ABSTRACT: We presented a comprehensive thermodynamic study of the gas-phase chemical reaction mechanism of the AlN growth by high-temperature metal-organic chemical vapor deposition, investigating the addition reactions, pyrolysis reactions, and polymerization of amide DMANH₂ and subsequent CH₄ elimination reaction. Based on the quantum chemistry calculations of the density functional theory, the main gas-phase species in different temperature ranges were predicted thermodynamically by comparing the enthalpy difference and free energy change before and after the reactions. When T > 1000 °C, it was found that MMAl, (MMAlNH)₂, and (MMAlNH)₃ are the three most probable end gas products, which will be the main precursors of surface reactions. Also, in high temperatures, the final product of the parasitic reactions is mainly (DMA1NH₂)₂ and (DMA1NH₂)₃, which are easy to decompose into small molecules and likely to be the sources of AlN nanoparticles.

1. INTRODUCTION
Aluminum nitride (AlN) film materials have particularly be attractive as important semiconductor materials because of the wide range of direct band gap, high piezoelectric coefficient and thermal conductivity, high acoustic wave propagation speed, excellent optical and mechanical properties, and so forth.¹⁻⁴ It has been explored for use in the fields of high-power microelectronic devices, blue and ultraviolet photodetectors, and light-emitting diodes.⁵ Metal organic chemical vapor deposition (MOCVD) is the dominant method of depositing AlN thin films, considering both production efficiency and crystallization quality.⁶ During the process of epitaxial growth, Al atoms and aluminum free radicals are less mobile, which leads to difficult migration process. To promote the surface migration of Al atoms and aluminum free radicals, the growth of high-quality AlN thin films has been intensively performed by high-temperature MOCVD (HT-MOCVD).⁷ At high growth temperature, AlN thin films can achieve a high surface growth rate, and the resultant AlN surface is atomically flat. However, contributed to high growth temperature and bond energy of Al–N, the gas-phase chemical reaction will become complicated, and especially, the parasitic reactions will unavoidably occur during the HT-MOCVD process.⁸ The parasitic reactions not only cause the waste of source gas but also seriously affect the growth rate, growth uniformity, and crystallization quality. Therefore, in order to understand the gas-phase chemical reaction mechanism in the growth of AlN during HT-MOCVD, we study the reaction paths, energy, and products. In the present study, Mihopoulos et al.⁹ first proposed that the formation of dimers and trimer is the major pathway for the decreased growth rate with increasing temperature and then decompose into AlN nanoparticles, and this kind of particles was observed in the experiment by Creighton,¹⁰ which further confirmed the validity of the model. Additionally, Nakamura et al.¹¹ proposed that under the condition of excess NH₃, the potential energy barrier of the methane elimination is reduced considerably. Despite progress in the gas-phase chemical reaction mechanism in the growth of AlN thin films by MOCVD, there are still many controversies about the reversible growth of the adducts, TMAl:NH₃, and the growth of AlN main gaseous products during the epitaxial growth process. Especially, the paths and conditions of the parasitic reactions and the products by HT-MOCVD are still unclear because of the limitations of experimental condition and the complexity of the intermediate reaction processes.

In this paper, we analyze the gas-phase chemical reaction mechanism in the growth of AlN thin films during HT-MOCVD comprehensively by a thermodynamics study. In fact, the growth rate, growth uniformity, and crystallization quality of AlN growth by MOCVD are influenced not only by
temperature but also by pressure and gas flow rate. However, the thermodynamics study in this paper focused on the microscopic molecules and the effect of high temperature on the gas-phase chemical reactions, so the calculation results avoid other factors. We have done the quantum chemistry calculations based on the density functional theory (DFT), showing that higher temperature is favorable for the parasitic reactions, and the gas-phase chemical reaction paths and products are temperature dependent.

2. GAS REACTION MECHANISM AND CALCULATION MODEL

2.1. Gas Reaction Mechanism. For the accuracy and simplicity of the model, on the basis of the previous studies, the gas-phase chemical reaction pathways of AlN growth used in our work are shown in Figure 1. We can conclude that the routes of AlN growth can mainly divide into three categories: adduct pathways (G1–G5), pyrolysis pathways (G6–G8), and parasitic pathways (G9–G20). TMAl can convert to a Lewis acid–base adduct (TMAl:NH3) by sharing an electron pair with NH3, which constitutes the foundation of adduct pathways by eliminating CH4 to produce DMAlNH2, or successively decompose into DMAI, MMAI, and Al during pyrolysis pathways. In addition, DMAlNH2 could polymerize in the gas phase to generate dimers and trimmers, which would decompose at high temperature and generate AlN small molecular substances. Gas-phase parasitic reactions lead to a serious waste of organic precursors and have negative effect on the efficacy and quality of AlN film. Therefore, the study of polymerization elimination reaction (parasitic reaction) is to understand the formation of nanoparticles in the process of AlN growth and the gas precursors that ultimately participate in surface reactions.

2.2. Calculation Model. The numerical simulation has been completed using the Gaussian 09 software package. In the mathematical theory, the electron orbitals in the system are called the basis group. The higher the level of the base group, the more detailed the description of the electron orbitals, which will not only greatly improve the accuracy of the calculation but also introduce complex calculations. There are many base groups to choose from in the Gaussian 09. The base groups used to calculate the gas-phase reaction path of growing AlN at high temperature are mainly as follows: (1) Group 6-31G(d)(6-31G*) atoms of H–Cl range elements, belonging to the polarized group. The base group is widely used and can be used for most calculations. (2) The base group 6-311G(d,p) is used for the atoms of the H–Br range element, which is the polarized base group. (3) The base group LANL2DZ is used for atoms of elements larger than the third period and is a pseudopotential group. Taking into account the advantages of computational complexity and accuracy, we use the B3LYP/6-31G(d) functional and basis set in DFT to optimize the geometric structure and calculate the frequency of reactants, products, and transition states during the growth process of AlN by HT-MOCVD. In order to determine the transition state, which can connect the reactants and products, the intrinsic reaction coordinate calculation of transition-state structure is carried out. Based on the structural optimization, the corresponding molecular energies have been calculated at the B3LYP/[LanL2DZ+6-311G(d,p)] level. For C, H, and N atoms, the 6-31G(d) basis set is used to optimize the molecular structure, and the 6-311G(d,p) basis set is used to calculate the energy. The molecular structure of the optimized main reactants is shown in Figure 2.

TMAl has the C₃ symmetry, where the Al–C bond length is 0.1975 nm, and the C–Al–C bond angle is 120°, which is consistent with the experimental value of 0.1957 nm. TMAl:NH3 has the Cᵥ symmetry, and the C–Al–C bond

Figure 1. Schematic diagram of main gas-phase reaction paths for MOCVD growth of AlN [adduct pathways (G1–G5), pyrolysis pathways (G6–G8), and parasitic pathways (G9–G20) 20–1400 °C].

Figure 2. Molecular structure of optimized main reactants (the pink, blue, gray, and white spheres represent the Al, N, C, and H elements, respectively) (a) TMAl, (b) TMAl:NH3, (c) TS1, (d) DMAINH₂, (e) NH₃:TMAl:NH₃, (f) TS2, (g) (DMAINH₂)_2, (h) (DMAINH₂)_3, (i) (AlN)_2, and (j) (AlN)_3.
angle decreases from 120 to 117.22°. This fact states that the metal atoms of Al in the adducts are no longer in the same plane with three C atoms when the N atom approaches to the metal atom and forms one coordination bond because the lone electron pair in the coordination bond occupies more space than each of the three bonding electron pairs. For the two-NH3 adduct, NH3:TMAl:NH3, the metal atoms Al are still located in the same plane with three C atoms, but the Al-N bond length extends from 2.13 Å in TMAl:NH3 with one coordination bond to 2.29 Å in NH3:TMAl:NH3 with two coordination bonds. These indicated that the strength of the first coordination bond is weakened by the recombination of a NH3 molecule. For the structures of the amide DMA1NH2 which is equivalent to TMAl in CH4 is replaced by NH3, the Al–N bond length is 0.1789 nm, and the C–Al–C bond angle is 123.52°, which is basically consistent with the calculated value in 0.1790 nm, 123.0°. Figure 2 also shows the transition-state (TS1 and TS2) structures for the decomposition of the two adducts. (DMA1NH2)2 has a ring structure, in which the Al–N bond length is 0.1990 nm, which is basically consistent with the structure in literature values.10 (AlN)2 and (AlN)3 are four-membered rings and six-membered ring structures, which are basically consistent with the structures in the document.11

### 2.3. Chemical Thermodynamics

In the growth of AlN thin films by HT-MOCVD, there is a large temperature gradient above the substrate during the nonisothermal flow of the gas in the reactor. The enthalpy difference ΔH and Gibbs free energy difference ΔG of the polymerization reaction are calculated at different temperatures. According to chemical thermodynamics, the relationships for internal energy E, enthalpy H, entropy S, and Gibbs free energy G of 1 mol ideal gas are

\[ G = H - TS \]  
\[ H = E + RT \]

To determine the direction of chemical reaction, the enthalpy difference between the reaction before and after the reaction is ΔH and ΔG. The former gives the reaction energy barrier (transition state), and the latter gives the probability of spontaneous reaction. During calculations on thermodynamic properties by Gaussian, the statistical mechanics theory is used, as is shown in Section 2.3 of ref 9 for the ideal gas assumption.

### 3. RESULTS AND DISCUSSION

#### 3.1. Adduct Decomposition

In the addition reaction, according to the conditions of NH3 in excess or not, we summed up five adduct reaction paths for AlN HT-MOCVD growth, and the reaction equation is as follows

\[ \text{G1: TMAl} + \text{NH}_3 \rightleftharpoons \text{TMAl:NH}_3 \]  
\[ \text{G2: TMAl:NH}_3 \rightarrow T S 1 \rightarrow \text{DMA1NH}_2 + \text{CH}_4 \]  
\[ \text{G3: DMA1NH}_2 + \text{NH}_3 \rightarrow \text{DMA1NH}_2: \text{NH}_3 \]  
\[ \text{G4: } \text{TMAl:NH}_3 + \text{NH}_3 \rightarrow \text{NH}_3: \text{TMAl:NH}_3 \]  
\[ \text{G5: } \text{NH}_3: \text{TMAl:NH}_3 \rightarrow T S 2 \rightarrow \text{NH}_3: \text{DMA1NH}_2 + \text{CH}_4 \]

The addition reaction of TMAl and NH3 forms adduct TMAl:NH3 at room temperature, and the adducts may also be decomposed into TMAl and NH3 (G1). Although at higher temperatures, TMAl:NH3 experiences transition-state TSI, eliminates CH4, and produces amide DMA1NH2 (G2). In adduct TMAl:NH3 when temperature T \( \leq 200 \) °C, TMAl:NH3 will be decomposed into TMAl and NH3, when T \( \geq 300 \) °C. By using the linear difference method in mathematics, it is concluded that when T = 268 °C, G1 is bidirectionally reversible, and the formation and dissociation are in equilibrium, and the same result can be obtained by the infrared spectrum, as shown in Figure 4. For the G2, the TMAl:NH3 undergoes a transition state (TS1) to form the amide DMA1NH2, the ΔG < 0 in all temperature ranges, and the reaction can react spontaneously. As the temperature increases, the reaction energy barrier changes very little while the difference of free energy changes a lot. When T = 1400 °C, ΔG reduces to –68.28 kcal/mol. Therefore, higher temperature is favorable for the G2 that TMAl:NH3 eliminates CH4 to generate DMA1NH2. For the G3, when the temperature is low and ΔG < 0, DMA1NH2 spontaneously combines one NH3 molecule. As the temperature increases, until about 1400 °C, ΔG increases to 44.09 kcal/mol, so G3 is hard to react.

It can be concluded that DMA1NH2 has the following three paths during the HT-MOCVD: (1) the amino DMA1NH2 undergoes a transition state and eliminates methane to

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**Figure 3.** When NH3 is not excessive, the enthalpy change of the addition pathway is H (a) and the free energy change G (b).

**Figure 2.** The calculation results of NH3 with nonexcessive G1, show that TMAl and NH3 spontaneously form coordination structures.
generate MMAlNH. (2) The amino DMAINH₄ generates (DMAINH₂)₂ by polymerization. (3) The amino DMAINH₂ generates (DMAINH₂)₃ by polymerization. The results of the relative energy show that the (2) and (3) paths are the spontaneous reaction. Therefore, it can be concluded that the main path of amino DMAINH₂ is to generate polymers instead of to decompose.

Because the molar ratio of NH₃ to TMAl in the gas phase is nearly 10,000, the probability of TMAl:NH₃ binding to NH₃ is large. As mentioned in 4, when the temperature is at or slightly above room temperature, there is evidence that NH₃ and TMAl form an adduct in a ratio of 2:1, and the energy of this compound is more stable.

It can be seen from Figure 5 that because of the excess of NH₃, the excess TMAl:NH₃ forms a more stable adduct NH₃:TMAl:NH₃ with NH₃ at a lower temperature; as the temperature reaches the intermediate temperature region, the temperature of NH₃:TMAl:NH₃ also increases. The heated adduct NH₃:TMAl:NH₃ crosses the energy barrier and undergoes TS2 to eliminate a methane molecule. In the high-temperature region, NH₃:TMAl:NH₃ is more prone to reverse decomposition to NH₃ and TMAl:NH₃ and then undergoes TS1 to eliminate methane molecules.

3.2. Pyrolysis Pathways. It can be seen from Figure 6 that the pyrolysis reaction of TMAl and MMAIN requires high-temperature activation while the demethylation of DMAIN to form MMAIN is relatively easy to occur with MMAIN. When T > 1000 °C, the pyrolysis reaction of DMAIN to MMAIN will proceed spontaneously. The pyrolysis path reaction equation is as follows

\[ G6: \text{TMAI} \rightarrow \text{DMAI} + \text{CH}_3 \]  
\[ G7: \text{DMAI} \rightarrow \text{MMAIN} + \text{CH}_3 \]  
\[ G8: \text{MMAIN} \rightarrow \text{Al} + \text{CH}_3 \]

3.3. Parasitic Reactions. The amide DMAINH₂ has strong chemical activity and can be oligomerized to form dimers or trimers. Meanwhile, the oligomers will further decompose and eventually become AlN polymers by eliminating methane, as shown in equations G9–G13. The paths G9–G13 represent the dimerization and elimination of amide.

\[ G9: 2\text{DMAINH}_2 \rightarrow (\text{DMAINH}_2)_2 \]  
\[ G10: (\text{DMAINH}_2)_2 \rightarrow \text{TS3} \rightarrow (\text{DMAINH})(\text{MMAINH}) + \text{CH}_4 \]  
\[ G11: (\text{DMAINH})(\text{MMAINH}) \rightarrow \text{TS4} \rightarrow (\text{MMAINH}) + \text{CH}_4 \]  
\[ G12: (\text{MMAINH})_2 \rightarrow \text{TS5} \rightarrow (\text{MMAINH})(\text{AlN}) + \text{CH}_4 \]  
\[ G13: (\text{MMAINH})(\text{AlN}) \rightarrow \text{TS6} \rightarrow (\text{AlN})_2 + \text{CH}_4 \]  

Figure 7 shows the enthalpy and free energy changes of the formation of (MMAINH)_2 by polymerization and decomposition of DMAINH₂ at different temperatures. For the G9, when T < 600 °C, ΔG < 0, and because the energy barrier (ΔH < 0), the dimer (DMAINH₂)₂ is generated. When T > 1000 °C and ΔG > 0, the dimer is more easily decomposed, and the reverse reaction of G9 reacts, and the ΔH ≈ 48.98 kcal/mol. The reaction reaches equilibrium at 880 °C, and the ΔG ≈ 0. Therefore, as the temperature increases, until about 1400 °C, the dimer is easily decomposed into small molecules, which are likely the sources of AlN nanoparticles. For the G10, when T > 460 °C and ΔG > 0, the G10 can react spontaneously. For the G11, at all calculated temperatures and ΔG > 0, the reaction can react spontaneously while will undergo a transition state, and the energy barrier is 34–37 kcal/mol. For the G12 and G13, ΔG > 0, and the energy
barrier is large (60−100 kcal/mol) in all temperature ranges. Therefore, the (MMAlNH)2 eliminates CH4 to generate (AlN)2, which is hard to react. To sum up, the main gas-phase reaction end product generated by polymerization and elimination reactions during the HT-MOCVD is (MMAlNH)2 instead of (AlN)2.

Similar to the decomposition of dimer, trimer may also decompose into polymers of AlN. The paths G14−G20 represent the trimerization and elimination of amide.

G14: \((\text{DMAlNH}_2) + (\text{DMAlNH}_2) \rightarrow (\text{DMAlNH}_2)_3\)

G15: \((\text{DMAlNH}_2)_3 \rightarrow \text{TS7} \rightarrow (\text{DMAlNH}_2)_2 \text{MMAlNH} + \text{CH}_4\)

G16: \((\text{MMAlNH})_2 \text{MMAlNH} \rightarrow \text{TS8} \rightarrow \text{DMAlNH}_2\)

G17: \((\text{MMAlNH}_2)_2 \text{MMAlNH} \rightarrow \text{TS9} \rightarrow (\text{MMAlNH})_3 + \text{CH}_4\)

G18: \((\text{MMAlNH})_3 \rightarrow \text{TS10} \rightarrow (\text{MMAlNH})_2 \text{AlN} + \text{CH}_4\)

G19: \((\text{MMAlNH})_2 \text{AlN} \rightarrow \text{TS11} \rightarrow (\text{MMAlNH})_2 + \text{CH}_4\)

G20: \((\text{MMAlNH})_2 \text{AlN} \rightarrow \text{TS12} \rightarrow (\text{AlN})_3 + \text{CH}_4\)

Figure 6. Enthalpy change of pyrolysis path \(\Delta H\) (a) and free energy change \(\Delta G\) (b).

Figure 7. Polymerization and elimination paths (dimer): (a) \(\Delta H\) and (b) \(\Delta G\).

Figure 8 shows the enthalpy change and free energy change of the formation of \((\text{DMAlNH}_2)_3\), and the decomposition reacts at different temperatures. For the G14, when \(T < 300^\circ\text{C}\) and \(\Delta G < 0\), there is no energy barrier, and it is easy to generate \((\text{DMAlNH}_2)_3\); when \(T > 600^\circ\text{C}\) and \(\Delta G > 0\), the trimer is more easily decomposed, the reverse reaction of G14 reacts, and \(\Delta H \approx 27\) kcal/mol. The reaction reaches equilibrium at \(372^\circ\text{C}\) and \(\Delta G \approx 0\). Therefore, as the temperature increases, until about \(1400^\circ\text{C}\), the trimer is easily decomposed into small molecules, which are likely the sources of AlN nanoparticles. For the G15, when \(T > 200^\circ\text{C}\) and \(\Delta G < 0\), the reaction can be spontaneous. Further eliminating the two CH4 for \((\text{DMAlNH}_2)_2(\text{MMAlNH})\), the \((\text{MMAlNH})_3\) is generated and is less than zero in all calculated temperature ranges. The transition states, TS8 and TS9, exist in the G16 and G17, respectively, and the energy barriers are \(\Delta H \approx 36−37\) kcal/mol and \(\Delta H \approx 26−28\) kcal/mol. For the G18−G20, \(\Delta G > 0\), and there is a need to overcome a high energy barrier about \(\Delta H \approx 55−70\) kcal/mol in all temperature ranges. Therefore, the \((\text{MMAlNH})_3\) eliminates CH4 to generate \((\text{AlN})_3\), which is hard to react. It is thus confirmed that the main gas-phase reaction end product generated by the polymerization and elimination reaction of the trimer during the HT-MOCVD is \((\text{MMAlNH})_3\) instead of \((\text{AlN})_3\).
Figure 8. Polymerization and elimination paths (trimer) (a) $\Delta H$ and (b) $\Delta G$.

4. CONCLUSIONS

In summary, we analyzed the gas-phase chemical reaction mechanism of the AlN growth by HT-MOCVD comprehensively by the thermodynamics study. According to the enthalpy difference and the change of free energy in thermodynamic analysis, the main mechanism of Al source participation reactions was clearly explained. The temperature range of each gas-phase reaction paths in AlN growth by HT-MOCVD was divided from the longitudinal temperature gradient. It was found that there was a critical temperature $T_*$ ($T_* \approx 268 ^\circ C$) for the formation of TMAI:NH$_3$ adduct. When $T > 1000 ^\circ C$, the pyrolysis of MMAI from DMAI will proceed spontaneously, and the DMAI is one of the main surface reaction precursors. The reaction of CH$_4$ elimination to MMAINH$_3$ by addition-derived (DMAINH$_3$)$_2$ is easy to occur at $460 ^\circ C < T < 880 ^\circ C$, and the reaction of CH$_4$ elimination to MMAINH$_3$ by addition-derived (DMAINH$_3$)$_2$ is easy to obtain at $175 ^\circ C < T < 372 ^\circ C$. Also, with the temperature increases, until about $1400 ^\circ C$, the (DMAINH$_3$)$_2$ and (DMAINH$_3$)$_3$ are easily decomposed into small molecules, which are likely the sources of AlN nanoparticles. In the HT-MOCVD process of AlN growth, MMAI, (MMAINH)$_2$, and (MMAINH)$_3$ are the most likely gas-phase reaction end precursors, which will determine the surface reaction growth of AlN.

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Notes

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