

Quasi-Thermodynamic Model of MOVPE of InAlN^{*}

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Abstract: A quasi-thermodynamic model of MOVPE growth of $\text{In}_x\text{Al}_{1-x}\text{N}$ alloy with TMAl, TMIn and ammonia as sources has been proposed. In this improved 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, Al and In. It is assumed that the alloy is synthesized by the reactions between ammonia and group III elements. The results show that it is more difficult to grow the $\text{In}_x\text{Al}_{1-x}\text{N}$ alloy, especially for the $\text{In}_x\text{Al}_{1-x}\text{N}$ lattice matched the GaN. In order to enhance the incorporation of indium into InAlN, we should use the lower growth temperature, optimized input V/III ratio and high nitrogen fraction in the carrier gas. In addition, the decomposed fraction of ammonia should be reduced. Indium droplets would be deposited if the growth conditions have not been selected properly.

Key words: InAlN; MOVPE; thermodynamic model

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1 Introduction

Group III-nitrides are very important materials, which are applied to the fabrication of green, blue and ultraviolet light emitting diodes(LEDs) and laser diodes(LDs)^[1]. $\text{In}_x\text{Al}_{1-x}\text{N}$ alloy is a kind of promising material for GaN-based short-wavelength-light devices, because $\text{In}_x\text{Al}_{1-x}\text{N}$ can be lattice-matched the GaN and or $\text{Ga}_{1-y}\text{In}_y\text{N}$. For example, $\text{In}_{0.17}\text{Al}_{0.83}\text{N}$ is lattice-matched the GaN with a larger band gap energy than GaN, therefore, it can be used as a cladding layer with no strain on the laser structure, leading to a reduction of defects. In addition, $\text{In}_x\text{Al}_{1-x}\text{N}$ can be adopted as an active layer for light-emitting devices in

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the spectral region from ultraviolet to red. A little attention has been paid to $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys experimentally^[2-4] or theoretically.

Thermodynamic analysis has been developed for many III-V and II-VI alloys, including the alloys with miscibility gaps. It is well known that these kinds of models can provide us with useful information on the growth of stable and unstable alloys. Koukitu and Seki have reported their thermodynamic calculations on MOVPE growth of $\text{In}_x\text{Ga}_{1-x}\text{N}$ ^[7] and we proposed a quasi-thermodynamic model to analysis MOVPE growth of AlGaIn and InGaIn^[5,6]. The following points are 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 of the sum number of molecules can not be neglected, which is caused by the reactions, especially by the decomposition of ammonia. Secondly, since the low-pressure process has advantages over the atmospheric one, we can take the effect of reactor pressure into consideration. The calculated composition and experimental one quite agree in AlGaIn and InGaIn systems. However, $\text{In}_x\text{Al}_{1-x}\text{N}$ system has not been calculated yet. The goal of this paper is to establish a quasi-thermodynamic model for MOVPE growth of $\text{In}_x\text{Al}_{1-x}\text{N}$ with TMAI, TMIn and NH_3 as source materials. The model used here is similar to that in references 5 and 6.

2 Model

To analyze $\text{In}_x\text{Al}_{1-x}\text{N}$, the following assumptions are used, as what have done for AlGaIn and InGaIn in reference 5 and 6.

1. Ignoring the pre-reactions between group III and V precursors. TMAI and TMIn are decomposed irreversibly near the vapor-solid interface at usual growth temperature.

2. Based on thermodynamic calculations, NH_3 is almost fully decomposed into N_2 and H_2 at the temperature higher than 300°C . However, without catalyst, the deposition rate of ammonia is very low. In order to calculate the influence of decomposition of ammonia, we introduce a decomposed fraction of NH_3 , η ,

$$\text{NH}_3(\text{g}) = (1 - \eta)\text{NH}_3(\text{g}) + \eta/2\text{N}_2(\text{g}) + 3\eta/2\text{H}_2(\text{g}). \quad (1)$$

3. Ignoring the reactions between N_2 and the group III elements in the temperature range of $500\text{--}900^\circ\text{C}$ since the N_2 molecule is inert.

Assumptions 2 and 3 make this model a quasi-equilibrium model.

4. Ternary alloys are formed by the reactions between NH_3 and the group III elements and the thermodynamic equilibrium established at the solid-vapor interface.

The following species are chosen as the necessary vapor species: Al, In, NH_3 , H_2 , N_2 , and CH_4 . The equations of mass action for synthesizing InAlN are as follows:

$$a_{\text{AlN}}P_{\text{H}_2}^{3/2}/(P_{\text{Al}}P_{\text{NH}_3}P_{\text{tot}}^{1/2}) = K_1 \quad (2)$$

$$a_{\text{InN}}P_{\text{H}_2}^{3/2}/(P_{\text{In}}P_{\text{NH}_3}P_{\text{tot}}^{1/2}) = K_2 \quad (3)$$

where P_i is the equilibrium partial pressure of i , P_{tot} is the total pressure, and K_i is the equi-

librium constant. a_{AlN} and a_{InN} are the activities of the solid AlN and InN respectively in In-AlN alloy and derived from the regular solution model.

The change of the total number of molecules can not be neglected, which is created by the reactions, mainly by the decomposition of ammonia. In this case, instead of partial pressure, we use molar quantity to express the mass conservation constraints of element N, H, In and Al.

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

$$f = n_{\text{H}_2}^{\circ} / (n_{\text{H}_2}^{\circ} + n_{\text{IG}}^{\circ}) \quad (4)$$

which f is the mole fraction of H_2 relative to the inert gas in the carrier gas, n_j° is the input number of moles j .

In this paper we did not show all the equations for the sake of simplicity, which are similar to those in Ref. 6, with the only difference being that Al instead of Ga in the equations.

3 Results and Discussions

Figure 1 shows that the calculated activities of InN and AlN in $\text{In}_x\text{Al}_{1-x}\text{N}$ deviate strongly from the ideal solution. The interaction parameter is taken as 47555.344 J/mole (11366 cal/mole)^[8]. In addition, the deviation varies greatly with the temperature.

Figure 2 shows the equilibrium partial pressure of gaseous species over $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys. For comparison, the dotted lines show the vapor pressure of pure In and Al metal (P_{In}° and P_{Al}°), respectively^[9]. The equilibrium partial pressures of indium and aluminum vary with the solid composition. The equilibrium partial pressure of In is significantly higher than that of Al due to the difference between the equilibrium constants, and this phenomenon influences the deviation of the vapor-solid distribution relationship. The equilibrium partial pressure of Al is very low, which means that most input aluminum is incorporated into the alloy. Therefore, we do not need to consider the formation of liquid aluminum droplets. The equilibrium partial pressures of In is very close to P_{In}° or even higher than of P_{In}° (see Fig. 2). Liquid indium droplets may deposit on the substrate surface.

Figure 3 shows theoretical curves of $\text{In}_x\text{Al}_{1-x}\text{N}$ solid composition as a function of the input mole ratio of $[\text{TMIn}]/[\text{TMIn} + \text{TMAI}]$ at different growth temperatures from 500°C to 800°C. The solid composition is a linear function of the input mole fraction ratio at 500 or 600°C. However, with the increase of growth temperature, the solid composition deviates

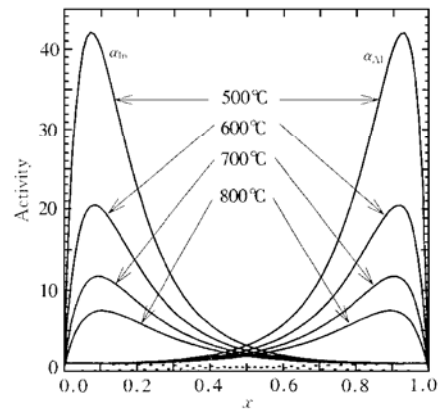


FIG. 1 Activities of InN and AlN at 700°C as Function of Solid Composition. The dotted lines show those in the case of ideal solid solution.

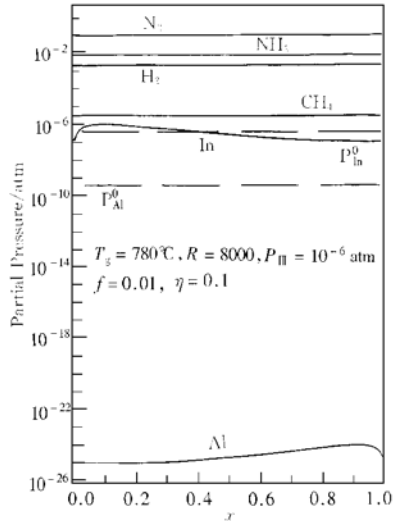


FIG. 2 Equilibrium Partial Pressures as Function of x in $\text{In}_x\text{Al}_{1-x}\text{N}$ Alloy.

The dotted lines show the vapor pressure of pure In and Ga metal, P_{In}^0 and P_{Al}^0 , respectively.

from the linear function dramatically. At lower temperature ($< 700^\circ\text{C}$ for example), we are able to grow metastable $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys throughout the entire range of solid composition. It can be seen that the solid-vapor distribution function curve becomes S-shaped when the growth temperature is higher than 750°C , which can be seen in InGaN system as well. One of the authors of this paper, Lu, has found that the S-shaped curve exists in ZnTeSe and ZnTeS systems, which are immiscible II-VI alloys^[10]. The critical temperature for the phase separation, T_c , is 465°C in ZnSeTe . It is interesting that the multi-valued behavior (or S-shaped curve) disappears when the growth temperature is higher than 465°C ^[10], which means that the multi-valued behavior is associated with the miscibility gap.

Figure 4 shows the theoretical curves of the $\text{In}_x\text{Al}_{1-x}\text{N}$ composition as a function of the input mole ratio of the group III metalorganic compounds, varying with the decomposition fraction of ammonia,

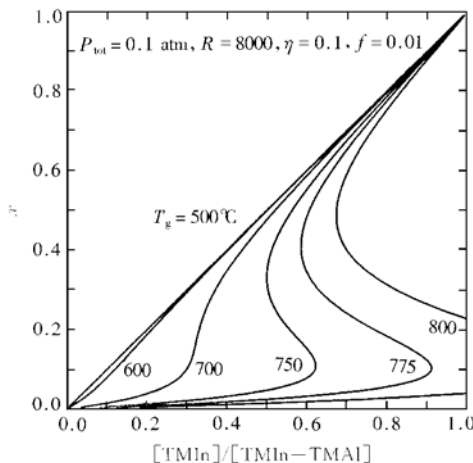


FIG. 3 Theoretical Curves of $\text{In}_x\text{Al}_{1-x}\text{N}$ Solid Composition as Function of Input Mole Ratio of Group III Metalorganic Compounds, Varying with Growth Temperature from 500 to 800°C .

For calculation, $P_{\text{tot}} = 0.1 \text{ atm}$, $P_{\text{III}} = 10^{-6} \text{ atm}$, $R = 8000$, $f = 0.01$ and $\eta = 0.1$.

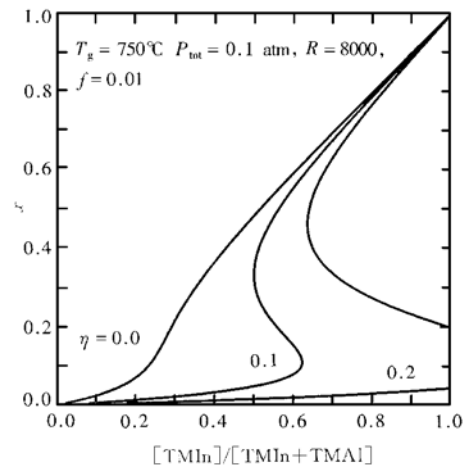


FIG. 4 Theoretical Curves of $\text{In}_x\text{Al}_{1-x}\text{N}$ Composition as Function of Input Mole Ratio of Group III Metalorganic Compounds, Varying With Input Decomposition Fraction of Ammonia, η , from 0.0 to 0.2.

For calculation, $T_g = 750^\circ\text{C}$, $P_{\text{tot}} = 0.1 \text{ atm}$, $P_{\text{III}} = 10^{-6} \text{ atm}$, $R = 8000$ and $f = 0.01$.

η . The η has a dramatic influence on the incorporation of indium. In Fig. 4, for example, the solid composition begins to deviate from linear function of the input mole ratio at $\eta = 0.0$. With the increase of η , the vapor-solid distribution relationship changes to S-shaped curve.

Figure 5 shows the theoretical curves of the $\text{In}_x\text{Al}_{1-x}\text{N}$ composition as a function of the input mole ratio of the group III metalorganic compounds, varying with the input V/III ratio from 5000 to 80000. The V/III ratio plays an important role in the control of indium incorporation. Note that the effect of the input V/III ratio on the indium incorporation is rather complicated. When $\eta = 0$, the InAlN composition increases with R . However, when $\eta > 0$, there is an optimum value of R for the indium incorporation as shown in Fig. 5. In Fig. 5, we keep the input group III metalorganic compounds constant, so that the partial pressure of NH_3 increases with R , so does the partial pressure of H_2 . But the effect of the partial pressure of H_2 on the P_{In} is stronger than that of NH_3 (see Eq. 3).

Figure 6 shows the theoretical curves of the $\text{In}_x\text{Al}_{1-x}\text{N}$ composition as a function of the input mole ratio of the group III metalorganic compounds, varying with the hydrogen fraction in carrier gas to be 0.01, 0.05 and 1. The predicted solid composition deviates from the linear function with the increase of the hydrogen fraction in carrier gas. Using inert gas (or nitrogen) as a carrier gas is desirable for the growth of the $\text{In}_x\text{Al}_{1-x}\text{N}$ alloy. The increase of partial pressure of H_2 drives the Eq. (5) to the left, and therefore less indium will be incorporated into the solid phase. Thus, the application of an inert gas or nitrogen is very important in the MOVPE growth of InAlN.

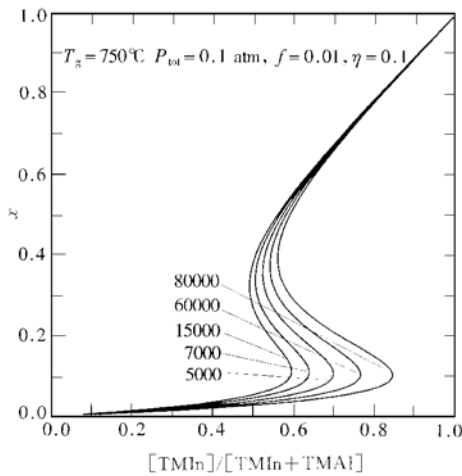


FIG. 5 Theoretical Curves of $\text{In}_x\text{Al}_{1-x}\text{N}$ Solid Composition as Function of Input Mole Ratio of Group III Metalorganic Compounds, Varying with Input V/III Ratio from 5000 to 80000. For Calculation, $T_g = 750^\circ\text{C}$, $P_{\text{tot}} = 0.1 \text{ atm}$, $P_{\text{III}} = 10^{-6} \text{ atm}$, $f = 0.01$ and $\eta = 0.1$

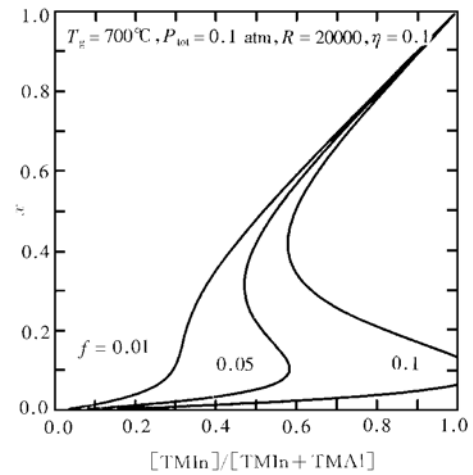


FIG. 6 Theoretical Curves of $\text{In}_x\text{Al}_{1-x}\text{N}$ Composition as Function of Input Mole Ratio of Group III Metalorganic Compounds, Varying with Hydrogen Fraction in Carrier Gas of 0.0, 0.05 and 0.1, Respectively.

4 Conclusions

A quasi-thermodynamic analysis for the MOVPE growth of $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys using TMAI, TMIn and ammonia has been proposed. The alloys were assumed which are synthesized by the reactions between ammonia and group III elements. The equilibrium partial pressures over $\text{In}_x\text{Al}_{1-x}\text{N}$ have been calculated. The relationship between the input vapor and the deposited solid composition for the $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys has been calculated. It is difficult to grow InAlN alloy, even harder than to grow InGaN, especially for the lattice-matched GaN, not only because $\text{In}_x\text{Al}_{1-x}\text{N}$ is an immiscible alloy but also InN has a very high In vapor pressure. The miscibility of InAlN alloy leads to a large fluctuation of indium or phase separation in alloys. It is also shown that aluminum has a strong preferential incorporation tendency into the $\text{In}_x\text{Al}_{1-x}\text{N}$ alloy. When growing InAlN, it is suitable to use lower growth temperature, optimized input V/III ratio and lower hydrogen fraction in the carrier gas and to reduce the decomposed fraction of ammonia. Indium droplets may be formed if the growth conditions are not selected properly.

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