

A Reaction Pathway of Surface-Catalyzed Ammonia Decomposition and Nitrogen Incorporation in Epitaxial Growth of Gallium Nitride

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Abstract

We report density-functional calculations that clarify atom-scale mechanisms of vapor-phase epitaxial growth of GaN with gas sources of trimethylgallium and ammonia. We identify various stable adsorption structures of a Ga atom and NH_x molecules ($x = 0 - 3$) on GaN(0001) surfaces and find that NH_2 and NH units spontaneously intervene in Ga-Ga surface bonds on Ga-rich GaN (0001) surface. We then explore the reaction in which NH_3 on the surface is decomposed and become an N-incorporated structure, $-\text{Ga}-(\text{NH})-\text{Ga}-$, on the Ga-rich GaN (0001) and find that the reaction occurs with the energy barrier of 0.63 eV. Further exploration reveals that a reaction of H_2 desorption occurs with the energy barrier of 2 eV, leaving the N atom incorporated in the Ga-N network. This barrier can be overcome when we consider the chemical potential of an H_2 molecule in the gas phase at the growth temperature. This N incorporation on GaN is a new growth mechanism catalyzed by the growing surface.

1 Introduction

The nitride semiconductor with group IIIb elements (Al, Ga, and In) is one of the most important semiconductors due to its wide range of direct band gaps, becoming a principal material in optoelectronic devices.¹⁻³ This premier status of the nitride semiconductor was triggered and established by a pioneering work on crystal growth of GaN:^{4,5} i.e., the introduction of the buffer AlN layer and the hydrogen removal by the electron-beam irradiation and later by thermal treatment⁶ in improving the thin-film quality in Metal-Organic Vapor-Phase Epitaxy (MOVPE).⁷

In addition to the optoelectronics applications, GaN has emerged as a key material in power electronics.⁸ This is obviously due to its wide band gap and robustness under harsh environment. In the power devices, interfaces between semiconductors and insulators inevitably include several interface alignments, thus demanding the higher quality of epitaxial GaN films.

Epitaxial growth is an atom-scale scrap-and-build process: The growing surface, though at high temperature, still keeps stable bond configurations, then the bonds are destructed, and finally a new bond configuration emerges in the growth process. Knowledge of the atom-scale mechanism for this bond destruction and creation is lacking so far but inevitable in future to advance science and technology of epitaxial growth.

The MOVPE with trimethylgallium (TMG) and ammonia (NH_3) as gas sources is regarded as the most suitable technique of growing GaN films.^{1,2} Many experimental and theoretical efforts have revealed that TMG is decomposed in the gas phase and the growing surface is generally Ga rich.⁹⁻¹¹ On the other hand, the mechanism of the decomposition of NH_3 is unclear though it is postulated without firm evidence to be decomposed in the gas phase and forms several NH_x unit, i.e., adduct formation.¹² Then some empirical parameters for the decomposition are used to analyze the growth rate of GaN.^{13,14}

In this paper, we report first-principle total-energy electronic-structure calculations that clarify reaction pathways and corresponding energy barriers for the decomposition of NH_3 and the incorporation of N with the forms of NH_2 , NH and N on GaN films. We concentrate on the growing GaN(0001) surface which is mostly used in typical MOVPE of GaN. The calculated energy barriers indicate that the whole reaction toward the formation of GaN network occurs under usual growth conditions. This is the first proposal based on the quantum theory of the surface-catalyzed atom incorporation during the epitaxial growth.

The organization of this paper is as follows. Section 2 describes the present density-functional calculations. Adsorption of a Ga atom and NH_x molecules and their reactions on GaN(0001) bare surfaces are described in Section 3.1 in order to identify the Ga-rich surface and clarify salient features of the adsorbed structures. Identification of the Ga-rich GaN(0001) surface and adsorbed structures of NH_x are presented in Section 3.2. Reaction pathways of the subsequent N incorporation and corresponding energy barriers are also revealed in Section 3.2. Section 4 summarizes our findings.

2 Methodology

All the calculations have been performed in the density functional theory (DFT)^{15,16} with the generalized gradient approximation¹⁷ to the many-body exchange-correlation energy functional. Nuclei and core electrons are described by norm-conserving pseudo-potentials.¹⁸ The Ga $3d$ states are treated as core-electron states. Computations have been done using our real-space-scheme code called RSDFT¹⁹ which has been developed so as to achieve the state-of-the-art high-performance computing.²⁰ The GaN (0001) surface is simulated by a repeating slab model in which each slab consisting of six GaN double layers are separated from its images by the 15-Å thick vacuum regions. The bottom N surface is passivated by fractionally charged (0.75 e) hydrogen to annihilate the dangling bonds and mimic the semi-infinite GaN substrate. In the lateral planes, we use 2×2 supercell periodicity. The spacing of the real-space grid points in RSDFT scheme is taken as 0.18 Å which corresponds to the 73-Ryd cutoff energy in the conventional plane-wave-basis calculations. The Brillouin-zone (BZ) integration has been done with the Monkhorst-Pack k -point sampling scheme and the $5 \times 5 \times 3$ sampling points are found to suffice for the BZ of wurtzite GaN. In the 2×2 slab calculations, this sampling corresponds to the $3 \times 3 \times 1$ sampling. These calculational parameters for the grid spacing and the k -point sampling lead to the lattice constants of 3.20 Å and 5.20 Å for wurtzite GaN, which are larger than the experimental values²¹ by 0.3 % and 0.2 %, respectively. In the geometry optimization, all the atoms in the slab except for the bottom two double layers and H atoms are fully relaxed until the remaining forces become less than 25 meV/Å.

Reaction pathways and corresponding energy barriers are calculated by using the hyper-plane constraint method (HPC).^{22,23} In this method, we first determine lines in the $3N_{\text{atom}}$ dimensional space (N_{atom} : the number of atoms in the simulation cell) which connect the initial $\{\mathbf{R}_i\}$ and the final or the intermediate metastable structures $\{\mathbf{R}_f\}$ for a selected reaction pathway. Here, we use the notation $\{\mathbf{R}\}$ for a $3N_{\text{atom}}$ dimensional vector which denotes the atomic geometry. Next, for each line in the selected pathway, the $(M - 1)$ vectors $\{\mathbf{P}_m\}$

($m = 1, \dots, M - 1$) along the line are selected as $\{\mathbf{P}_m\} \equiv \{\mathbf{R}_i\} + m(\{\mathbf{R}_f\} - \{\mathbf{R}_i\})/M$ and then a hyperplane perpendicular to the line at each $\{\mathbf{P}_m\}$ is defined. On each hyperplane, we perform geometry optimizations to find the most probable reaction pathways.

3 Results and Discussion

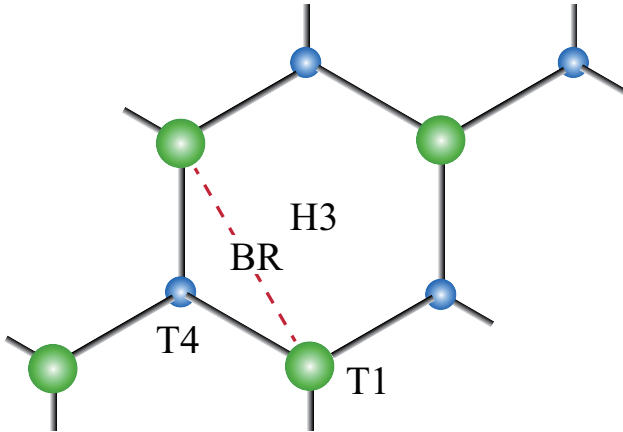


Figure 1: Top view of the GaN(0001) surface and its several atomic sites: T1, T4, H3 and BR (see text). Green (large) and blue (small) balls depict the Ga and N atoms, respectively.

3.1 Adsorption and reaction on Ga-faced GaN (0001) surface

We start with the GaN(0001) bare surface terminated with Ga atoms where the stoichiometry is the same as that in the bulk. This is for the sake of the clarification of the general features of the adsorbed structures on the GaN surface and then the identification of the Ga-rich surface which is regarded as the stage of MOVPE. The geometry optimization leads to a relaxed surface in which the top-layer Ga atoms are buckled alternately, as is already reported in the previous density-functional calculation.²⁴ We have found that this surface relaxation hardly affects the stable structures of adsorbed species and their energetics explained below. Figure 1 depict representative atomic sites on such surface: T1 (on-top) site above the top-layer Ga atom, T4 (hcp) site above the top-layer N atom, BR (bridge) site between the two

top-layer Ga atoms and H3 (fcc) site above the hollow of the hexagonal network. We have placed a Ga atom or NH_x species on those sites and examined their stability. It is noteworthy that not only the surface atoms but also the ad-species are allowed to be relaxed toward the total-energy minimized structures. The binding energy E_{bind} defined below is the measure of the stability of each adsorbed structure:

$$E_{\text{bind}} = -(E_{\text{sur-ad}} - E_{\text{sur}} - E_{\text{ad}}),$$

where $E_{\text{sur-ad}}$, E_{sur} and E_{ad} are the total energies of the GaN surface plus the ad-species, the GaN surface, and the adsorbed species in the gas phase, respectively.

Table 1: Calculated binding energies in eV for Ga adatom and NH_x molecule at the atomic sites, T1, T4, H3 and BR (see text), on the bare GaN(0001) surface. The sites at which the adsorbed species is unstable are depicted by hyphens.

adsorbed species	T1	T4	H3	Br
Ga	2.48	3.77	3.49	-
NH_3	1.30	-	-	-
NH_2	4.70	-	-	4.81
NH	-	6.67	7.39	-
N	-	8.19	8.94	-

For the Ga adatom, we have found that T4, H3 and T1 sites show positive binding energies (Table 1), meaning the exothermic adsorption, whereas BR site is unstable for the Ga adsorption. The most stable adsorption site is T4 where the Ga adatom form a bond with each of the three top-layer Ga atoms (Fig. 2). The H3 site provides smaller but comparable binding energy while the T1 site does much smaller binding energy. Previous density-functional calculations have also shown that the T4 site is most energetically favorable for a Ga adatom.^{25,26} When we count the number of Ga dangling bonds in the 2×2 lateral cell, it is four on the bare surface. When a Ga adatom is adsorbed on either T4 or H3 site, the number of the Ga dangling bond becomes two. At T4 and H3 sites, 3 electrons of the

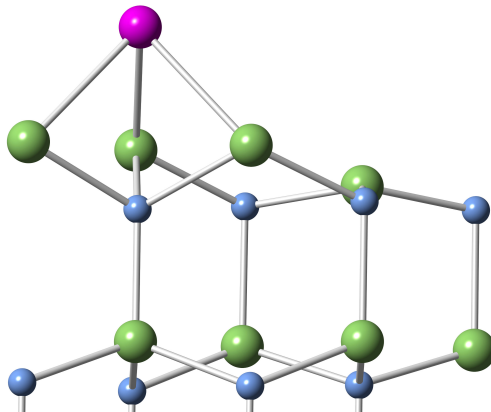


Figure 2: Most stable adsorption structure for a Ga adatom (purple ball) at T4 site on the GaN(0001) surface. Green (large) and blue (small) balls depict Ga and N atoms, respectively.

additional Ga atom plus 0.75 electrons nominally accommodated in the other Ga dangling bond is used to form the three Ga-Ga back-bonds. Hence the 2 cation (Ga) dangling bonds, which have higher orbital energy, in the 2×2 lateral cell becomes empty. This electron counting, which has been recognized as the electron counting rule (ECR),^{27,28} explains the stability at T4 and H3 sites. The T4 site is more favorable than the H3 site. This is due to the attractive interaction between the Ga adatom and the N atom located beneath the Ga adatom. In the most stable T4 site, the bond length between the Ga adatom and one of the top Ga atoms is 2.48 Å which is comparable with the Ga-Ga distance (2.7 Å) in the bulk Ga metal.

Ammonia is the source of nitrogen in MOVPE. Hence the identification of the adsorption sites of NH_3 and its possible adsorbates, NH_2 , NH and N on the GaN (0001) bare surface is important to identify typical forms of the nitrogen-related species on the GaN (0001). Figure 3 shows obtained stable adsorbed structures for the NH_3 , NH_2 , NH and N on the GaN (0001) bare surface. We have found that NH_3 is stable only at the T1 site in which all the N and Ga atoms are four-fold coordinated as shown in Fig. 3(a). At other sites, such coordination number energetically favorable is impossible. The adsorption energy is calculated as 1.30 eV (Table 1). The resulting Ga-N and average N-H bond lengths on the surface are 2.07 Å

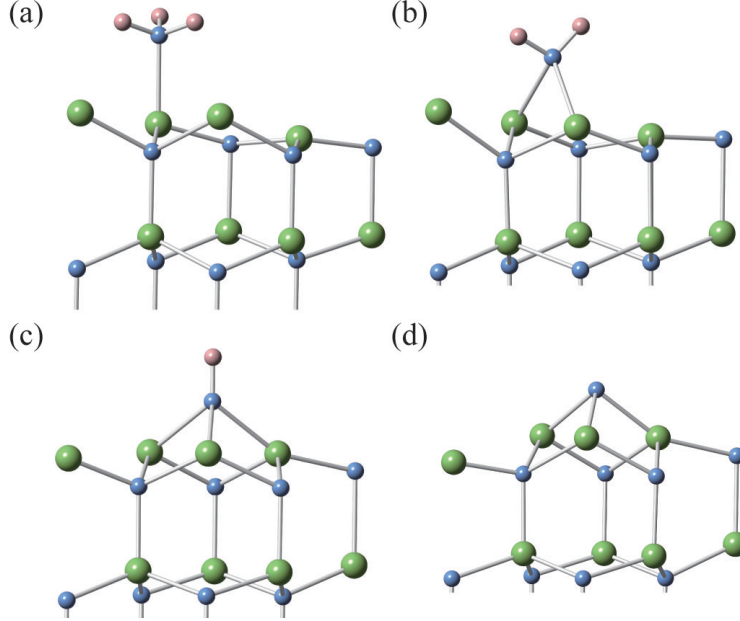


Figure 3: Most stable adsorption structure for (a) NH_3 at T1, (b) NH_2 at Br, (c) NH at H3 and (d) N at H3 sites on the $\text{GaN}(0001)$ surface. Color code is the same with Fig. 2. Salmon pink balls depict H atoms in NH_x units.

and 1.02 \AA , respectively, whereas the H-N-H angles are 111.3° , 111.0° , and 106.8° . These structural parameters are close to those of an isolated ammonia.

The first two possible adsorbate, NH_2 and NH , show bistability in their adsorption forms. The stable forms are well interpreted in terms of the coordination number. For NH_2 , the BR and T1 sites are energetically favorable with the binding energies of 4.81 eV and 4.70 eV , respectively (Table 1). In both adsorption forms, the NH_2 attached Ga is four-fold coordinated whereas the N is either four-fold or three-fold coordinated [Fig. 3(b)]. For NH , the H3 and T4 sites are favorable with the binding energies of 7.39 eV and 6.67 eV , respectively (Table 1). In those adsorption forms, N in the NH unit becomes four-fold coordinated which assures the stability [Fig. 3(c)].

The final possible adsorbate is the N atom itself. We have found that the energetically favorable adsorption sites for N are the H3 and T4 sites with the binding energies of 8.94 eV and 8.19 eV , respectively. Upon the adsorption on these sites, there remain a single Ga dangling bond and a single N dangling bond in the 2×2 lateral cell. At other sites,

the N adatom is not effective to erase the surface Ga dangling bonds. In addition to that, the H3- and the T4-site configurations satisfy ECR: the electron accommodated in the Ga dangling bond (nominally 3/4 electrons) is transferred to the N dangling bond (nominally 5/4 electrons accommodated), thus resulting in an N lone pair and an empty Ga dangling bond. The T4 site is less favorable than the H3 site. This is due to the repulsion between the N adatom and the N atom beneath.

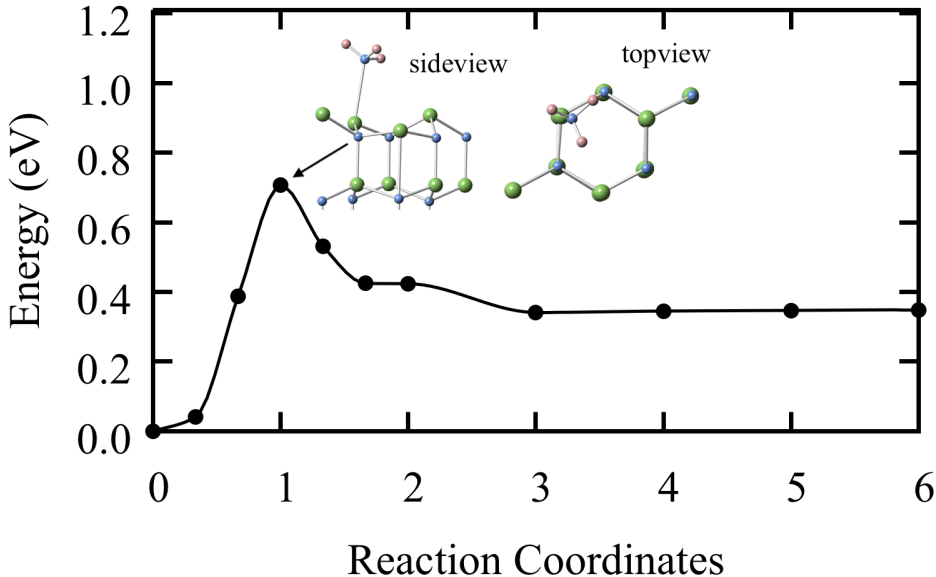


Figure 4: Calculated energy profile for the reaction of NH_3 decomposition to NH plus an adsorbed H_2 molecule on the bare $\text{GaN}(0001)$ surface (see text). The inset is the transition-state geometry.

To examine characteristics of atomic reactions related to NH_x species on the $\text{GaN}(0001)$ bare surface, we consider a decomposition reaction of ammonia: NH_3 at T1 [Fig. 3(a)] \rightarrow NH at H3 [Fig. 3(c)] + desorbed H_2 . We have identified the transition-state geometry in which N in NH_3 moves from T1 to H3, elongating its bond with surface Ga from 2.0 Å to 2.7 Å (Fig. 4). In the geometry, two H atoms in NH_3 move upward whereas the third H keeps its original position. This transition state leads to the activation barrier of 0.7 eV in this reaction as shown in Fig. 4. Decomposition of ammonia is possible in this way on the GaN surface.

3.2 Incorporation of N after adsorption and decomposition of NH_3 and related species on Ga-rich GaN(0001) surface

Thermodynamical analyses¹⁰ have shown that the growing surface in GaN MOVPE at the typical range of temperature and pressure of gas sources is Ga rich. Calculated results in the previous subsection have clarified that the T4 site is the most favorable for the adsorption of the Ga adatom (Fig. 2). We therefore consider the Ga-faced GaN(0001) surface with an additional Ga atom at the T4 site in the 2×2 lateral cell as a representative of the Ga-rich GaN(0001). The corresponding coverage of the Ga adatom is $\theta = 0.25$. It is noteworthy that this coverage, i.e., n^2 Ga adatoms in a $2n \times 2n$ lateral cell satisfies the ECR. In this subsection, we explore reaction pathways and corresponding energy barriers for the nitrogen incorporation after the adsorption and decomposition of ammonia and related species on the growing Ga-rich GaN surface.

Table 2: Calculated binding energies in eV for NH_x molecule at the atomic sites, T1, H3, BR and T_{ad} (see text), on the Ga-rich GaN(0001) surface. The sites at which the adsorbed species is unstable are depicted by hyphens.

adsorbed species	T1	H3	Br	T_{ad}
NH_3	1.27	–	–	0.33
NH_2	3.96	–	3.25	3.07
NH	6.36	5.14	6.19	3.50
N	–	8.34	–	–

Recent high-resolution time-of-flight (TOF) measurements^{11,29} show that ammonia is rarely decomposed in the gas phase but that small amount (0.1 %) of NH_2 indeed exists. Hence we first identify the stable adsorption structures of NH_3 on the Ga-rich surface. As shown in the previous section, NH_3 is adsorbed only at T1 site on the bare GaN (0001) surface. This is due to the strong bond formation between the N atom in NH_3 and the top Ga atom. Hence on the Ga-rich surface, the site on the Ga adatom (T_{ad} site hereafter) in addition to the T1 site is a candidate for the NH_3 adsorption. We have indeed found that

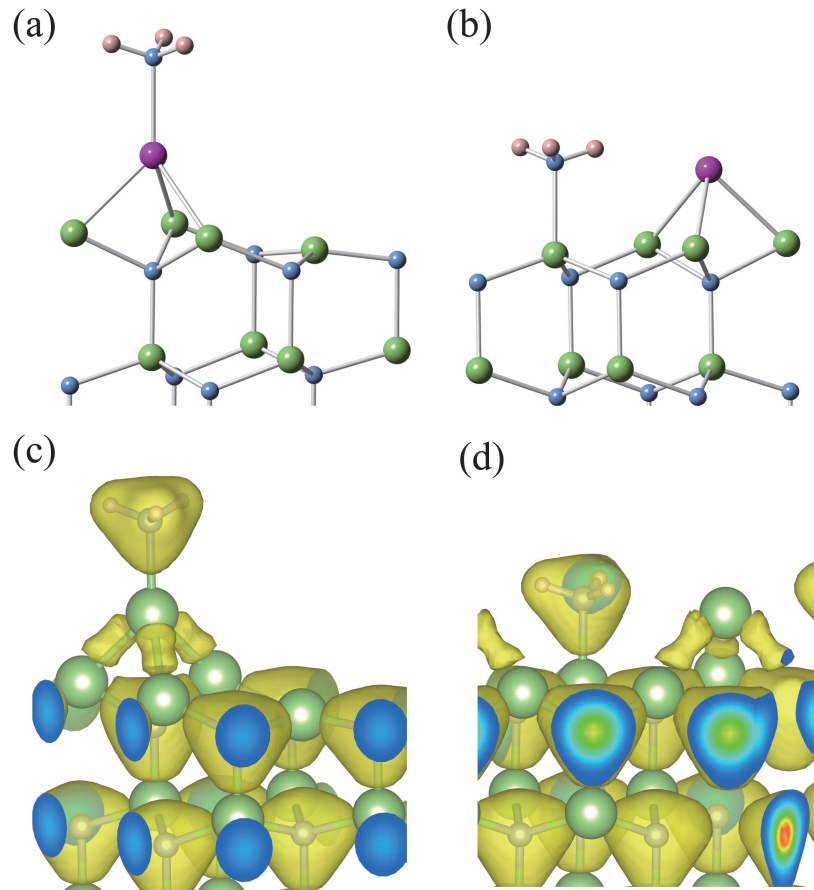


Figure 5: Stable adsorption structure and corresponding electron density of NH₃ at T_{ad} site [(a) and (c)] and at T1 site [(b) and (d)] on the Ga-rich 2 × 2 GaN (0001) surface. Color code in (a) and (b) is the same with Fig. 2 and Fig. 3. Electron density is represented by yellow equi-value surfaces and by contour color plots at the cross-sections.

the T_{ad} and T1 are the stable adsorption sites with the binding energies of 0.33 eV and 1.27 eV, respectively (Table 2). The optimized geometries of adsorbed NH_3 are shown in Fig. 5. The structures of the NH_3 unit at the T_{ad} and T1 sites are almost identical: The N-Ga bond length and the averaged N-H bond length are 2.18 Å (2.08 Å) and 1.01 Å (1.02 Å), respectively, at T_{ad} (T1) site; the H-N-H bond angles are $111.1^\circ \pm 1.2^\circ$ for both sites. It is of interest that both the T_{ad} and the T1 configurations satisfy the ECR with the Ga dangling bond unoccupied. Calculated electron densities for the adsorbed NH_3 at these sites are shown in Figs.5 (c) and (d). Formation of the covalent bond between N of NH_3 and top Ga is evident. Furthermore, we have found that the Ga-Ga bonds in the structures are rather weak, as is shown by the smaller equivalent surfaces. This weak spots may be a candidate place for the N incorporation (see below).

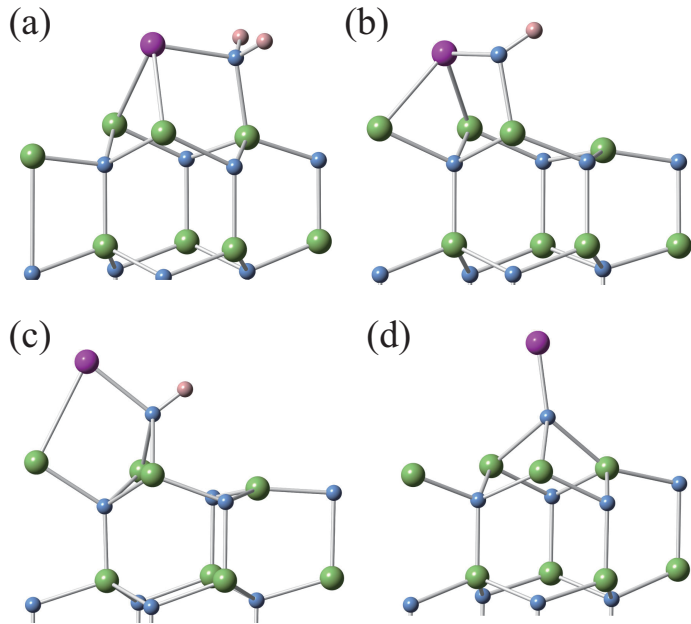
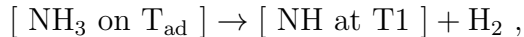


Figure 6: Stable adsorption structures of NH_x units on the Ga-rich GaN (0001) surface. (a) NH_2 on the T1 site, (b) NH on the T1 site, (c) NH on the BR site, and (d) N on the H3 site. The color code is the same as in Fig. 5.

As stated above, recent TOF measurements show the existence of NH_2 in the gas phase. This NH_2 , though the minority, may play a role in MOVPE and its behavior should be clarified. Behaviors of other species, NH and N , are also important since they may constitute

stable or metastable geometries appearing in the reactions of NH_3 and NH_2 . For NH_2 , we have found that the most stable site is the T1 site ($E_{\text{bind}} = 3.96$ eV) followed by the BR site ($E_{\text{bind}} = 3.25$ eV) and then the T_{ad} site ($E_{\text{bind}} = 3.07$ eV) (Table 2). It is of note that the NH_2 unit intervenes in the Ga-Ga bond after the geometry optimization for the NH_2 at T1 site: i.e., almost barrierless destruction of the weak Ga-Ga bond [Fig. 6 (a)]. We have also found the variances of the T1 structure in which the NH_2 unit intervenes into the left Ga-Ga bond in Fig. 6 (a). The calculated E_{bind} is same with that for the structure shown in Fig. 6 (a). The NH unit is adsorbed at any site, presumably due to the unstable form of an isolated NH, with the binding energies of 6.36 eV (T1), 6.19 eV (BR), 5.14 eV (H3), and 3.5 eV (T_{ad}). We have found that in the most and the next stable NH geometries the NH unit intervenes in the Ga-Ga bond again with an undetected energy barrier [Fig. 6 (b) and(c)]. The N atom is adsorbed only at H3 site with $E_{\text{bind}} = 8.34$ eV. This is obviously due to the limitation of the bonding ability of a single N atom (Table 2). The final geometry shown in Fig. 6(d) is surprising: The N approaches the H3 site and at the same time Ga adatom moves from the adatom site to the top of the N atom with the four-fold coordinated N appearing. Similar barrierless substitutional adsorption has been observed for a Si adatom on the hydrogen covered Si(100) surface due to the multiplicity of the H bond in the Si-H system.³⁰ In the present case, the weakness of the Ga-Ga bond causes this substitutional adsorption.

The calculations for NH_2 and NH above show that the weak Ga-Ga bond is likely to be the reaction site. Hence we next explore a pathway and a corresponding energy barrier for the reaction,



using the HPC method. Figure 7 shows the obtained energy profile of the reaction from NH_3 at the T_{ad} [Fig. 5(a)] toward NH near the T_1 [Fig. 6(b)] with the H_2 molecule being desorbed. It is noteworthy that the final configuration satisfies ECR with the N dangling bond being occupied by 2 electrons and the two Ga dangling bonds being unoccupied. The energy barrier

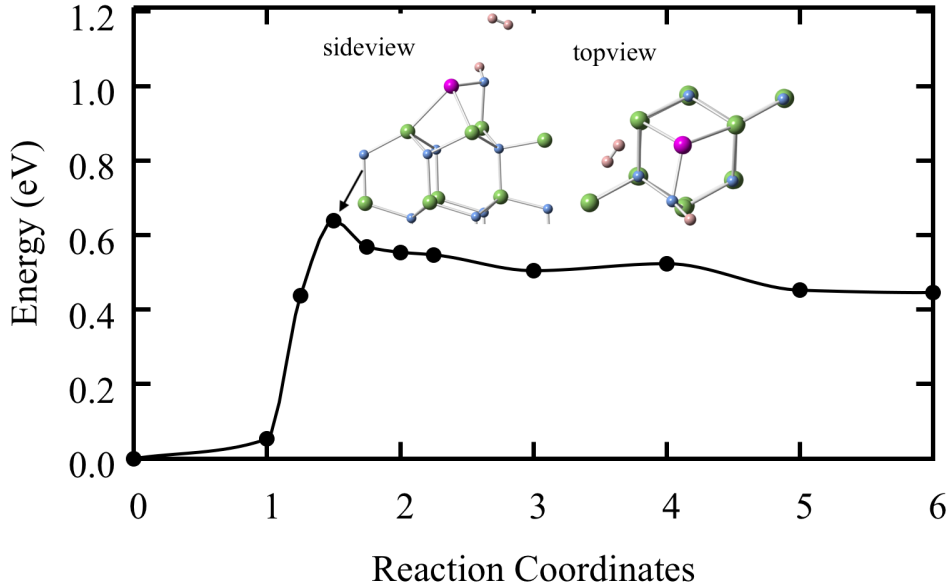


Figure 7: Calculated energy profile for the reaction of the NH_3 decomposition and the NH incorporation (see text) on the Ga-rich $\text{GaN}(0001)$ growing surface. The transition-state geometry is also shown. .

for this reaction of the NH_3 decomposition and the subsequent NH incorporation in the GaN bond network is calculated to be 0.63 eV. This value is surprisingly small in spite that the reaction involves the destruction of a Ga-Ga bond. The transition-state geometry is shown in Fig. 7. In the geometry, the Ga adatom is moved from the T_{ad} site to the H3 site, thus providing room for the NH unit to intervene in the Ga-Ga backbond. The distance from the incorporated N of the NH unit to the two Ga atoms are 1.90 Å and 1.92 Å, indicating that Ga-N bonds are already formed. In this sense the reaction is certainly concerted.

Figure 8 shows calculated valence electron density at the final structures of the decomposition and the subsequent incorporation reaction. The relative weakness of the Ga-Ga bond in the initial geometry of the NH_3 at T_{ad} site is demonstrated by the small equi-value surfaces in the region [Fig. 5 (c)]. In the final geometry of the incorporated NH , we have found that two strong Ga-N bonds are formed, as shown by the larger equi-value surfaces in Fig. 8.

Our RSDFT and RSDFT-HPC calculations have unequivocally clarified that both NH_3 and NH_2 react with the Ga-rich surface and the N atom in the forms of NH_2 or NH intervenes

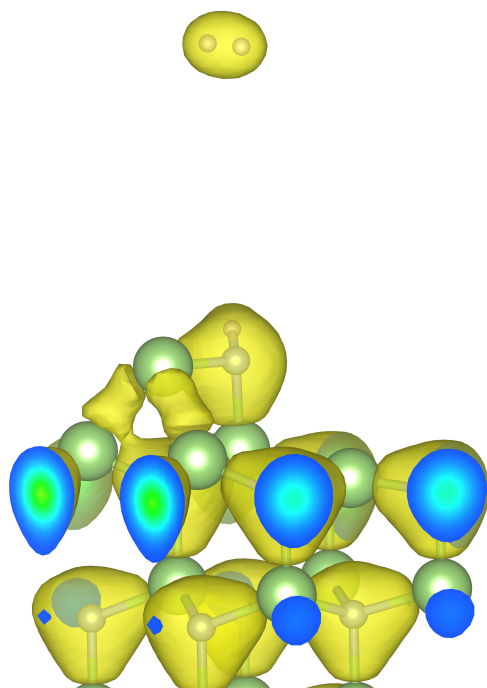


Figure 8: Electron density of the incorporated NH near the T_{ad} site after the decomposition and the subsequent incorporation reaction on the Ga-rich surface. Electron density is presented by yellow equi-value surfaces and by contour color plot at the cross-sections.

in the Ga-Ga bond spontaneously or with the small barrier of a half eV. The weak Ga-Ga bond on the Ga-rich surface acts as a catalyst for these decomposition and incorporation reactions.

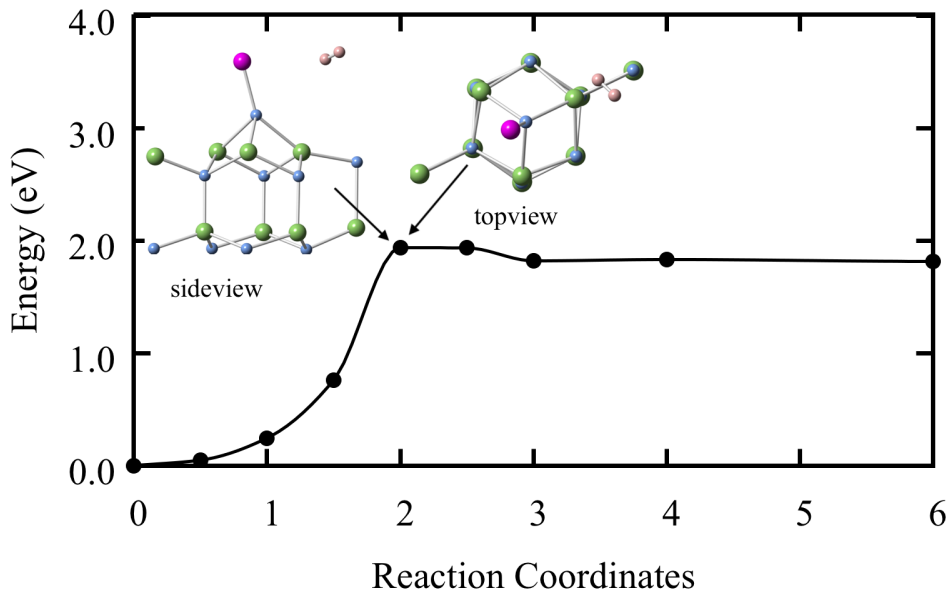


Figure 9: Calculated energy profile for the nitrogen incorporation reaction from the NH_2 unit [Fig. 6(a)] toward the fourfold-coordinated N structure [Fig. 6(d)] with H_2 being desorbed. The transition-state geometry is also shown.

The next issue is how the hydrogen atoms are desorbed in a form of H_2 and leaves the N atom surrounded by 4 neighboring Ga atoms. We have explored several possibilities. Since the $-(\text{Ga adatom})-(\text{NH})-\text{Ga}-$ structure [Fig. 6(b)] is formed after the decomposition of NH_3 , we first consider the reaction in which two $-(\text{Ga adatom})-(\text{NH})-\text{Ga}-$ structures nearby become Ga-N network with an H_2 being desorbed. In the final structure, the N atom intervenes in the subsurface and is indeed fourfold coordinated with Ga atoms. However, the energy cost for the H_2 desorption is calculated to be 3 eV. Hence this reaction is unlikely. Secondly, we have examined the reaction in which H_2 in the $-(\text{Ga adatom})-(\text{NH}_2)-\text{Ga}-$ structure [Fig. 6(a)] is desorbed. The calculated reaction barrier is again 3eV. Thirdly, We have examined the reaction in which the $-(\text{Ga adatom})-(\text{NH}_2)-\text{Ga}-$ structure [Fig. 6(a)] becomes the incorporated N being four-fold coordinated with Ga atoms [Fig. 6(d)]. We have identified the transition

state geometry and the calculated energy barrier is 2.0 eV, as shown in Fig. 9. This four-folded N configuration is important in GaN MOVPE since the capture of N with Ga species is imperative in the usual epitaxial growth under the extremely low ratio of group III to group V gas pressure.² Exploration of reactions from the structure [Fig. 6(d)] toward the formation of the nitrogen over-layer is certainly necessary in the future.

From the energy profile in Fig. 9, the barrier is found to be an energy cost to make the final state with H₂ being desorbed. Hence, when the energy of the final state is lowered, the reaction is likely to occur. This indeed happens in the typical growth conditions: the hydrogen chemical potential at 1300 K in the gas phase is evaluated to be - 2.1 eV, considering translation, vibration and rotation motions of H₂. This value of the chemical potential compensates for the zero-temperature energy barrier computed above. Then the whole reaction of the formation of GaN unit and the H₂ desorption that we have found is possible in GaN MOVPE.

4 Conclusions

We have performed density-functional calculations that clarify an atom-scale mechanism for the growth of GaN using the Metal-Organic Vapor-Phase Epitaxy (MOVPE) with the gas sources of TMG and NH₃. First, we have determined stable adsorption structures for Ga, NH₃, NH₂, NH and N on the bare Ga (0001) surface, obtained the binding energy for each adsorption structure, and examined a decomposition reaction of NH₃. We have found that no catalytic reaction for the N incorporation occurs on the bare surface. Based on the obtained adsorption structure of Ga atoms, we have identified Ga-rich GaN (0001) surface in which Ga-Ga bonds exist. We have explored various adsorption structures of NH₃, NH₂, NH and N on this Ga-rich GaN (0001) and found that NH₂ and NH units spontaneously intervene in the relatively weak Ga-Ga bond, forming a - Ga - (NH_x) - Ga - bond network. We have then explored a reaction in which NH₃ on the surface is decomposed toward the - Ga - NH

- Ga - configuration with an H_2 molecule being desorbed. We have determined the reaction pathway and obtained the small energy barrier of 0.63 eV. Considering that the growing surface is this Ga-rich surface and that NH_3 along with the small amount of NH_2 exists in the gas phase, we have explored reaction pathways in which N of NH_3 or NH_2 is incorporated into the Ga-N network and surrounded by four Ga atoms. We have found such a reaction pathway with the barrier of 2 eV which can be overcome by the free-energy gain of the H_2 molecule in the usual growth condition. The reaction process for the N incorporation that we have found based on the first-principle calculations is a new growth mechanism catalyzed by the growing surface.

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Graphical TOC Entry

