

# Regional Density Functional Theory for Parasitic Reaction in III-V Nitride Semiconductor Crystal Growth

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## Introduction

Wide-band-gap GaN and related nitrides have attracted much attention because of their application for blue light-emitting diodes and lasers. Rapid progress in the metal-organic vapor phase epitaxy (MOVPE) technology makes it possible to fabricate highly efficient GaN and InGaN devices in atmospheric pressure. However, the growth of AlGaN layers in atmospheric-pressure MOVPE is inhibited by gas-phase reactions among precursors leading to adduct formation, called “parasitic reactions.”

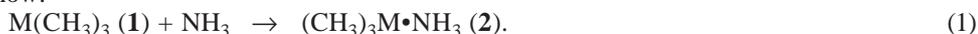
In this study, we have investigated the detailed reaction mechanism of the parasitic reactions and related gas-phase reactions in  $M(\text{CH}_3)_3/\text{H}_2/\text{NH}_3$  systems following the elimination of methane, where M denotes Al, Ga, or In for trimethylaluminum (TMA), trimethylgallium (TMG), or trimethylindium (TMI) respectively, by carrying out *ab initio* quantum chemical calculations. Furthermore, we have studied the electronic processes of the formation of coordinate bond between TMA, TMG, TMI, and ammonia in terms of the regional density functional theory [1-3], and discussed the characteristics of the M–N coordination interaction, which should be a key factor in the control of the parasitic reactions.

## Computational Methods

*Ab initio* quantum chemical calculations were performed with the Gaussian 94 program package [4]. The geometries of model reaction species and transition states (TSs) for the methane elimination were optimized by the analytical energy gradient method at the Lee-Yang-Parr gradient-corrected correlation functional with the Becke’s 3 hybrid parameters (B3LYP), using LanL2DZ\* basis set. The Mulliken population analysis was carried out by means of the Kohn-Sham (KS) orbitals.

## Results and Discussions

$M(\text{CH}_3)_3$  molecule (**1**) makes a very stable complex with ammonia,  $(\text{CH}_3)_3M\cdot\text{NH}_3$  (**2**), due to the M–N coordinate bond as you know:

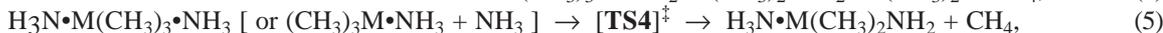
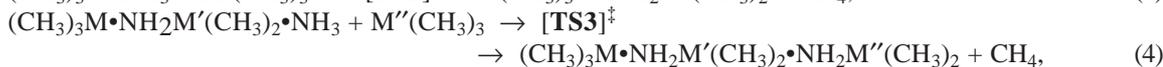
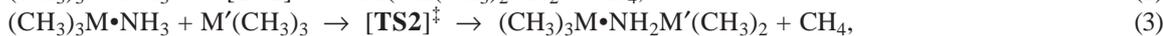


As shown in Table 1, both of the stabilization energy of complex formation and the M–N bond order are the largest in the TMA +  $\text{NH}_3$  system, but the quantities of charge transfer from ammonia to TMA and to TMG are almost equal to each other in terms of the Mulliken population analysis. We found that each of TMA monomer, the  $\text{Al}(\text{CH}_3)_3$  part and the  $\text{NH}_3$  part in  $(\text{CH}_3)_3\text{Al}\cdot\text{NH}_3$  complex is polarized more remarkably than the corresponding TMG monomer and parts in  $(\text{CH}_3)_3\text{Ga}\cdot\text{NH}_3$  complex. Therefore it is considered that the difference in the M–N bonding energies between  $(\text{CH}_3)_3\text{Al}\cdot\text{NH}_3$  and  $(\text{CH}_3)_3\text{Ga}\cdot\text{NH}_3$  is caused by the dipole-dipole interaction between **1** and ammonia. In the TMI +  $\text{NH}_3$  system, the largest polarization of the same kind is observed, but the stabilization energy of complex formation is small because the charge transfer from ammonia to TMI is poor.

Fig. 1 shows electron acceptor region  $P$  and an electron donor region  $Q$  which we set up for the analyses in terms of the regional density functional theory. The region  $P$  consists of two sub-regions  $P_1$  and  $P_2$ . The former is the inside of a cubic box, where the nucleus of M puts on the center. The latter is made up of three cubic boxes with symmetry of 3-fold rotation, including a  $\text{CH}_3$  group respectively. The regional electron number of the electron acceptor region,  $N_P$ , was computed by means of the analytical integration algorithm [2]. Fig. 2 shows change of the regional electron numbers of sub-region,  $N_{P1}$  and  $N_{P2}$ , along the reaction coordinate, respectively. The increase of  $N_{P1}$  is mainly due to intermolecular influx of the lone-pair electrons of ammonia into the  $P_1$  box by the coordinate bond, when the complex formation proceeds. Curves of  $N_{P1}$  indicate that charge transfer acceptabilities of TMA and TMG are almost equal, and that of TMI is inferior to others. On the other hand, the increase of  $N_{P2}$  is caused by intramolecular flow of the electrons from the M atom to  $\text{CH}_3$  groups as an ammonia molecule approaches. It means that the polarization in the  $M(\text{CH}_3)_3$  part is intensified when the complex **2** is fabricated. This tendency is accordance with the result of the Mulliken population analysis that the negative charge in the  $M(\text{CH}_3)_3$  part is raised after the formation of complex **2**, as shown in Table 1.

Furthermore, we have discussed the regional electronic energy  $E_P$  for the region  $P$ , which can be calculated by using the regional electron number in terms of recent study of the regional density functional theory [1].  $E_P$  is reduced by electron transfer processes due to the redistribution of electrons with respect to the approach of ammonia. In the early stage of the complex formation,  $E_P$  for the TMI +  $\text{NH}_3$  system is the lowest by the large polarization, but  $E_P$  for  $(\text{CH}_3)_3\text{Al}\cdot\text{NH}_3$  is much more lower by the charge transfer in fabrication of the coordinate bond.

We have also discussed many sorts of the gas-phase reactions in  $M(\text{CH}_3)_3/\text{H}_2/\text{NH}_3$  systems following the elimination of methane as follows:



and so on. It is clearly shown that the Al source gases enhance reactivity, and the adduct-derived chain compounds grow successively with high exothermicity, as listed in Table 2. In the presence of excess ammonia (reactions 5 and 6), we have indicated that potential energy barrier of the methane elimination is reduced considerably.

## Conclusions

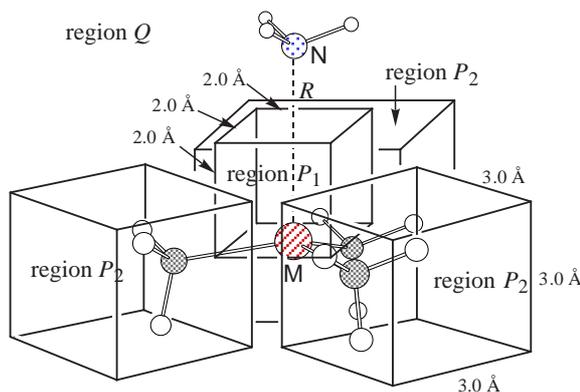
We have demonstrated that the strong Al–N coordination interaction contributes remarkably to the stabilization of the reaction system, by means of the detailed analysis of the electronic process and the reaction mechanism. The regional density functional theory has disclosed the driving force of the stability in electronic process. The fine control of the Al–N coordination interaction would make possible it to control the parasitic reactions; for example, the substitution of metal source may have a possibility of inhibiting the parasitic reactions. In the presence of excess ammonia, we have proved that potential energy barrier of the methane elimination is further reduced.

## References

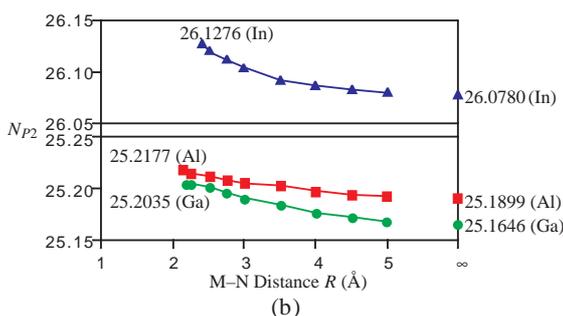
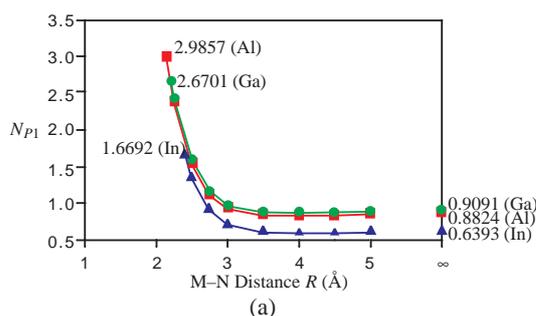
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**Table 1.** Stabilization energy (kcal/mol) and Mulliken population analysis of  $(\text{CH}_3)_3\text{M}\cdot\text{NH}_3$  complex formation.

M =	Al	Ga	In
Stabilization energy	-23.17	-18.92	-18.22
Bond order of M–N in <b>2</b>	0.337	0.287	0.194
Mulliken charge transfer for $\text{NH}_3 \Rightarrow \mathbf{1}$ in <b>2</b>	0.179	0.179	0.128
Atomic charge in <b>1</b>			
M	0.962	0.869	1.054
CH <sub>3</sub> part	-0.321	-0.290	-0.352
Atomic charge in <b>2</b>			
M	1.008	0.878	1.112
CH <sub>3</sub> part	-0.396	-0.352	-0.414
N	-0.943	-0.925	-0.966
amino-H	0.374	0.368	0.365



**Fig. 1.** Regional partitioning for the regions  $P$  and  $Q$ .



**Fig. 2.** Regional electron numbers of sub-region, (a)  $N_{P1}$  and (b)  $N_{P2}$ , in  $\text{M}(\text{CH}_3)_3 + \text{NH}_3$  system.

**Table 2.** Relative energies of  $\text{CH}_4$  elimination by bimolecular mechanism (reactions 3 and 6) (kcal/mol).

M/M' =	Al/Al	Al/Ga	Ga/Al	Ga/Ga	Ga/In	In/Ga	In/In
$\text{M}(\text{CH}_3)_3 + \text{M}'(\text{CH}_3)_3 + 2\text{NH}_3$	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$(\text{CH}_3)_3\text{M}\cdot\text{NH}_3 + \text{M}'(\text{CH}_3)_3 + \text{NH}_3$	-23.17	-23.17	-18.92	-18.92	-18.92	-18.22	-18.22
<b>TS2</b> + $\text{NH}_3$	2.97	8.40	4.85	11.54	10.78	10.90	10.04
$(\text{CH}_3)_3\text{M}\cdot\text{NH}_2\text{M}'(\text{CH}_3)_2 + \text{CH}_4 + \text{NH}_3$	-45.09	-41.91	-40.65	-37.41	-37.91	-36.78	-36.69
$(\text{CH}_3)_3\text{M}\cdot\text{NH}_3 + (\text{CH}_3)_3\text{M}'\cdot\text{NH}_3$	-46.34	-42.09	-42.09	-37.83	-37.14	-37.14	-36.45
<b>TS5</b>	-10.56	-2.90	-5.51	2.39	-3.19	2.93	-2.78
$(\text{CH}_3)_3\text{M}\cdot\text{NH}_2\text{M}'(\text{CH}_3)_2\cdot\text{NH}_3$	-68.62	-61.63	-63.80	-56.74	-56.70	-55.67	-56.15