

Thermodynamic Modeling and Phase Diagrams of Hexagonal and Cubic GaN Single-Crystal Film Growth by ECR-PEMOCVD Method*

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Abstract: Based on thermodynamic equilibrium theory, a chemical equilibrium model for GaN growth is given in electron cyclotron resonance plasma enhanced metalorganic chemical vapor deposition (ECR-PEMOCVD) system. Calculation indicates that the growth driving force are functions of growth conditions: group III input partial pressure, input V/III ratio, and growth temperature. Furthermore, the growth phase diagrams of hexagonal and cubic GaN film growth are obtained, which are consistent with our experimental conditions to some extent. Through analysis, it is explained the reason that high temperature and high input V/III ratio are favorable for hexagonal GaN film growth. This model can be extended to the similar systems used for GaN single-crystal film growth.

Key words: GaN; ECR-PEMOCVD; thermodynamic analysis; growth phase diagram

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1 Introduction

GaN is one of the most promising wide band gap semiconductors for applications in short-wave-length light emitters and high-temperature electronic devices^[1,2]. It is found that the kinetics and thermodynamics of GaN film growth relate to the following factors strongly: the kinds of source gases, substrate, growth pressure, growth temperature, carrier gas and geometry configuration of reactor chamber, which is explained by equilibrium

thermodynamic and fluid dynamics^[2]. Many investigators have made successful predictions for Al-GaInAsP III-V group materials using thermodynamic equilibrium models^[3~5]. Thermodynamic studies on metalorganic vapor phase epitaxial growth^[6~8] or molecular beam epitaxial growth^[9] of group III nitrides have been also reported and discussed recently.

This paper reports the thermodynamic study on GaN film grown in ECR-PEMOCVD system. In low-pressure MOCVD system, diffusion is the main mechanism of various molecules propagation,

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so the quasi-thermodynamic equilibrium can be reached at the gas-solid interface. The suitable growth phase diagrams of hexagonal and cubic GaN are calculated. The different growth mechanisms of hexagonal and cubic GaN are discussed.

2 The theoretical analysis of GaN growth in ECR-PEMOCVD system

In our ECR-PEMOCVD system, trimethylgallium (TMG) was used as the Ga source; H_2 was used as carrier gas. The N source was produced by discharge of N_2 in the ECR zone^[10]. GaN was epitaxially grown on Si(001)^[11], or GaAs(001) substrates^[12, 13]. In low-pressure MOCVD system, the growth area locates at the downstream of glow discharge of plasma, which is far away from magnetic fields in ECR zone, so we assume that no magnetic field exists in growth area on substrate surface. Thus the movement of active particles and gas molecules produced by ECR discharge is mainly a diffusion process, so we can divide GaN film growth process into following stages:

(1) Mixed gases and excited particles were delivered to the deposition area;

(2) Reactant molecules which remained gas phase diffused onto substrate surfaces from main flow;

(3) Reactant molecules were absorbed onto substrate surface;

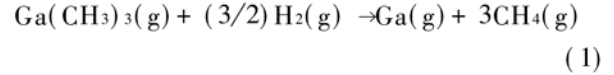
(4) Chemical reactions occurred between absorbed molecules or between absorbed molecules and gas molecules, desired deposition particles and reaction byproducts were produced, at the same time desired deposition particles migrated on substrate surface and combined into crystal lattice;

(5) Reaction byproduct molecules desorbed from substrate surface;

(6) Reaction byproduct molecules diffused into main flow outwards, then were vented to ambient atmosphere.

In such a system, a quasi-thermodynamic equilibrium can be reached to the gas-solid interface.

It is reported^[14, 15], when mixed with H_2 , TMG was decomposed irreversibly above 600°C according to the following homogeneous reaction near the vapor-solid interface:



Then $Ga(g)$ reacted with reactive nitrogen atoms delivered from gas phase to gas-solid phase interface, resulted in GaN film growth, namely



where g and s denote gas phase and solid phase, respectively.

The equilibrium constant expression of reaction

$$(2) \text{ is } K_p = \frac{1}{p_{Ga}p_N} \quad (3)$$

The following condition of restriction can be obtained from reaction (2)

$$p_{Ga}^0 - p_{Ga} = p_N^0 - p_N \quad (4)$$

where p_{Ga}^0 and p_N^0 denote input partial pressure of corresponding element respectively, p_{Ga} and p_N denote equilibrium partial pressure of corresponding element respectively. The driving force of reaction (2) can be obtained from expression (3) and (4)

$$\begin{aligned} \Delta p &= p_{Ga}^0 - p_{Ga} \\ &= p_{Ga}^0 - \frac{p_{Ga}^0(1-x) + \sqrt{p_{Ga}^0(1-x)^2 + 4/K_p}}{2} \\ &= p_{Ga}^0/2(1+x - \sqrt{(1-x)^2 + 4/(K_p p_{Ga}^0)}) \end{aligned} \quad (5)$$

where $x = p_N^0/p_{Ga}^0$, denotes input V/III ratio.

The equilibrium constant of reaction (3) is the following expression

$$\Delta G^0 = -RT \ln K_p \quad (6)$$

ΔG^0 can be obtained from the following expression^[16-20]

$$\Delta G^0 = A + B/T + CT \ln T + DT + ET^2 \quad (7)$$

where $A = -2.090 \times 10^2$, $B = 8.484 \times 10^2$, $C = -2.547 \times 10^{-3}$, $D = 9.189 \times 10^{-2}$, $E = 2.570 \times 10^{-11}$

As is pointed out, the above analysis is suitable for both hexagonal and cubic GaN, but the value of ΔG^0 is different for hexagonal and cubic GaN growth. The above value of ΔG is for hexagonal GaN growth. Because the value of ΔG^0 for cubic GaN is unknown now, we consider the different

value of ΔG^0 for that between graphite and diamond^[21]. Within the temperature range of 600~900°C, the value of ΔG (absolute value) of diamond is 4%~13% of that of graphite, however, when the structure difference of hexagonal and cubic GaN is considered not so large as that of graphite and diamond, we assume that the value of ΔG^0 (absolute value) of cubic GaN is 30% of that of hexagonal GaN. The reason for adopting the above assumption is that the following calculated growth phase diagrams of cubic GaN are well fit to our experimental data, and the calculating deviation is 5% or so, according to our recent theoretical calculation based on the thermodynamic and statistical physics^[22]. In the following discussion, GaN is referred to hexagonal GaN if cubic GaN or hexagonal GaN is not used in the text.

3 Results and discussion

Figure 1 shows the equilibrium partial pressure of Ga(g) and N(g) over GaN films as a function of input V/III ratio. The dotted denotes p_{Ga}^0 ; the dashed denotes vapor pressure of Ga metal, p_{Ga}^v . We can see that the equilibrium partial pressure changes dramatically when V/III ratio equals to 1, and that almost all Ga elements are segregated into solid phase when V/III ratio is greater than 1. So the equilibrium partial pressure of Ga(g) is very low. Contrary to this situation, almost all of N elements are segregated into solid phase when V/III ratio is less than 1. So the equilibrium partial pressure of N element will become very low.

Figure 2 shows the driving force for GaN deposition, Δp as a function of input V/III ratio for several input pressure of p_{Ga}^0 at 700°C. The driving force depends on input V/III ratio and input partial pressure of the group III elements. The Δp decreases with the decrease of Δp_{Ga}^0 , when Δp_{Ga}^0 remains constant, the Δp increases with the increase of the V/III ratio up to 1, then it becomes constant for V/III > 1, reflecting the deposition of Ga into the solid phase as shown in Fig. 1.

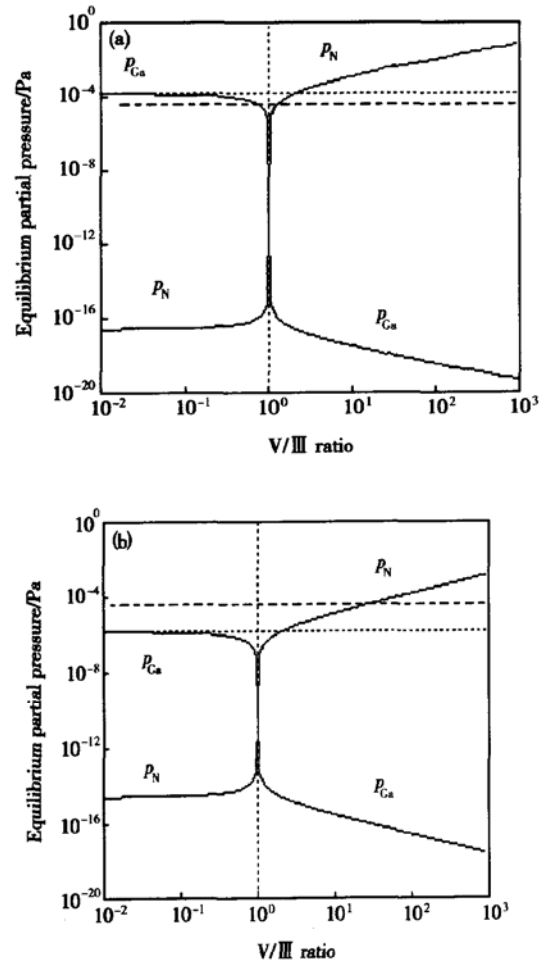


Fig. 1 Equilibrium partial pressure of Ga(g) and N(g) over GaN films as a function of input V/III ratio with p_{Ga}^0 is 1.33×10^{-4} Pa (a), 1.33×10^{-6} Pa (b) at 700°C, respectively

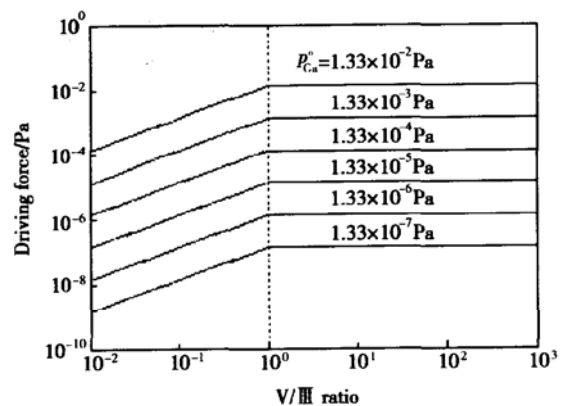


Fig. 2 Driving force for GaN deposition, Δp as a function of input V/III ratio for several input pressure of p_{Ga}^0 at 700°C

Figure 3 shows the calculated phase diagrams for hexagonal GaN(a), cubic GaN(b) deposition at different growth temperatures. In Figures, abscissa represents input V/III ratio, ordinate represents

the input partial pressure of III group source gas. There are three deposition modes^[5,6]: etching area ($p_{\text{Ga}} > \Delta p_{\text{Ga}}^0$), droplet area ($p_{\text{Ga}}^v < p_{\text{Ga}} < p_{\text{Ga}}^0$), and growth area ($p_{\text{Ga}} < \Delta p_{\text{Ga}}^v, p_{\text{Ga}} < p_{\text{Ga}}^0$).

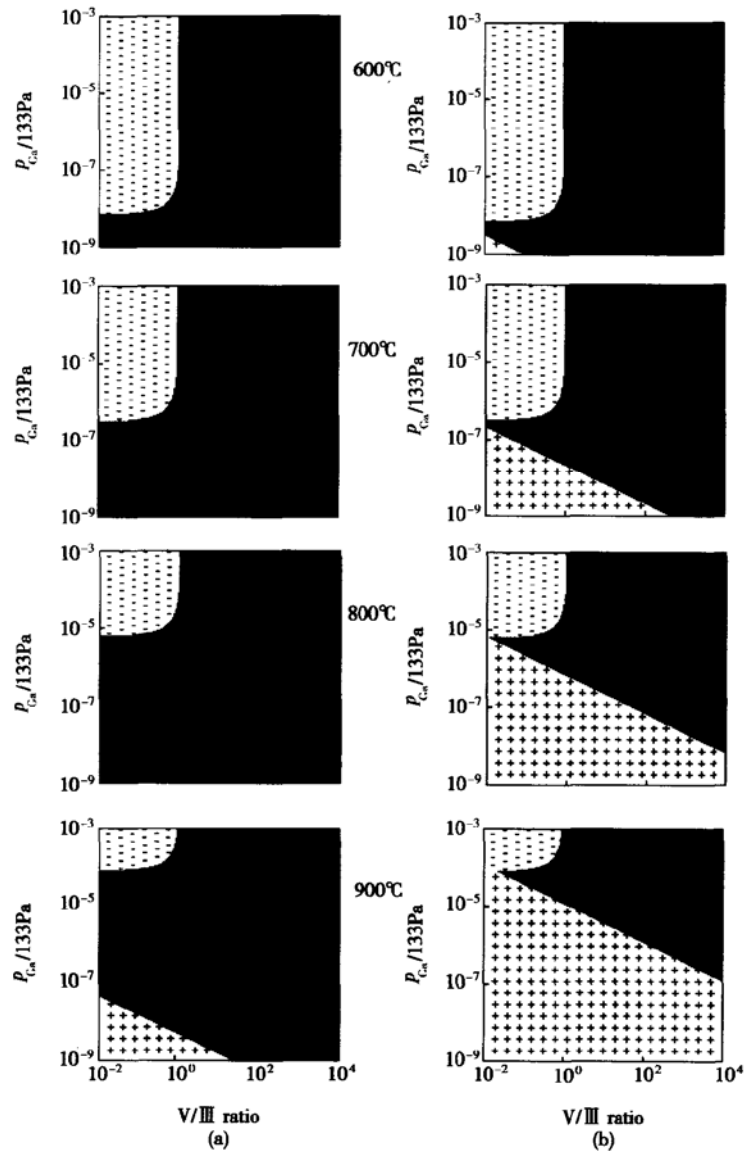


Fig. 3 Calculated phase diagrams for hexagonal GaN(a), cubic GaN (b) deposition at different growth temperatures — : droplet area; + : etching area; ■ : growth area

From Fig. 3(a), we can get the suitable conditions for hexagonal GaN growth. When V/III ratio is less than 1, the droplet area expands when the growth temperature is decreased. Moreover, the etching area emerges at high growth temperature.

Combined with the effect of the driving force of GaN growth, GaN growth areas should be located within the region that V/III ratio is greater than 1. It is well known that the growth at high temperature is favorable for improving the crystal quality

of GaN, so when selecting experimental parameters, high growth temperature and high V/III ratio are desired. Nevertheless, if selected growth temperature is too high, we can see that the etching area emerges except the droplet and growth areas, moreover, the etching area enlarges with increasing temperature, at the same time the growth area is restricted.

From Fig. 3 (b), the suitable conditions for cubic GaN growth can be obtained, which are different from those of hexagonal GaN growth. There is almost no growth area when V/III ratio is less than 1, the droplet area dominates in low temperature area, which will be constricted with increasing growth temperature, while the etching area will be enlarged quickly. As can be seen, the suitable growth conditions for cubic GaN is 600~700°C growth temperature and the V/III ratio should be greater than 1. In our experiments, the growth conditions for hexagonal and cubic GaN films growth are^[23]: $p_{\text{Ga}}^0 \approx 1.33 \times 10^{-2}$ Pa, growth temperature: 600~700°C, 580~650°C; input V/III ratio: 10~100, 2~20, respectively. Which are both located in the growth area of calculated growth phase diagrams.

From Fig. 3, as can be seen, at higher growth temperature (for example, 800°C), even at the same V/III ratio value (for example, 100), when p_{Ga}^0 is low (for example, 1.33×10^{-6} Pa), the cubic GaN is located in the etching area, while the hexagonal GaN is located in the growth area, so hexagonal GaN can be epitaxially grown on GaAs(001)^[24] or Si(001) substrate. That is, high temperature is favorable for hexagonal GaN growth.

It is well known that high input V/III ratio is favorable for hexagonal GaN growth, which can be explained from Fig. 4. At a given growth temperature, for example, 800°C, with the increasing input V/III ratio, the hexagonal and cubic GaN growth both trend to the growth area, but, unfortunately, the growth area of cubic GaN is less than that of hexagonal GaN. At the low p_{Ga}^0 range, a etching area emerges for cubic GaN, so with the increasing

input V/III ratio, p_{Ga}^0 is reduced and the cubic GaN growth will be located in the etching area gradually, but at the same time, the hexagonal GaN growth is located in the growth area already. That is, high input V/III ratio is favorable for hexagonal GaN growth^[25].

4 Summary

The theoretical analysis for hexagonal and cubic GaN film growth is carried out with equilibrium thermodynamic method in our ECR-PEMOCVD system. The driving force for GaN growth is dependent on the growth conditions including the input partial pressure of III group source (p_{Ga}^0), the input V/III ratio, and growth temperature. Through calculations the growth phase diagrams of hexagonal and cubic GaN film growth are obtained, which are consistent with our experimental conditions to some extent. Through analysis, we explained the reasons that high temperature and high input V/III ratio are favorable for hexagonal GaN film growth. The above model and analysis can be easily extended to similar systems, such as gas source molecular beam epitaxy (GSMBE)^[26], metalorganic molecular beam epitaxy (MOMBE)^[27], for growing GaN single-crystal film.

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采用 ECR-PEMOCVD 方法进行立方和六方 GaN 单晶薄膜生长的准热力学模型和相图*

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摘要: 基于热力学平衡理论, 对在电子回旋共振等离子体增强金属有机化学气相沉积系统中的 GaN 薄膜生长给出了一个化学平衡模型. 计算表明, GaN 生长的驱动力 Δp 是以下生长条件的函数: III 族输入分压, 输入 V/III 比, 生长温度. 计算了六方和立方 GaN 的生长相图, 计算结果和我们的实验结果显示出一定的一致性. 通过分析, 解释了高温和高 V/III 比生长条件适合六方 GaN 的原因. 上述模型可以延伸到用于 GaN 单晶薄膜生长的类似系统中.

关键词: GaN; ECR-PEMOCVD; 热力学分析; 生长相图

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