effect of temperature on the

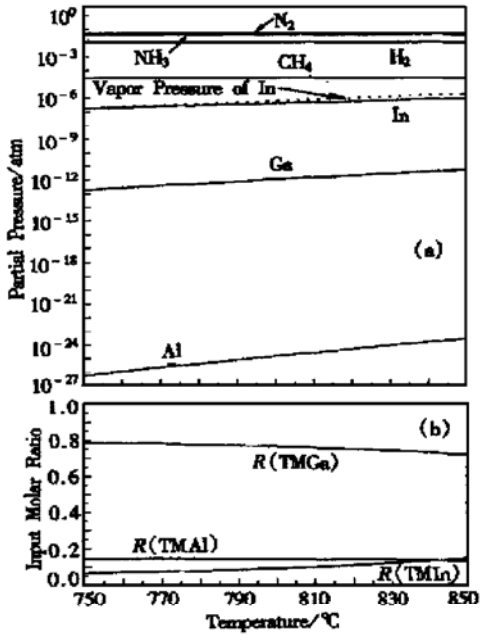

FIG. 1 Equilibrium Partial Pressure (a) and Input Mole Ratio of TMGa, TMAl and TMIn (b) as Function of Temperature in $Ga_{0.8}Al_{0.15}In_{0.05}N$ Alloys $P_{tot} = 0.1$atm, $P_{Ⅲ} = 10^{-5}$atm, $f = 0.01$, $\eta = 0.15$, $R = 5000$.

input molar ratio of TMGa, TMAl and TMIn. The R (TMGa) is defined as $n^0_{TMGa}/(n^0_{TMGa}+n^0_{TMAl}+n^0_{TMIn})$, $R(TMAl)=n^0_{TMAl}/(n^0_{TMGa}+n^0_{TMAl}+n^0_{TMIn})$ and $R(TMIn)=n^0_{TMIn}/(n^0_{TMGa}+n^0_{TMAl}+n^0_{TMIn})$, respectively.

A typical composition triangle can be used to describe the composition of the input molar ratio of group Ⅲ metal organic compounds and the solid composition of quaternary, as is shown in figure 2, where the first triangle, representing the composition of input metalorganic compounds, coincides with the second triangle, representing the GaAlInN solid composition. Therefore, the relationship between the composition of input metalorganic compounds and the solid composition of quaternary can be described in one triangle. Much attention has been paid to the gallium-rich corner of the quaternary, because the GaAlInN is usually used as a cladding layer, with the energy gap a little higher than that of GaN or InGaN. In addition, the growth of high content of Ga or Al quaternary is much easier than that of high In. The composition of the solid $Ga_{0.825}Al_{0.144}In_{0.031}N$ lattice matched to GaN is shown as the solid circle in Fig. 2, while the corresponding composition of metalorganic compounds in gas phase is as an open circle. The pair equilibrium solid-gas composition is linked up with a string line (linking line). Dash line (in Fig. 2) represents the quaternary composition lattice matched to GaN. All points on the open circle are located on the right side of the corresponding solid one, which means that indium are enriched in gas phase. In order to obtain the same solid composition GaAlInN, higher TMIn is needed when the reactor pressure is increased from 0.1atm to 1atm, which proves that low-pressure process is suitable for the growth of GaAlInN.

It is important to determine the optimal growth temperature of the GaAlInN alloy. Aluminum-based nitrides generally require higher growth temperatures, because of the higher bonding energy of AlN bond and high reactivity of aluminum with oxygen. Higher temperature is

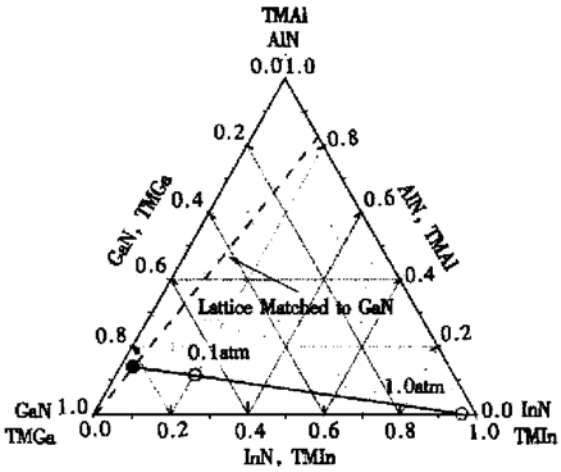

FIG. 2 Relationship Between Solid $Ga_{0.825}Al_{0.144}In_{0.031}N$ and Input Mole Ratio of TMGa, TMAl and TMIn, as Function of Reactor Pressure P_{tot} = 1atm and 0.1atm, Respectively The solid line links the equilibrium solid and the gas phases. T_g = 800℃, P_{III} = 10^{-5}atm, R = 20000, f = 0.01 and η = 0.15. Dash line represents the GaAlInN quaternary composition lattice matched to GaN.

helpful in obtaining better crystalline quality and preventing oxygen from incorporating into the film. Lower temperature, however, are required for indium-based compounds to increase the indium incorporation owing to the lower bonding energy of In—N bond. The growth temperature will therefore determine if both Al and In can be incorporated into the GaAlInN quaternary alloy. Figure 3 shows the theoretical input mole ratio of the group Ⅲ metalorganic compounds as a function of temperature in the $Ga_xAl_yIn_{1-x-y}N$ alloys, which is lattice matched to GaN. In order to determine the lattice constant of the $Ga_xAl_yIn_{1-x-y}N$ alloys, we assume that the Vagary's low is suitable for:

$$a_{[Ga_xAl_yIn_{1-x-y}N]}=xa_{GaN}+ya_{AlN}+(1-x-y)a_{InN} \quad (27)$$

the lattice constants of binaries are: a_{GaN} = 0.3189nm, a_{AlN} = 0.3112nm and a_{InN} = 0.3548nm. We can see that with the increase of growth temperature, the input mole ratio of metalorganic compounds varies dramatically to obtain a same solid composition. When the growth temperature

increases, more TMIn is needed. It is difficult to grow a wider band gap GaAlInN alloy if the growth temperature is higher than 850℃. All the linking lines point towards the TMIn angle, as can also be seen in Figures 2 and 4, which indicates that all input Ga and Al incorporate into the alloy under the calculated conditions.

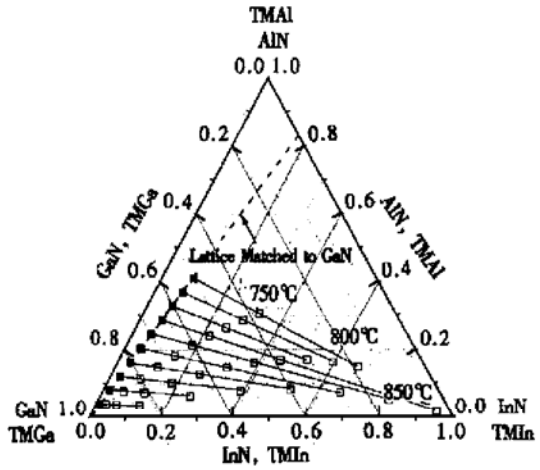

FIG. 3 Relationship Between Solid $Ga_xAl_yIn_{1-x-y}N$ and Input Mole Ratio of TMGa, TMAl and TMIn as Function of Growth Temperature Ranging from 750℃ to 850℃ η= 0.15, R= 20000, P_{tot}= 0.1atm, and f = 0.002. Dash line represents the GaAlInN quaternary composition lattice matched to GaN.

Figure 4 shows the theoretical curves of the GaAlInN composition as a function of the input mole ratio of the group Ⅲ metalorganic compounds, when we varying the decomposition fraction of ammonia, η, from 0.1 to 0.2. The η has a dramatic inference on the incorporation of indium. Decomposition rate of ammonia can be affected by many factors, such as growth temperature, total flow rate in the reactor, reactor pressure, reactor geometry, the nature of carrier gas and catalyst if exist. The most important thing is to reduce the decomposition of ammonia before it reaching the growing surface.

Figure 5 shows the theoretical curves of the GaAlInN composition as a function of the input Ⅴ/Ⅲ ratio, with R varying from 10000 to 30000. R of high value is required, like In-content ternary

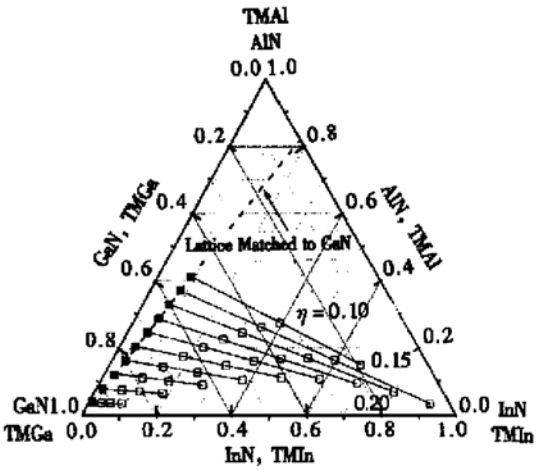

FIG. 4 Relationship Between Solid $Ga_xAl_yIn_{1-x-y}N$ Matched to GaN and Input Mole Ratio of TMGa, TMAl and TMIn as Function of Decomposition Fraction of Ammonia, η, from 0.1 to 0.2 Growth temperature= 800℃, P_{tot}= 0.1atm, R= 20000, and η= 0.002. Dash line represents the GaAlInN quaternary composition lattice matched to GaN.

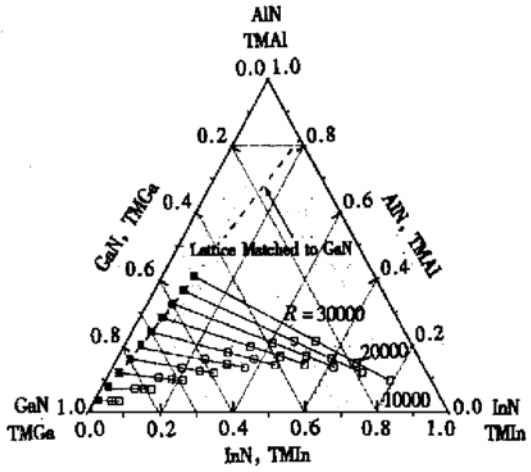

FIG. 5 Relationship Between Solid $Ga_xAl_yIn_{1-x-y}N$ and Input Mole Ratio of TMGa, TMAl and TMIn as Function of Ⅴ/Ⅲ ratio R, Which Varying from 10000 to 30000 Growth temperature= 800℃, P_{tot}= 0.1atm, η= 0.15, f= 0.002 and $P_{Ⅲ}$= 10^{-6}atm. Dash line represents the GaAlInN quaternary composition lattice matched to GaN.

alloy[7,8]. We also calculate the influence of mole fraction of H_2 in the mixed carrier gas (f). In Fig. 6, one can find that it is very important to

reduce the content of H_2 in the H_2-N_2 carrier gases to increase the In content in the quaternary.

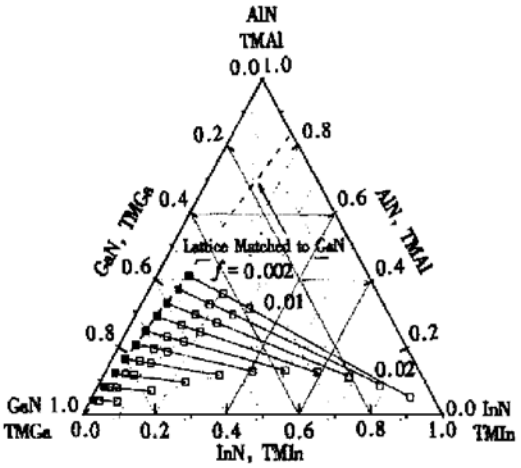

FIG. 6 Relationship Between Solid $Ga_xAl_yIn_{1-x-y}N$ and Input Mole Ratio of TMGa, TMAl and TMIn as Function of Mole Fraction of H_2 in Mixed Carrier Gas (f) Growth temperature = 750℃, P_{tot} = 0.1atm, η = 0.10, R = 20000 and $P_{III} = 10^{-6}$ atm. Dash line represents the GaAlInN quaternary composition lattice matched to GaN.

4 Conclusions

A quasi-thermodynamic model of MOVPE growth of $Ga_xAl_yIn_{1-x-y}N$ alloys with TMGa, TMAl, TMIn and ammonia as sources has been proposed. In this model, the effect of low decomposition rate of ammonia has been considered and the number of moles is used to express the mass conservation constraints of element N, H, Ga, Al and In. It is assumed that the alloy is synthesized by the reactions between ammonia and group III elements. This model can be used to calculate the relationship between the composition of GaAlInN alloy and input molar ratio of group III metalorganic compounds. Almost all the aluminum and gallium reaching the growing surface are incorporated into the alloy. In order to enhance the incorporation of indium into $Ga_xAl_yIn_{1-x-y}N$, lower growth temperature and higher input V/III ratio should be used and the decomposed fraction of ammonia should be reduced. Indium droplets will deposit if the growth conditions are not selected properly.

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MOVPE 生长 $Ga_xAl_yIn_{1-x-y}N$ 的准热力学模型*

陆大成[1]　段树坤[2]

(1 中国科学院半导体研究所 半导体材料科学实验室，北京　100083)
(2 中国科学院半导体研究所，北京　100083)

摘要：提出一个以 TMGa、TMAl、TMIn 和 NH_3 为源，用 MOVPE 方法生长 $Ga_xAl_yIn_{1-x-y}N$ 四元合金的准热力学模型. 该模型假设四元合金是由氨和Ⅲ族元素之间反应合成的，其特点是考虑了 NH_3 的分解效率，并用 N、H、Ga、Al 及 In 的摩尔分数代替惯用的分压来表示质量守衡方程. 计算了各种生长条件对于与 GaN 晶格匹配的 $Ga_xAl_yIn_{1-x-y}N$ 四元合金与注入反应室的Ⅲ族金属有机化合物之间关系的影响. 计算表明，几乎所有达到生长表面的 Al 和 Ga 都并入到 $Ga_xAl_yIn_{1-x-y}N$ 四元合金中，而 In 则富集在气相. 为增强铟的并入，应采用低的生长温度，高的Ⅴ/Ⅲ比，氮载气而且须要设法降低到达生长界面前氨的分解.

关键词：GaAlInN；MOVPE；热力学；Ⅲ族氮化物
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* 国家重点基础(973)资助项目(合同号：G20000683).
陆大成　男，1937 年出生，研究员，从事半导体材料和光电器件的研究.
段树坤　女，1938 年出生，研究员，从事半导体材料和光电器件的研究.
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