An ab initio-based approach to the stability of GaN(0001) surfaces under Ga-rich conditions

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Abstract

Structural stability of GaN(0001) under Ga-rich conditions is systematically investigated by using our ab initio-based approach. The surface phase diagram for GaN(0001) including (2×2) and pseudo-(1×1) is obtained as functions of temperature and Ga beam equivalent pressure by comparing chemical potentials of Ga atom in the gas phase with that on the surface. The calculated results reveal that the pseudo-(1×1) appearing below 684~973 K changes its structure to the (2×2) with Ga adatom at higher temperatures beyond 767~1078 K via the newly found (1×1) with two adlayers of Ga. These results are consistent with the stable temperature range of both the pseudo-(1×1) and (2×2) with Ga adatom obtained experimentally. Furthermore, it should be noted that the structure with another coverage of Ga adatoms between the (1×1) and (2×2)-Ga does not appear as a stable structure of GaN(0001). Furthermore, ghost island formation observed by scanning tunneling microscopy is discussed on the basis of the phase diagram

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1. Introduction

GaN thin films are usually fabricated by metal organic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE), where temperature and pressure of species are crucial growth parameters. Atomic structure of the reconstructions during and after MBE growth on the GaN(0001) surface under Ga-rich conditions have been subjects of a number of experimental and theoretical investigations. The (2×2) and pseudo-(1×1) surfaces have been observed on the GaN(0001) under Ga-rich conditions by scanning tunneling microscopy (STM) [1,2]. Furthermore, Xie et al. found that 'ghost' island with the (2×2)-like structure coexists with normal island with the pseudo-(1×1) structure under excess Ga fluxes [3]. In order to clarify surface structures on the GaN(0001), there have been some theoretical studies based on ab initio calculations for surface structures and adsorption behavior on the surfaces. Northrup et al. proposed the structure of the pseudo-(1×1) as the most stable state under Ga-rich limit to clarify the relative stability among various surface structures[4]. Ishii investigated stable adsorption behavior on the (2×2) under N- and Ga-rich conditions [5]. Although these ab initio studies successfully elucidate some aspects in the surface-related problems of GaN, their results are limited at 0 K without incorporating the growth parameters such as temperature and beam equivalent pressure (BEP). In order to make up the deficiency in the previously reported ab initio calculations, we have successfully developed ab initio-based approach to include temperature and BEP to investigate the surface reconstructions and elemental growth processes on the GaAs and GaN surfaces [6-9]. In this study, we apply our ab initio-based approach to Ga adsorption-desorption behavior on the GaN(0001)-(2×2) and –pseudo-(1×1) surfaces and predict phase diagram as functions of temperature and Ga BEP. The relative stability among the (2×2), (1×1), and pseudo-(1×1) surfaces is also discussed on the basis of the surface phase diagrams obtained in this study and relative energy obtained by conventional thermodynamic approach using ab initio calculations.

2. Computational methods

Figure 1 shows the schematic of the (2×2) with Ga adatom and pseudo-(1×1) considered in this study. The pseudo-(1×1) structure shown in this figure corresponds to registry B proposed by Northrup et al. [4], which consists of two monolayers of excess Ga on the GaN(0001). On these surfaces, the adsorption-desorption behavior of Ga can be described by comparing the free energy of ideal gas per one particle (chemical potential) μ with the adsorption energy E_{ad}. The chemical potential μ_{Ga} of the ideal gas such as Ga atom is given by the following equations [10,11].

$$\mu_{Ga} = -k_B T \ln\left[k_B T / p_{Ga} \times g \times \zeta_{trans}\right], \quad (1)$$

Here, k_B is Boltzmann's constant, T the gas temperature, g the degree of degeneracy of electron energy level, p the beam equivalent pressure (BEP) of the particle, ζ_{trans} is the partition function for the translational motion. The adsorption energy E_{ad} is obtained by total energy for the solid

phase and chemical potential in the gas phase. In the total energy calculations for the (2×2) and pseudo-(1 × 1) surfaces with various atomic arrangements, we used the first-principles pseudopotential method based on the density functional formalism [12] within the generalized gradient approximation [13], combined with Troullier-Martins pseudopotential for Ga [14] and Vanderbilt pseudopotential for N [15]. The wave functions are expanded by the plane-wave basis set corresponding to sufficient kinetic energy cut-off of 28 Ry. The conventional repeated slab geometry is employed to simulate the surface. The unit super cell consists of six atomic layers of GaN, an atomic layer of fictitious H atoms and a vacuum region equivalent to about 15 atomic layers in thickness.

Using these chemical potentials μ and adsorption energies E_{ad}, the adsorption-desorption behavior of Ga on the the (2×2) and pseudo-(1×1) surfaces is clarified as functions of temperature and Ga BEP. Relative stability between various surface structures is determined by comparing μ with E_{ad}. That is, net adsorption proceeds when E_{ad} is less than μ, whereas net desorption occurs when μ is less than E_{ad}. Based on these results, we obtain phase diagrams of the (2×2) and pseudo-(1×1) surfaces as functions of temperature and Ga BEP. Furthermore, to discuss the stability of surface structures obtained in this study, we also employ the conventional thermodynamic formalism wherein the difference in energies between structures depends linearly on the Ga chemical potential as follows [16]:

$$\Delta E=\Delta E(\text{Ga-rich})+(\Delta n_{\text{N}}-\Delta n_{\text{Ga}})\,(\mu_{\text{Ga}}-\mu_{\text{Ga(bulk)}}). \qquad (2)$$

In this expression Δn_{N} and Δn_{Ga} are differences, per unit area, in the numbers of N and Ga atoms in the structures, μ_{Ga} is the chemical potential for Ga, and $\mu_{\text{Ga(bulk)}}$ is the energy per atom of bulk Ga. The maximum allowable value for μ_{Ga} is $\mu_{\text{Ga(bulk)}}$. Thus, by definition we have $\Delta E=\Delta E$(Ga-rich) in the Ga-rich limit.

3. Results and Discussion

Figure 2(a) shows the calculated phase diagrams of the GaN(0001) surfaces as functions of temperature and Ga BEP. Schematic of the stable structures are also shown in this figure. The pseudo-(1×1) is stable in the temperature range less than 684 K at 10^{-8} Torr and less than 973 K at 10^{-2} Torr. This is qualitatively consistent with experimental stable temperature range for the pseudo-(1×1) shown in this figure [17]. It should be noted that (1×1) with two Ga adlayers shown in Fig. 2(b) appears at higher temperatures and lower Ga BEP. This structure is realized by desorption of Ga atom at the A-site in the topmost layer due to smaller adsorption energy (2.67 eV) than those at the B-, C-, and D-sites (~3.0 eV) in the topmost layer. The desorption of Ga atom from the A-site induces large atomic displacement of Ga atom at the B-, C-, and D-sites from the initial lattice sites (denoted by dotted circles in Fig. 2(b)) to lower the system energy. Furthermore, the structure with another coverage of Ga adatoms between the (1×1) and (2×2)-Ga does not

appear as a stable structure of GaN(0001), since Ga adsorption energy keeps almost constant (2.6~2.8 eV) independent of Ga coverage between them.

This figure also reveals that the (2×2) with Ga adatom (hereafter (2×2)-Ga) is stable in the temperature range of 767 K to 1017 K at 10^{-8} Torr and 1078 K to 1420 K at 10^{-2} Torr. This is consistent with experimental stable temperature range for the (2×2)-Ga shown in this figure [18]. Lower Ga BEP and higher temperature favors the (2×2)-VGa, since Ga desorption is enhanced at lower Ga BEP and higher temperature. Moreover, ideal (2×2) does not appear in the phase diagram. This is because the ideal surface does not satisfy the electron counting model (ECM) to make adsorption energy of Ga on the ideal surface (3.34 eV) smaller than that on the (2×2)-Ga satisfying the ECM (4.01 eV). Thus the (2×2) surface directly changes its structure from the (2×2)-Ga to the (2×2)-VGa satisfying the ECM at lower Ga BEP and higher temperature.

Smith et al. theoretically considered possible structures of GaN(0001) using conventional thermodynamic formalism with ab initio total energy calculations and claimed that the (2×2)-VGa is not stable on the (0001) surface [19]. Figure 3 shows the calculated relative energy for the surfaces considered in this study as a function of Ga chemical potential similarly to their study. Here the energy for (2×2) with N adatom is energy origin. It is found that the energy of the (2×2)-VGa is higher than other structures near Ga-rich limit with μ_{Ga}-$\mu_{Ga(bulk)}$=0 eV. However, this does not necessarily mean that the (2×2)-VGa is unstable, since this approach does not incorporate temperature but only consider μ_{Ga}-$\mu_{Ga(bulk)}$ qualitatively corresponding to Ga BEP. Consequently, the (2×2)-VGa as a stable phase results from incorporating adsorption or desorption of Ga at finite temperatures in our ab initio-based approach.

From experimental viewpoints, it is well known that the (2×2) surface is often observed following an interruption in the Ga flux [20]. The phase diagram shown in Fig. 2 qualitatively agrees with this experimental finding, since decrease of Ga BEP prefers the (2×2)-Ga to the pseudo-(1×1) and (1×1) at a certain temperature (for example ~800 K). Furthermore, the STM observations by Xie et al. clarified that the pseudo-(1×1)-like normal and (2×2)-like ghost islands coexist during submonolayer deposition of GaN at 673-773 K by MBE [3]. They also found that the ghost island easily converts to the normal island by STM. The shaded area in Fig. 2 denotes the deposition temperature range of submonolayer deposition of GaN. This temperature range includes the stable regions of the pseudo-(1×1), (1×1), and (2×2)-Ga. These results suggest that Ga adsorption or desorption can easily change the pseudo-(1×1) or (1×1) to the (2×2)-Ga and vice versa depending on Ga BEP. This is consistent with their STM observations. Although further study incorporating another structures such as (5×5) and (4×6) and N BEP should be necessary to exactly consider these experimental results, the calculated phase diagram shown in Fig. 2 gives one possible interpretation for them.

4. Conclusion

We have systematically investigated the phase diagram of GaN(0001) surfaces including (2 $\times$2) and pseudo-(1 $\times$1) using our ab initio-based approach. The phase diagram calculations for the pseudo-(1 $\times$1) implies that the pseudo-(1 $\times$1) is stable in the temperature range less than 684 K at 10^{-8} Torr and less than 973 K at 10^{-2} Torr. The calculated phase diagram for the (2 $\times$2) reveals that the (2 $\times$2) with Ga adatom is stable in the temperature range of 767 K to 1017 K at 10^{-8} Torr and 1078 K to 1420 K at 10^{-2} Torr. Furthermore, the newly found (1 $\times$1) phase appears between the (2 $\times$2) and pseudo-(1 $\times$1). On the basis of the phase diagram of GaN(0001) surfaces, it is conjectured that Ga adsorption or desorption during GaN MBE growth can easily change the pseudo-(1 $\times$1) or (1 $\times$1) to the (2 $\times$2) with Ga adatom and vice versa depending on Ga BEP. This gives one possible explanation for STM observations where the pseudo-(1 $\times$1)-like normal and the (2 $\times$2)-like ghost islands coexist during submonolayer deposition of GaN at ~673-773 K by MBE. According to these results, this approach is feasible for investigating realistic surface phase diagram for GaN in addition to previously reported GaAs as functions of temperature and BEPs.

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Figure captions

Fig. 1. Schematic of top view for (a) GaN(0001)-(2 × 2) and (b) –pseudo-(1 × 1) surfaces considered in this study. Dotted line denotes (2 × 2) surface unit cell. Thin solid lines in Fig. 1(b) represent interatomic bonds between N in the fourth layer and Ga in the third layer.

Fig. 2. (a) Calculated phase diagram of GaN(0001) surfaces as functions of temperature and Ga BEP. Experimental results are attached to temperature axis. Shaded area denotes MBE growth temperature range in Ref. 3. (b) Schematic of top view of newly found (1 × 1) with lattice sites for Ga atoms in the topmost layer on the pseudo-(1 × 1) denoted by dotted circles and A-D.

Fig.3. Calculated relative energy for GaN(0001) surfaces considered in this study as functions of temperature and Ga chemical potential. Here, energy origin is the energy for the (2 × 2) with N adatom.

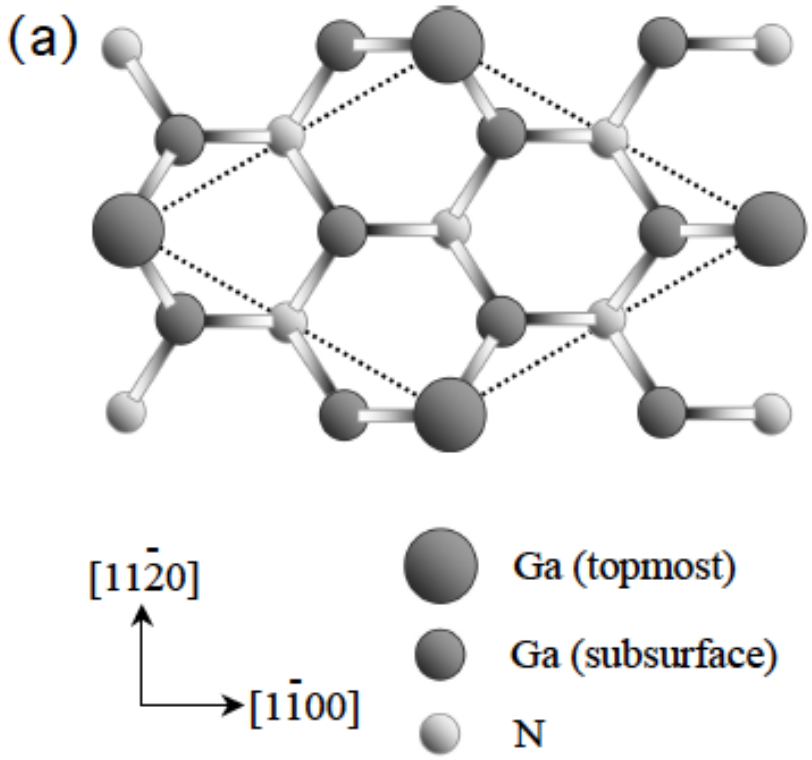

Fig. 1

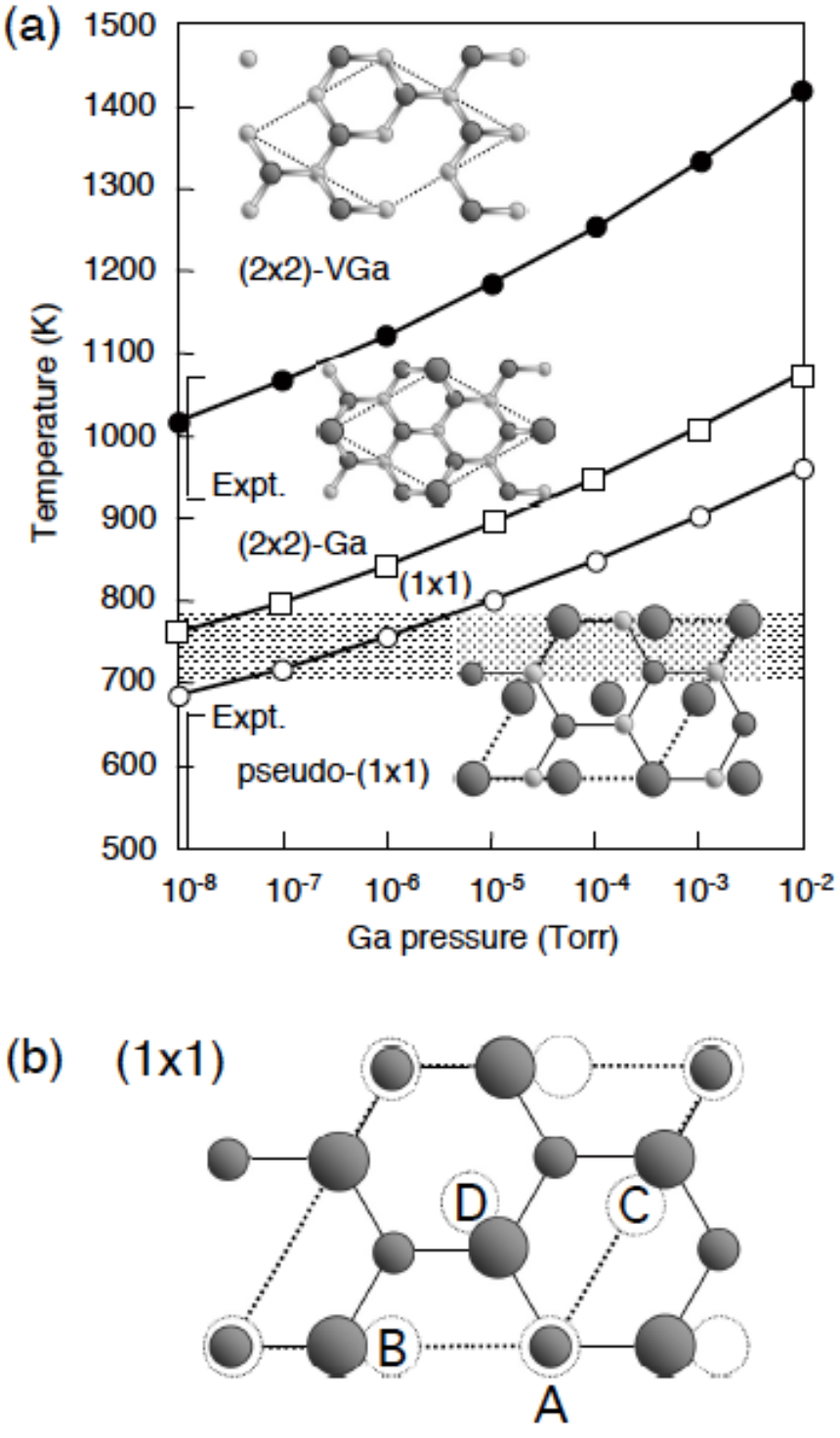
(a)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
Temperature (K)
(2x2)-VGa
Expt.
(2x2)-Ga
(1x1)
Expt.
pseudo-(1x1)
10-8
10-7
10-6
10-5
10-4
10-3
10-2
Ga pressure (Torr)
(b) (1x1)
D
C
B
A

Fig.2

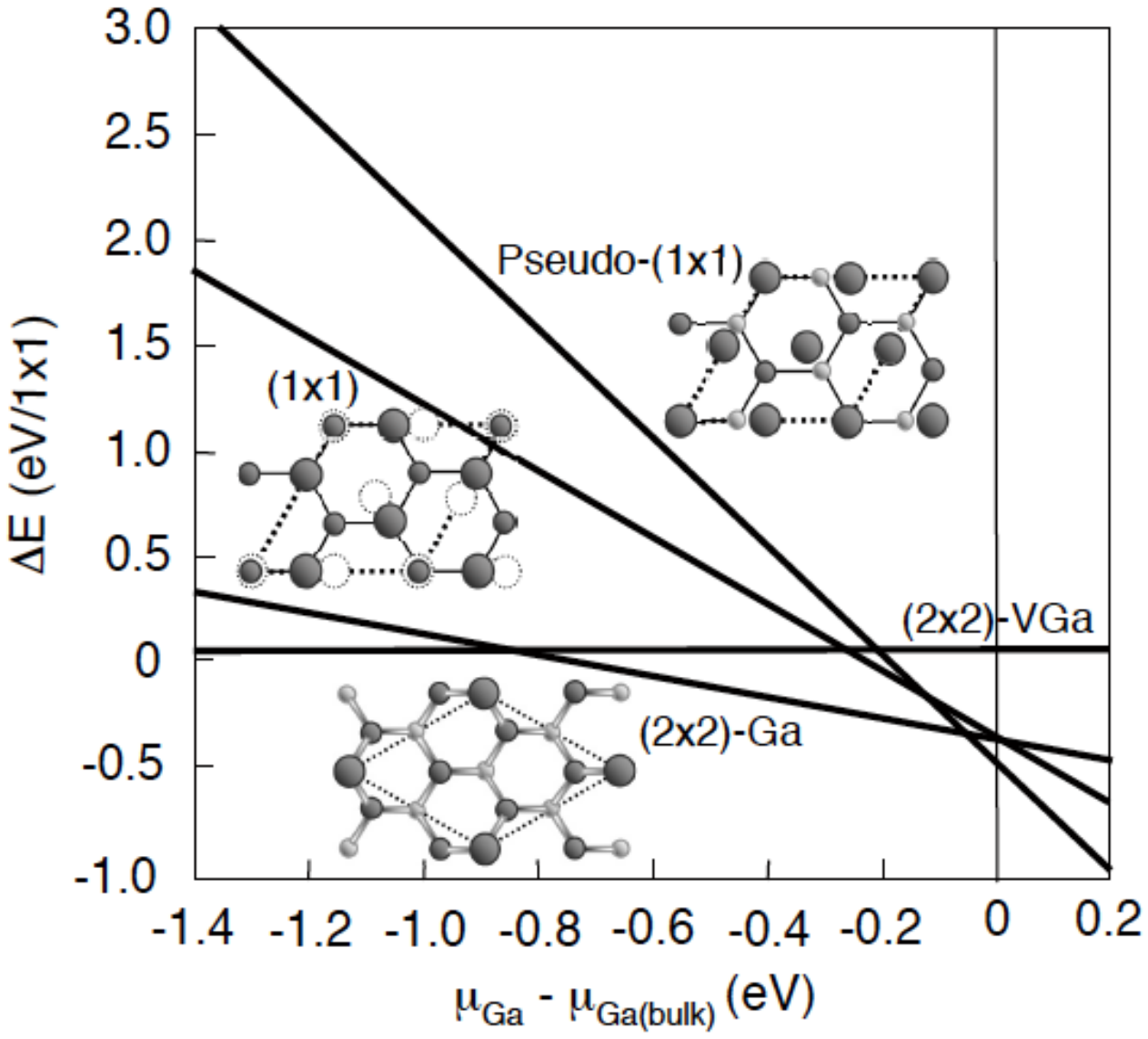
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
-1.0
ΔE (eV/1x1)
-1.4
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0
0.2
μGa - μGa(bulk) (eV)
Pseudo-(1x1)
(1x1)
(2x2)-VGa
(2x2)-Ga

Fig. 3