

## Incorporation of Nitrogen-related species on Ga-rich GaN (0001) surfaces

Cơ chế hấp thụ của các hợp chất Nitơ trên bề mặt giàu Ga của GaN (0001)

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### Abstract

We present features in the incorporation of Nitrogen-related species on the Ga-rich GaN (0001) surface based on first-principles total energy calculations. We find that the N adatom spontaneously substitutes for the Ga adatom upon adsorption and forms 4-fold N structure. Surprisingly, this substitutional adsorption does not have any activation energy. Also, we find that NH<sub>2</sub> and NH units intervene in the Ga-Ga weak bonds and form - Ga - (NH<sub>x</sub>) - Ga - structure during the adsorption. This finding gives an insight into the fate of ammonia species during adsorption on the Ga-rich GaN (0001) surface.

**Keywords:** Gallium Nitride; epitaxial growth; first principle simulation.

### Tóm tắt

Chúng tôi trình bày cơ chế hấp thụ các hợp chất Nitơ trên bề mặt giàu Ga của GaN (0001) dựa trên các tính toán năng lượng toàn phần theo nguyên lý đầu tiên. Chúng tôi thấy rằng nguyên tử Nitơ dễ dàng thay thế nguyên tử Ga khi hấp thụ và tạo thành cấu trúc Nitơ bậc bốn. Điều ngạc nhiên là sự hấp thụ này không cần vượt qua bất kỳ hàng rào năng lượng kích hoạt nào. Ngoài ra, chúng tôi nhận thấy NH<sub>2</sub> và NH còn tham gia vào liên kết yếu Ga-Ga và hình thành cấu trúc - Ga - (NH<sub>x</sub>) - Ga - trong quá trình hấp thụ. Phát hiện này mang lại cái nhìn tổng quan và sâu sắc về số phận của các hợp chất Nitơ trong quá trình hấp thụ trên bề mặt giàu Ga của GaN (0001).

**Từ khóa:** Gallium Nitride; trồng xếp lớp epitaxy; mô phỏng nguyên lý đầu tiên.

### 1. Introduction

Nitride (III-V) semiconductor materials, which include aluminum nitride (AlN), gallium nitride (GaN), and indium nitride (InN), are

changing our lives significantly with two main applications in optoelectronic devices and power devices [1–3]. These materials, known for having a wide band gap, have the power to pay

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less (less electricity, less waste heat) but gain more (more light, more power). Among that, GaN is becoming a promising material for the next generation of light-emitting diodes (LEDs), high-power and energy saving devices [4–9]. For the massive production of GaN, it is highly demanding to fabricate a high-quality GaN. For the fabrication of optoelectronic devices, the (0001) surface of GaN is often used [10–12].

Metalorganic vapor phase epitaxy (MOVPE) is known to massively produce the best quality GaN crystals [1,2,13]. In MOVPE, trimethylgallium (TMG) and ammonia are generally used as source gases which are carried to the growth section by a carrier gas,  $H_2$  or  $N_2$ . Kusaba *et al.* [8] reported that for the  $N_2$  carrier gas, the Ga adatom surface was observed at low temperatures. More recently, theoretical studies show that the T4 site is the most favorable adsorption site of the Ga adatom [15–18]. As seen in Fig. 1a which presents adsorption sites on the GaN (0001) bare surface, four high symmetry sites for the surface adsorption are addressed: T1 (on-top), BR (bridge), T4 (hcp), and H3 (fcc) sites. Fig. 1b from Bui *et al.* [19] shows the  $2 \times 2$  Ga adatom surface at the T4 site. It is seen that, the Ga adatom and three Ga atoms at the topmost layer on the surface form Ga-Ga weak bonds with smaller equivalent surface. These weak bonds can be a candidate for the N incorporation. Hereafter, the Ga adatom at the T4 site can be considered as a representative of the Ga-rich GaN (0001) surface.

Recently, Nagamatsu *et al.* [20] reported that ammonia is rarely decomposed in the gas phase using the high-resolution time-of-flight (TOF) measurements. Or in another word,  $NH_3$  reaches the surface. Also, a small amount (0.1%) of  $NH_2$  indeed exists on the surface. After approaching the surface, some reaction occurs and results in the product of  $NH_2$ ,  $NH$ , and  $N$  species. Thus, it is important to identify the typical forms of the

nitrogen-related species on the Ga-rich GaN (0001) and then examine what the fates of these species are on the Ga-rich surface.

In this article, we present the incorporation of nitrogen-related species on the Ga-rich GaN (0001) surfaces based on first-principles total energy calculations. We study how  $NH_x$  ( $x = 0-2$ ) species adsorb on the surface and incorporate in the Ga-Ga weak bond. The rest of this article is organized as follows: In section II, we describe the methodology used; In section III, we show the characteristic of  $NH_x$  ( $x = 0-2$ ) adsorption on various adsorption sites on the Ga rich GaN (0001) surface; Section IV summarizes our works.

## 2. Methodology

Here, first principle total energy calculation is performed in density functional theory (DFT) [21,22], as implemented in our real space density functional theory (RSDFT) package [23,24]. Exchange-correlation energy was treated by the Perdew-Burke-Ernzerhof (PBE) [25] exchange-correlation functional using the norm-conserving pseudo-potentials where the Ga 3d electrons are treated as core electrons [26]. In order to examine the adsorption on the surface, we first optimized the structure of the bulk GaN. The obtained lattice parameters are in agreement with experiment ( $a = 3.20 \text{ \AA}$  and  $c = 5.20 \text{ \AA}$ ) [27]. We then built a periodic slab of six double layers of GaN and a  $(2 \times 2)$  supercell. In order to avoid any interaction between surface and its periodically repeated images, we added  $15 \text{ \AA}$  of vacuum region between slabs. During the optimization, a  $3 \times 3 \times 1$   $k$ -point is used. The atoms in the bottom layer were passivated with Pseudo-hydrogens of charged  $0.75e$  to mimic the semi-infinite GaN substrate [28]. The top four double layers were allowed to relax until the maximum force acting on each atom becomes less than  $25 \text{ meV/\AA}$ . The cutoff energy of 73 Ry was used. The bottom

two bilayers and pseudohydrogens were kept fixed to mimic bulk-like behavior.

### 3. Results

In order to study the adsorption of  $\text{NH}_x$  species on the Ga-rich GaN (0001) surface, we put them on high symmetry sites shown in Fig. 1a and examine their stability by calculating the binding energy. The binding energy  $E_{\text{bind}}$  is defined as:

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

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

We first examine the adsorption of one N atom on the Ga-rich GaN (0001) surface. It is found that the N atom binds stably at the H3 site with the binding energy of 8.34 eV. Here, a striking feature of the geometry is found: there happens substitutional adsorption in which the N atom flips and makes bond with topmost Ga atoms on the surface (bond length: 2.12 Å), and the Ga adatom is in turn bonded with thus incorporated N atom (bond length: 1.89 Å) as depicted in Fig. 2b. The N adatom and topmost Ga atoms form strong covalent bonds and are therefore stabilized.

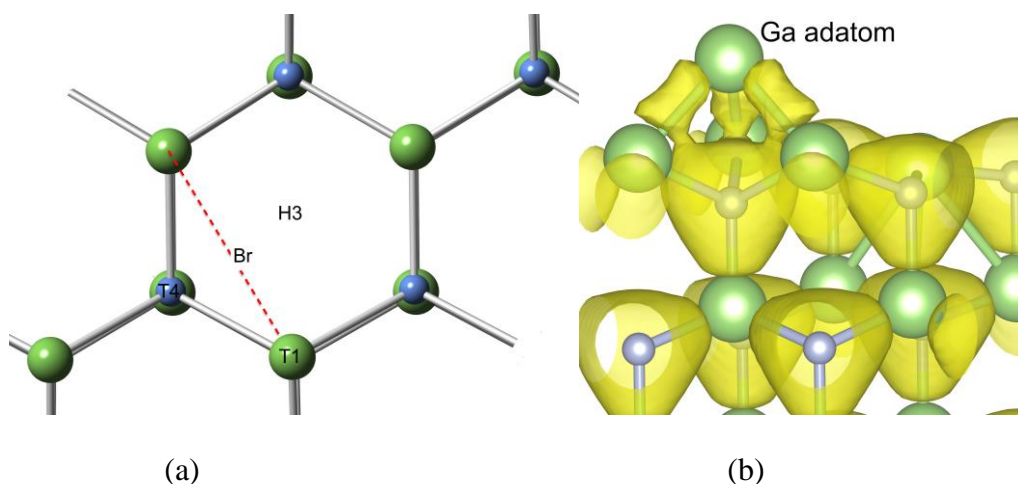


Figure 1. a) Top view of the GaN (0001) surface and adsorption sites: T1, T4, H3, and BR (see text). Green (large) and blue (small) balls depict the Ga and N atoms, respectively. b) Electron density for the Ga adatom at the T4 site.

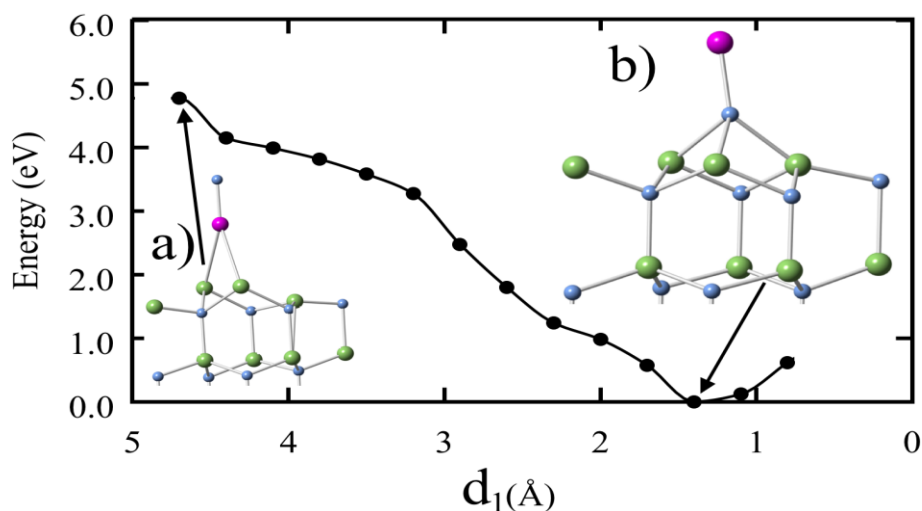


Figure 2. Total energy as a function of N-surface distance  $d_1$  (Å). a) Optimized structure of the N atom at  $d_1 = 4.7$  Å, b) Optimized structure of the N atom at  $d_1 = 1.4$  Å. Color code is the same as Fig. 1 with the Ga adatom shown in pink.

In order to obtain activation energies for such substitutional adsorption, we have performed the total energy calculation for fixed vertical distances,  $d_1$ , between the N atom and the surface. Fig. 2 shows the total energy as a function of the N-surface distance  $d_1$ . The energy keeps decreasing as the N atom comes closer to the surface when  $d_1 > 1.4 \text{ \AA}$ . If the N atom comes too close to the surface ( $d_1 < 1.4 \text{ \AA}$ ), a repulsion between the N atom and surface leads to the energy increase. Surprisingly, the energy barrier for such substitutional adsorption is absent. In other words, the N atom spontaneously substitutes for the Ga adatom upon adsorption. Previous studies by Jeong and Oshiyama. [29] also found the substitutional adsorption with no activation energy for the

adsorption of Si adatom on hydrogenated Si (100) surfaces. Such spontaneous substitutional adsorption is caused by the small atomic radius of the H atom and the strong covalency of group IV atoms. For our case, the reason is that the N adatom is attracted to the surface by Ga atoms on the surface while there is repulsion between the Ga adatom and the surrounding Ga atoms on the surface. Also, since the bonds between the Ga adatom and topmost Ga atoms are rather weak, they are easy to cleave. As a result, there is such substitutional adsorption on the Ga-rich GaN (0001) surface. This substitutional adsorption is an essential process for the crystal growth since it helps to form a new basic unit constituting the GaN film without overcoming any energy barrier.

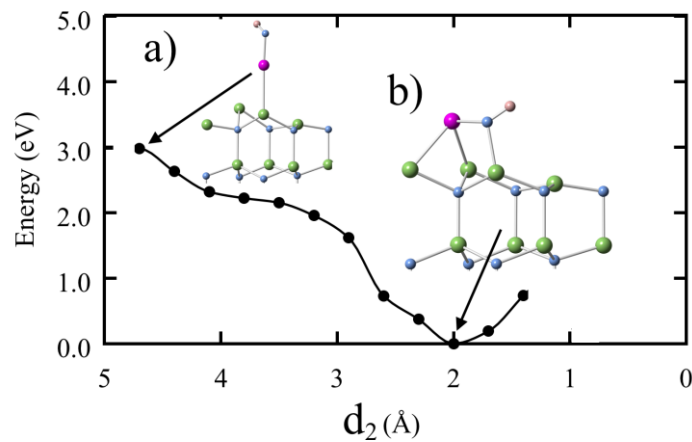


Figure 3. Total energy as a function of NH-surface distance  $d_2$  (Å). a) Optimized structure of NH at  $d_2 = 4.7 \text{ \AA}$ , b) Optimized structure of NH at  $d_2 = 2.0 \text{ \AA}$ . Green (large) and blue (small) balls depict the Ga and N atoms, respectively. The Ga adatom and the H atoms are shown in pink and salmon pink, respectively.

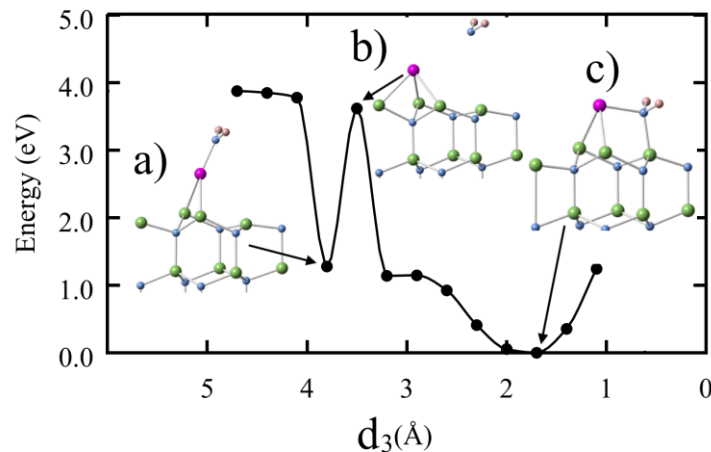


Figure 4. Total energy as a function of  $\text{NH}_2$ -surface distance  $d_3$  (Å). a) Optimized structure of  $\text{NH}_2$  at  $d_3 = 3.8 \text{ \AA}$ , b) Optimized structure of  $\text{NH}_2$  at  $d_3 = 3.5 \text{ \AA}$ , c) Optimized structure of  $\text{NH}_2$  at  $d_3 = 1.7 \text{ \AA}$ . The color code is the same as in Fig. 3.

Next, we explore the stability of NH on the Ga-rich GaN (0001) surface. T1 is found to be the most stable configuration of NH, being followed by BR, H3, and T<sub>ad</sub> site with the binding energies of 6.36 eV, 6.19 eV, 5.14 eV, and 3.45 eV, respectively. The Ga–N and N–H bond lengths at the T1 site are 1.88 Å and 1.02 Å, respectively. The geometry of NH adsorption at the T1 site is shown in Fig. 3b. Surprisingly, NH intervenes in the Ga-Ga weak bond and forms - Ga - (NH) - Ga - structure. Similar to the N atom case, we have done the examination of the total energy calculation for the fixed vertical distance,  $d_2$ , between NH and the surface. Fig. 3 shows that when  $d_2 > 2$  Å, the closer NH to the surface, the smaller total energy is. Then, this N atom incorporation is a barrierless process.

Interestingly, the feature of N atom incorporation into the Ga-Ga weak bond also works for NH<sub>2</sub>. Indeed, NH<sub>2</sub> at the T1 site is found to intervene in the Ga-Ga weak bond and form - Ga - (NH<sub>2</sub>) - Ga - structure as shown in Fig. 4c. The calculated binding energy at the T1, BR, and T<sub>ad</sub> site are 3.96 eV, 3.25 eV, 3.07 eV, respectively. For the T1 structure, the average Ga–N and N–H bond lengths on the surface are 2.06 Å and 1.02 Å, respectively. The H–N–H angle is calculated to be 105.6°. Fig. 4 shows the total energy as a function of the NH<sub>2</sub>-surface distance  $d_3$ . While the adsorption of N and NH is barrierless, that of NH<sub>2</sub> has the energy barrier of 2.34 eV. Above 4.1 Å, NH<sub>2</sub> is still far away and does not make a bond with any atom, thus NH<sub>2</sub>-surface at  $d_3 = 4.1$  Å has high energy. At 3.8 Å, since the Ga adatom makes the bond with NH<sub>2</sub> as shown in Fig. 4a, energy suddenly drops there. At 3.5 Å, NH<sub>2</sub> does not have a bond again with any atom, thus energy suddenly jumps up again as depicted in Fig. 4b. NH<sub>2</sub> has to climb energy of 2.34 eV to go from 3.8 Å to 3.5 Å. After that, energy keeps decreasing until NH<sub>2</sub> feels the repulsion from the surface at  $d_3 = 1.7$  Å.

## 4. Conclusions

Based on the density functional theory (DFT), we have theoretically investigated the spontaneous incorporation of nitrogen-related species on the Ga-rich GaN (0001) surface. First, the incorporation of NH<sub>x</sub> ( $x = 0-2$ ) on the Ga-rich GaN (0001) surface is clarified. To our surprise, the N atom is found to spontaneously adsorb on the surface and form 4-fold N configuration. NH units are found to spontaneously intervene in the Ga-Ga weak bonds on the Ga-rich GaN (0001) surface and form - Ga - (NH) - Ga - structure. NH<sub>2</sub> is also found to intervene in the Ga-Ga weak bonds but it needs to climb energy of 2.34 eV. These findings give an insight into the fate of ammonia species during adsorption on the Ga rich GaN (0001) surface.

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