

Effect of Step Edges on Adsorption Behavior for GaN(0001) Surfaces during Metalorganic Vapor Phase Epitaxy: An *Ab Initio* Study

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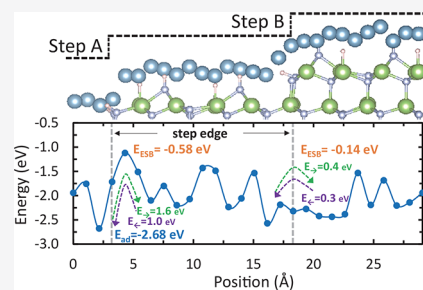
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**ABSTRACT:** The adsorption behavior of adatoms on stepped GaN(0001) surfaces during metalorganic vapor phase epitaxy (MOVPE) is theoretically investigated on the basis of *ab initio* calculations. The calculations using vicinal surfaces consisting of single layer step edges along the  $[1\bar{1}00]$  direction reveal that the structure of step edges depends on the growth condition. The vicinal surface with H-terminated N atoms ( $N_{ad}\text{-H+Ga-H}$ ) and that with both H-terminated N atoms and  $NH_2$  ( $N_{ad}\text{-H+Ga-NH}_2$ ) are found to be stabilized under the MOVPE growth condition. Furthermore, different adsorption sites and energies of Ga and N adatoms are obtained depending on the atomic configurations of step edges and terraces. The most stable adsorption site of the Ga adatom is located at the step edge irrespective of the reconstructions, but the adsorption energy for the surface with  $N_{ad}\text{-H+Ga-NH}_2$  ( $-3.54$  eV) is much lower than that with  $N_{ad}\text{-H+Ga-H}$  ( $-2.68$  eV). One of the striking results of the adsorption behavior of the Ga adatom is the presence or absence of the Ehrlich–Schwoebel barrier, depending on the structure of step edges. On the basis of the calculated adsorption energies and energy barriers, the adsorption behavior at the step edges on GaN(0001) surfaces depending on the growth condition of MOVPE is successfully explained.



## INTRODUCTION

Group-III nitrides, including GaN, have been given much attention due to their wide range of applications, such as optoelectronic and electronic devices. Since the epitaxial growth of group-III nitrides has been generally performed on a polar GaN(0001) surface, the structure and growth processes on a GaN(0001) surface have been studied both experimentally and theoretically. These efforts have been partly motivated to understand growth morphology and dopant incorporation, which are crucial for the application of group-III nitrides to optoelectronic and electronic devices.

The surface morphology during epitaxial growth on a GaN(0001) surface has been the subject of a number of experimental investigations. To reduce structural defects, controlling the smooth surface and interface morphology is of prime importance, and the incorporation of indium in InGaN quantum wells is strongly influenced by the local surface misorientation. It is well-known that flat GaN layers in the step-flow mode can be obtained by both metalorganic vapor phase epitaxy (MOVPE)<sup>1,2</sup> and Ga-rich plasma-assisted molecular beam epitaxy (PAMBE)<sup>3,4</sup> On the other hand, hexagonal hillocks have been observed in PAMBE<sup>2–4</sup> and ammonia MBE<sup>5,6</sup> under N-rich conditions. It has also been reported that the surface morphology, such as step-flow and the step-bunching of AlN, can be controlled by growth parameters such as the substrate off-angle and the V/III ratio.<sup>7,8</sup> These experimental findings thus imply that the morphology is caused by kinetic effects rather than the static

stability on the surface. In particular, Kaufmann et al. have suggested that the Ehrlich–Schwoebel barrier (ESB)<sup>9,10</sup> is an important kinetic factor in determining the surface morphology.<sup>2</sup> The ESB is defined as an energy barrier located at the step edges, where adatoms need to overcome diffusion down the step and attach to the lower step edge. The presence of the ESB causes the asymmetry of the adsorption–desorption behavior, resulting in surface-related phenomena, such as step-bunching and step-meandering.<sup>11–13</sup>

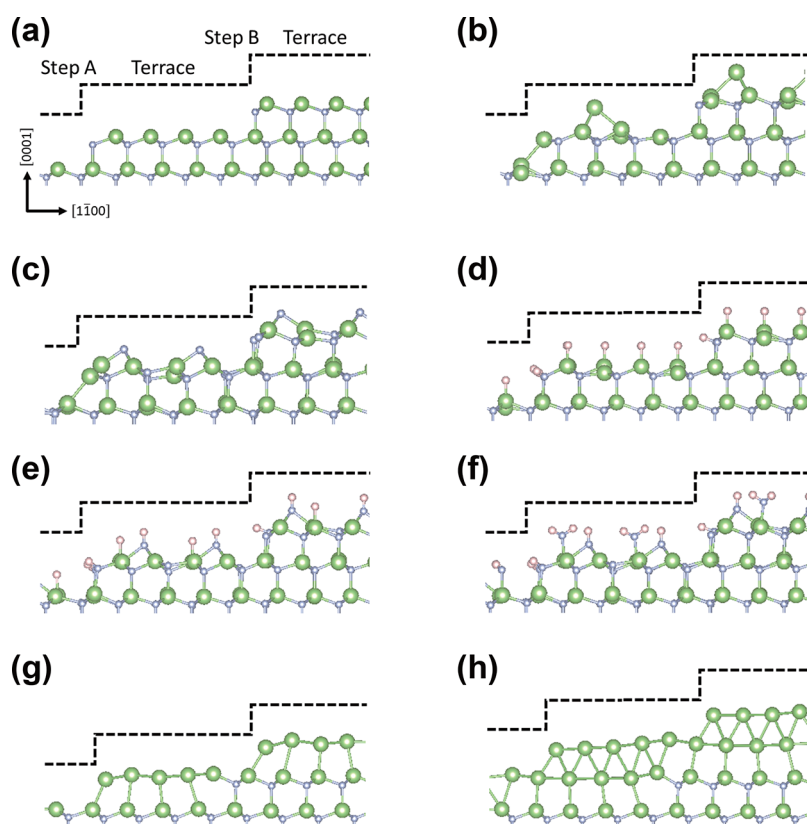
More importantly, observations of GaN(0001) surfaces during MOVPE by atomic force microscopy (AFM) have definitely clarified these kinds of behaviors.<sup>2</sup> AFM images have shown step-flow and step-meandering modes that depend on the carrier gas. In particular, the step-flow mode has been observed at both a high temperature (1050 °C) and a low temperature (840 °C) under H<sub>2</sub> carrier gas conditions, while step-meandering has been observed on GaN grown at a low temperature with a N<sub>2</sub> carrier gas in MOVPE.<sup>2</sup> This suggests that flat GaN layers can be obtained over a wide temperature range and that step-flow growth is possible under the H<sub>2</sub>

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**Figure 1.** Schematics of the vicinal ( $2 \times 9$ ) surface with single layer step edges along the  $[1\bar{1}00]$  direction for (a) ideal atomic configurations and the surface with (b) Ga atoms ( $\text{Ga}_{\text{ad}}$ ), (c) N atoms ( $\text{N}_{\text{ad}}$ ), (d) H atoms ( $3\text{Ga-H}$ ), (e) H-terminated N atoms ( $\text{N}_{\text{ad}}\text{-H+Ga-H}$ ), (f) H-terminated N atoms and  $\text{NH}_2$  ( $\text{N}_{\text{ad}}\text{-H+Ga-NH}_2$ ), (g) 1 monolayer (ML) of excess Ga, and (h) 2 MLs of excess Ga considered in this study. Green, purple, and pink circles represent Ga, N, and H atoms, respectively. Dotted stepwise lines indicate the step and terrace regions along the  $[1\bar{1}00]$  direction. Note that periodic boundary conditions are imposed along the  $[1\bar{1}00]$  direction and that two single layer steps with a height of 2.62 Å are included in the unit cell.

carrier gas condition due to the negligible contribution of the ESB. However, the relationship between the step-flow growth and the ESB from atom-scale viewpoints has never been examined.

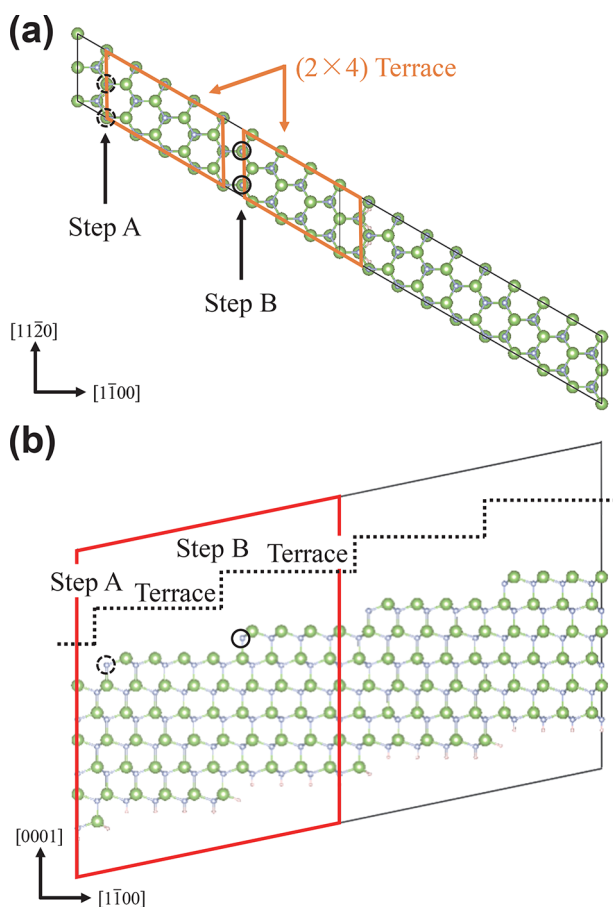
From theoretical viewpoints, the adsorption and desorption behavior on III-nitride surfaces during epitaxial growth has been carried out, and characteristic features of adatom kinetics that depend on the growth condition such as temperature and pressure have been clarified.<sup>14–18</sup> More recently, we have examined the adsorption behavior of adatoms at step edges of the GaN(0001) surface during MBE growth on the basis of *ab initio* calculations.<sup>19,20</sup> Different from MBE growth, the growth condition of the carrier gas is crucial for the step-flow growth in MOVPE. Therefore, investigating the adsorption behavior at the step edges under the MOVPE condition is a challenging issue. To clarify the effects of step edges on the growth processes that depend on the growth condition of MOVPE, the adsorption behavior of adatoms for stepped GaN(0001) surfaces during MOVPE growth is systematically examined on the basis of *ab initio* calculations. The difference in the adsorption behavior at the step edges and the ESB dependency on the growth condition are discussed.

## COMPUTATIONAL DETAILS

We perform total-energy calculations within density functional theory using a pseudopotentials approach. We use the generalized gradient approximation for exchange-correlation functionals,<sup>21</sup> norm-conserving pseudopotentials for Ga and H atoms,<sup>22</sup> and ultrasoft

pseudopotential<sup>23</sup> for N atoms to simulate nuclei and core electrons. Ga 3d orbitals are adopted by nonlinear core corrections.<sup>24</sup> The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 30.25 Ry. The conjugate-gradient technique<sup>25,26</sup> is utilized for both electronic structure calculations and geometry optimization. We use *k*-point sampling corresponding to 216 *k* points in the  $(1 \times 1)$  unit cell, which gives sufficient convergence of the total energy for discussing the relative stability. The computations are performed using the extended Tokyo *ab initio* program package (xTAPP).<sup>27,28</sup>

In the present study, stepped surface models during MOVPE growth are considered to clarify the behavior of adatoms at the step edges and terrace regions. The stepped surface models are constructed using vicinal ( $2 \times 9$ ) slab models ( $\sim 276$  atoms) consisting of six bilayers of GaN whose bottom surface is terminated by artificial H atoms.<sup>29</sup> The slab models contain 15 Å vacuum region to eliminate the interaction between adjacent slabs. We consider various atomic configurations, as schematically shown in Figure 1. The models, barring the ideal vicinal GaN(0001) surface shown in Figure 1(a), are constructed on the basis of the electron counting (EC) rule<sup>30</sup> and previously reported reconstructions on GaN(0001) surfaces under the MOVPE growth condition.<sup>14,15,31–33</sup> In these models, terrace regions are constructed by multiplying the  $(2 \times 2)$  periodicity satisfying the EC rule.<sup>30</sup> The surfaces of periodic  $(2 \times 9)$  vicinal slab models comprise two  $(2 \times 4)$  terrace regions and two single layer steps. Details of the whole unit cell of vicinal  $(2 \times 9)$  slab models are described in Figure 2. For the most stable adsorption sites, we have performed calculations of the adsorption energy using the  $(4 \times 9)$  vicinal slab models and found that the energy difference between  $(2 \times 9)$  and  $(4 \times 9)$  unit cells is less than 0.11 eV. It is thus likely that the errors of adsorption energies and energy barriers caused by the



**Figure 2.** (a) Top and (b) side views of the vicinal slab model for an ideal GaN(0001) surface. Green, purple, and pink circles denote Ga, N, and artificial H atoms, respectively. Black circles represent the atoms of step edges. The side view of the unit cell is represented by a red rectangle. Dashed stepwise lines in the side view indicate step and terrace regions along the  $[1\bar{1}00]$  direction. The surface consists of two  $(2 \times 4)$  terrace regions (orange rectangles in top view) and two single layer steps, which result in a  $(2 \times 9)$  vicinal slab model. Note that the unit cell is multiplied for visual understanding.

narrow unit cell are around 0.1 eV. We note that two different atomic configurations, described as step A and step B shown in Figure 1(a) and Figure 2, appear due to the stacking sequence (AB stacking) of the wurtzite structure along the  $[0001]$  direction. The stepped surface with Ga atoms ( $\text{Ga}_{\text{ad}}$ ) shown in Figure 1(b) is constructed based on the  $(2 \times 2)$  surface, with the Ga adatom stabilized under moderately Ga-rich conditions.<sup>14</sup> The surface with N atoms ( $\text{N}_{\text{ad}}$ ), as shown in Figure 1(c), is constructed based on the  $(2 \times 2)$  surface, with the N adatom stabilized under N-rich conditions.<sup>14</sup> In MOVPE, many types of surface structures with H atoms and  $\text{NH}_2$  have been proposed.<sup>31</sup> Thus, we consider a H-terminated stepped surface ( $3\text{Ga-H}$ ) shown in Figure 1(d), which is based on a H-terminated  $(2 \times 2)$  surface with three Ga-H bonds in the surface unit cell, stabilized under moderately Ga-rich conditions with high  $\text{H}_2$  pressures.<sup>31</sup> We also consider the surface with a H-terminated N adatom ( $\text{N}_{\text{ad}}\text{-H+Ga-H}$ ), as shown in Figure 1(e), which is based on the  $(2 \times 2)$  surface cell with a Ga-H bond and a H-terminated N adatom, stabilized under moderately N-rich conditions with high  $\text{H}_2$  pressures. Furthermore, we take the stepped surface with both a H-terminated N adatom and  $\text{NH}_2$  ( $\text{N}_{\text{ad}}\text{-H+Ga-NH}_2$ ) shown in Figure 1(f) into account. This is based on the  $(2 \times 2)$  surface stabilized under N-rich conditions with high  $\text{H}_2$  pressures. For the reconstructions under extreme Ga-rich conditions, the surfaces with 1 monolayer (ML) and 2 MLs of excess Ga shown in Figure 1(g) and Figure 1(h) are taken into accounts, respectively.

In order to clarify the stability of step edges, we evaluate the formation energy of the step edge,  $E_{\text{form}}$  as a function of the Ga chemical potential,  $\mu_{\text{Ga}}$ . The formation energy is given by

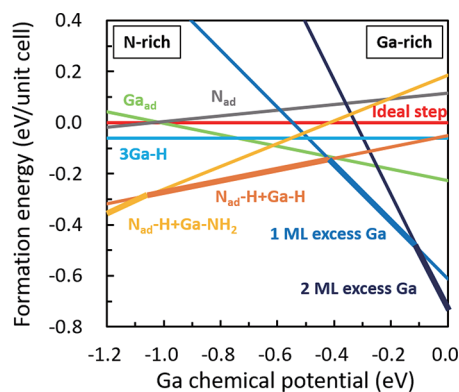
$$E_{\text{form}}(\mu_{\text{Ga}}) = E_{\text{tot}} - E_{\text{ref}} - (n_{\text{Ga}} - n_{\text{N}})\mu_{\text{Ga}} - n_{\text{N}}\mu_{\text{GaN}}^{\text{bulk}} - n_{\text{H}}\mu_{\text{H}} \quad (1)$$

where  $E_{\text{tot}}$  and  $E_{\text{ref}}$  are the total energies of the slab model under consideration and of the reference (i.e., the ideal vicinal surface shown in Figure 1(a)), respectively.  $n_{\text{Ga}}$ ,  $n_{\text{N}}$ , and  $n_{\text{H}}$  are the number of excess or deficit Ga, N, and H atoms with respect to the reference, respectively.  $\mu_{\text{GaN}}^{\text{bulk}}$  is the total energy per formula unit of bulk GaN. The relationship between  $\mu_{\text{Ga}}$  and the chemical potential of N ( $\mu_{\text{N}}$ ), expressed as  $\mu_{\text{Ga}} + \mu_{\text{N}} = \mu_{\text{GaN}}^{\text{bulk}}$ , is used as the equilibrium condition.  $\mu_{\text{Ga}}$  can vary in the thermodynamically allowed range. This range corresponds to the formation enthalpy, expressed as  $\Delta H_f = \mu_{\text{Ga}}^{\text{bulk}} - E_{\text{tot}}^{\text{bulk-Ga}} - E_{\text{tot}}^{\text{N}_2}$ , where  $E_{\text{tot}}^{\text{bulk-Ga}}$  and  $E_{\text{tot}}^{\text{N}_2}$  are the total energies per atom of bulk Ga and  $\text{N}_2$  molecules. Therefore, the range of  $\mu_{\text{Ga}}$  is  $\mu_{\text{Ga}}^{\text{bulk}} + \Delta H_f \leq \mu_{\text{Ga}} \leq \mu_{\text{Ga}}^{\text{bulk}}$ , where  $\mu_{\text{Ga}}^{\text{bulk}}$  is the chemical potential of bulk Ga. The calculated value of  $\Delta H_f$  for GaN is  $-1.20$  eV, which agrees with the experimental value.<sup>34</sup> The lower and upper limits correspond to N-rich and Ga-rich conditions, respectively. For the chemical potential of H atoms, we assume a  $\text{H}_2$  carrier gas in MOVPE growth, which corresponds to H-rich conditions. The value of the hydrogen chemical potential of  $\mu_{\text{H}} - \mu_{\text{H}_2} = -1.05$  eV at 76 Torr of  $\text{H}_2$  pressure and 1370 K<sup>35</sup> is used, where  $\mu_{\text{H}_2}$  is the chemical potential (per atom) for a single  $\text{H}_2$  molecule at 0 K.

Moreover, the adsorption energies are calculated at various positions to understand the adsorption behavior along the  $[1\bar{1}00]$  direction. In order to reveal the adsorption and diffusion of adatoms on the stepped surface, we calculate the potential-energy profile by fixing the adatom in the  $[1\bar{1}00]$  direction at various positions and allowing the relaxation of the adatom perpendicular to the  $[1\bar{1}00]$  direction and the full relaxation of the other atoms. To determine the initial position of adatoms at each position of vicinal surfaces, we also perform the calculations of adatoms on the planar GaN(0001) surface. To obtain the energy profiles, 27 inequivalent linear positions are totally sampled. The adsorption energy ( $E_{\text{ad}}$ ) is calculated by the total energy difference between the stepped surface with and without the adatom. One concern for calculating the adsorption energies is the dipole correction for slab models with different atomic configurations for bottom and top surfaces.<sup>36</sup> The calculations using slab models with large numbers of bilayers and vacuum region thicknesses are also performed. We find that the adsorption energies at the most stable site converge within 0.01 eV/Å. This small energy difference reflects the absence of a macroscopic field in the slab models passivated by artificial H atoms.<sup>37</sup> Details of the calculation procedure are explained elsewhere.<sup>38</sup>

## RESULTS AND DISCUSSION

Prior to the calculations of the adsorption behavior, stable vicinal surfaces under the growth condition should be determined based on the formation energy in eq 1. Figure 3 shows the calculated formation energy of vicinal  $(2 \times 9)$  surfaces as a function of the Ga chemical potential. The calculated formation energy clearly shows the chemical potential dependence in the stable structure of the vicinal surface. The surface with  $\text{N}_{\text{ad}}\text{-H+Ga-H}$  shown in Figure 1(e) is stabilized over a wide range of Ga chemical potentials for  $-1.04 \text{ eV} \leq \mu_{\text{Ga}} - \mu_{\text{Ga}}^{\text{bulk}} \leq -0.42 \text{ eV}$ . On the other hand,  $\text{N}_{\text{ad}}\text{-H+Ga-NH}_2$ , as shown in Figure 1(f), is stabilized close to the N-rich limit ( $\mu_{\text{Ga}} - \mu_{\text{Ga}}^{\text{bulk}} \leq -1.04 \text{ eV}$ ). The surface with 1 ML and 2 MLs of excess Ga is stabilized under Ga-rich conditions ( $\mu_{\text{Ga}} - \mu_{\text{Ga}}^{\text{bulk}} \geq -0.42 \text{ eV}$ ). Therefore, there are four types of reconstructions that depend on the growth condition of the MOVPE. The  $\mu_{\text{Ga}}$  dependence of atomic configurations in the terrace region of the vicinal surface is similar that of the planar



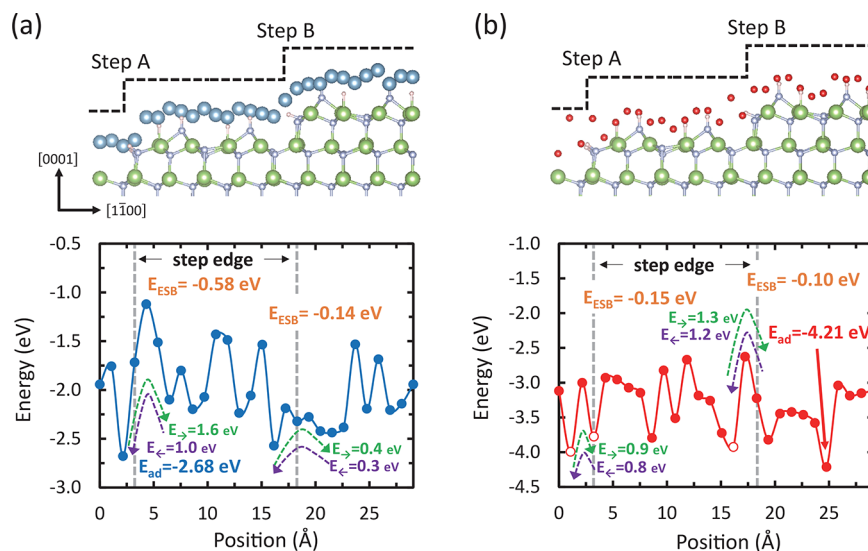
**Figure 3.** Calculated formation energy  $E_{\text{form}}(\mu_{\text{Ga}})$  in eq 1 of various step edge structures on the GaN(0001) surface as a function of the Ga chemical potential,  $\mu_{\text{Ga}} - \mu_{\text{Ga}}^{\text{bulk}}$ , under H-rich conditions. The origin of Ga chemical potential is set to the energy of the bulk Ga. The value of the hydrogen chemical potential of  $\mu_{\text{H}} - \mu_{\text{H}_2} = -1.05$  eV, corresponding to a  $\text{H}_2$  pressure of  $p = 76$  Torr at 1370 K,<sup>35</sup> is used. Structures of step edges and terrace regions are shown in Figure 1.

GaN(0001) surface.<sup>31</sup> It should be noted that the dangling bonds of the step edges in Figure 1(e) and Figure 1(f) are terminated by H atoms to satisfy the EC rule.<sup>30</sup>

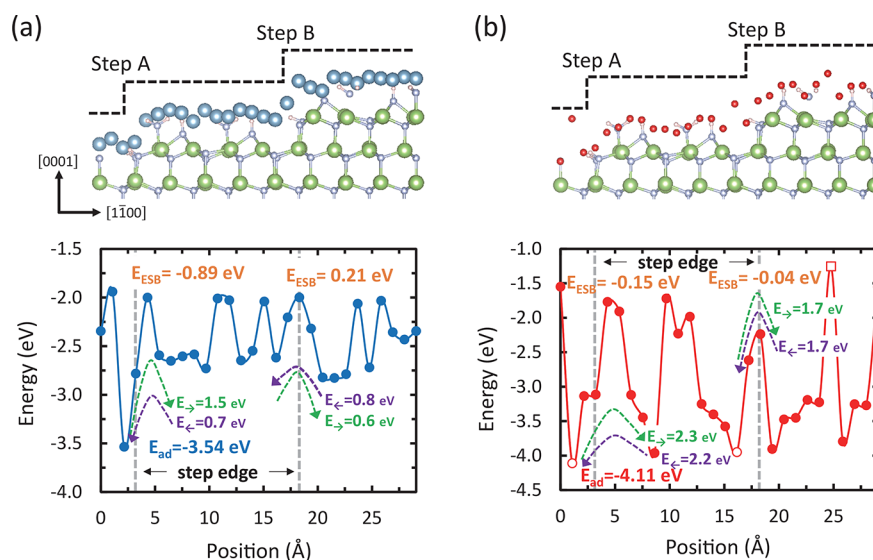
On the basis of the step edge structures determined by the formation energies shown in Figure 3, the adsorption of the Ga and N adatoms is examined for the surfaces with  $\text{N}_{\text{ad}}\text{-H+Ga-H}$  and  $\text{N}_{\text{ad}}\text{-H+Ga-NH}_2$ . This is because MOVPE growth is usually performed under N-rich conditions. According to the results shown in Figure 3 and the comparison of  $\mu_{\text{Ga}}$  with gas chemical potentials, the surface with  $\text{N}_{\text{ad}}\text{-H+Ga-H}$  ( $\text{N}_{\text{ad}}\text{-H+Ga-NH}_2$ ) corresponds to the reconstruction under low (high) temperatures.<sup>39</sup> Figure 4 shows the positions of Ga and N adatoms and their potential-energy profiles along the  $[\bar{1}100]$  direction on the stepped surface with  $\text{N}_{\text{ad}}\text{-H+Ga-H}$  shown in Figure 1(e). From the potential-energy profile of the Ga

adatom shown in Figure 4(a), the most stable adsorption site is found to be located close to step A with  $E_{\text{ad}} = -2.68$  eV. This value is much lower than the adsorption energy on the planar GaN(0001) surface of  $E_{\text{ad}} = -1.88$  eV such that the Ga adatom is easily incorporated at the step edge. The lower adsorption energy originates from the formation of two Ga-N bonds, with the topmost N atoms at step A in Figure 1(e). Furthermore, there is a difference in the energy barriers for diffusing up and down the step, which corresponds to the ESB. The value of the ESB ( $E_{\text{ESB}}$ ) is estimated from the difference of the energy barriers for the step attachment between the upper and lower terraces, which is written as  $E_{\text{ESB}} = E_{\leftarrow} - E_{\rightarrow}$ , where  $E_{\rightarrow}$  and  $E_{\leftarrow}$  are the energy barriers for diffusing up and down, respectively. As shown in Figure 4(a), the values of  $E_{\leftarrow}$  ( $E_{\rightarrow}$ ) are 1.57 (0.98) and 0.38 (0.25) eV for step A and step B, respectively. Therefore, the values of the ESB are  $-0.58$  eV for step A and  $-0.14$  eV for step B. The presence of negative (inverse) ESB values suggests that Ga adatoms can easily migrate from the upper terrace to the lower terrace at both step A and step B.

For the adsorption of the N adatom shown in Figure 4(b), there is an energy difference of about 1 eV that depends on the position of adsorption sites. It is found that the most stable adsorption site is located in the terrace region rather than step edges. The value of the adsorption energy at the most stable site in the terrace region is  $-4.21$  eV. From Figure 4(b), the values of  $E_{\leftarrow}$  ( $E_{\rightarrow}$ ) are found to be 0.93 (0.78) eV for step A and 1.30 (1.19) eV for step B. The values of the ESB for the N adatom are thus estimated to be  $-0.15$  and  $-0.10$  eV for step A and step B, respectively. However, it is likely that the surface diffusion of the N adatom rarely occurs during MOVPE because of the large energy difference of more than 1 eV between the most stable site and the other metastable site. It should be noted that the  $\text{N}_2$  molecule is formed near step A and step B (open circles in Figure 4(b)). Owing to the presence of the topmost N atom at the step edges, N atoms can desorb at the step edges by forming a stable  $\text{N}_2$  molecule.



**Figure 4.** One-to-one correspondence between the position of the adatom and its adsorption energy along the  $[\bar{1}100]$  direction for (a) Ga and (b) N adatoms near the step edges on the vicinal GaN(0001) surface with  $\text{N}_{\text{ad}}\text{-H+Ga-H}$  shown in Figure 1(e). Side views of Ga and N adatoms at each position on the stepped GaN(0001) surface are shown by blue and red circles, respectively. Notations of atoms are the same as those in Figure 2. Calculated adsorption energies of Ga and N adatoms at the most stable site are also shown. The open circle in the adsorption energy indicates the desorption of  $\text{N}_2$ . Note that the range of the adsorption energy is different from each other for the Ga and N adatoms. Energy barriers for diffusing up and down ( $E_{\rightarrow}$  and  $E_{\leftarrow}$ ) are described by green and purple dashed arrows, respectively.



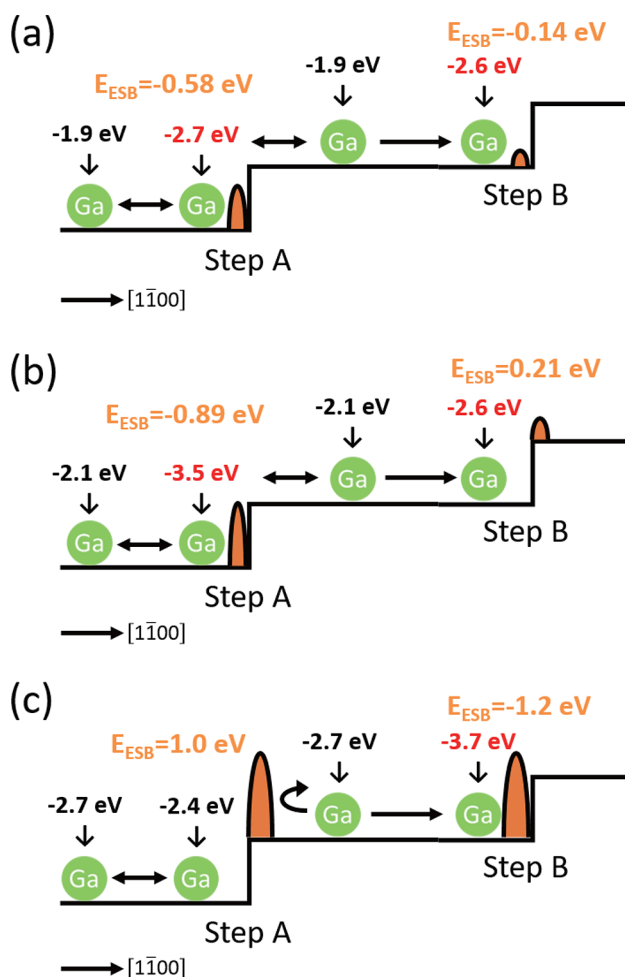
**Figure 5.** One-to-one correspondence between the position of the adatom and its adsorption energy along the  $[1\bar{1}00]$  direction for (a) Ga and (b) N adatoms near the step edges on the vicinal GaN(0001) surface with  $N_{ad}\text{-H+Ga-NH}_2$  shown in Figure 1(f). Notations of atoms are the same as those in Figure 2. Open circles and squares in the adsorption energy indicate the desorption of  $N_2$  and  $N_2H_2$  molecules, respectively. Calculated adsorption energies of Ga and N adatoms at the most stable site are also shown. Energy barriers for diffusing up and down ( $E_{\rightarrow}$  and  $E_{\leftarrow}$ ) are described by green and purple dashed arrows, respectively.

As a result, the surface is stabilized by either the desorption of the  $N_2$  molecule at step edges or the capture of the N adatom in the terrace.

Figure 5 shows the positions of Ga and N atoms and their potential-energy profiles along the  $[1\bar{1}00]$  direction on the vicinal surface with  $N_{ad}\text{-H+Ga-NH}_2$  shown in Figure 1(f), which corresponds to the reconstruction under the N-rich limit. The potential-energy profile of the Ga adatom shown in Figure 5(a) clarifies that the most stable adsorption site is located near step A with  $E_{ad} = -3.54$  eV, which is much lower than the adsorption energy on the planar GaN(0001) surface of  $E_{ad} = -2.09$  eV. This indicates that the Ga adatom on the surface with  $N_{ad}\text{-H+Ga-NH}_2$  is easily incorporated in the step edge, similar to the case of the surface with  $N_{ad}\text{-H+Ga-H}$ . However, the calculated energy barriers around the step edges of the surface with  $N_{ad}\text{-H+Ga-NH}_2$  are different than those with  $N_{ad}\text{-H+Ga-H}$ . The values of  $E_{\rightarrow}$  ( $E_{\leftarrow}$ ) in Figure 5(a) are 1.54 (0.66) eV for step A and 0.62 (0.83) eV for step B, so the values of the ESB estimated from the difference in the barriers for the step attachment between the upper and lower terrace are  $-0.89$  and  $0.21$  eV for step A and step B, respectively. Compared with the results for the surface with  $N_{ad}\text{-H+Ga-H}$  shown in Figure 4(a), a positive value of the ESB is recognized at step B of the surface with  $N_{ad}\text{-H+Ga-NH}_2$ . However, the value at step B is not so large; the contribution of the ESB to Ga adatom diffusion might be negligible, indicating that Ga adatoms can migrate from the upper terrace to the lower terrace at both step A and step B. Although the adsorption energy at stable sites and the energy barriers of the Ga adatom on the surface with  $N_{ad}\text{-H+Ga-NH}_2$  are different from those on the surface with  $N_{ad}\text{-H+Ga-H}$ , a similar adsorption behavior for the Ga adatoms on the vicinal surfaces can be deduced from the similarity of the most stable adsorption site and the ESB at step A. The amplitudes of the ESB at step B for these surfaces are negligibly small, and the difference in the ESB at step A is within 0.3 eV, which could be a negligible difference under high-temperature conditions.

In the case of a vicinal surface with  $N_{ad}\text{-H+Ga-NH}_2$ , the most stable adsorption site for the N adatom is located in the terrace with  $E_{ad} = -4.11$  eV. The adsorption of the N adatom near the step edge results in the formation of a  $N_2$  molecule with the topmost H-terminated N atom at the step edge (open circles in Figure 5(b)). Furthermore, there is a position with a high adsorption energy near 25 Å in the energy profile of Figure 5(b). This originates from the formation of  $N_2H_2$  molecules from the N adatom and the pre-adsorbed  $NH_2$  molecule. The energy barrier for the diffusion of the N adatom in the terrace is about 2 eV. It is thus expected that the N adatom hardly diffuses on terrace regions due to the large diffusion barrier (about 2 eV) and the formation of  $N_2$  and  $N_2H_2$  molecules. Even if we assume the diffusion of N adatoms by admitting the formation of these molecules, the values of  $E_{\rightarrow}$  ( $E_{\leftarrow}$ ) in Figure 5(b) are 2.34 (2.19) eV for step A and 1.71 (1.67) eV for step B, and therefore, the estimated values of the ESB are at most  $-0.15$  eV. Consequently, it is concluded that the step edges are stabilized by either the desorption of a  $N_2$  molecule or the capture of a N adatom in the terrace. It is thus likely that the behavior of the N adatom on the surface with  $N_{ad}\text{-H+Ga-NH}_2$  is similar to that on the surface with  $N_{ad}\text{-H+Ga-H}$ .

The calculated results on the vicinal surfaces shown in Figure 4 and Figure 5 suggest that Ga adatoms diffuse much faster than N adatoms. Although the diffusion of N adatoms should be carefully examined, we now try to deduce the growth modes on the basis of the calculated results for the adsorption and diffusion of Ga adatoms that depend on the growth condition. Figure 6 illustrates the behavior of Ga adatoms on vicinal GaN(0001) surfaces that depend on the surface reconstruction. Here, the adsorption energies in the terraces in Figure 6 are obtained from the calculations on the planar GaN(0001) surface. For the surface with  $N_{ad}\text{-H+Ga-H}$  shown in Figure 6(a), the presence of an inverse ESB suggests that Ga adatoms easily diffuse down the step edge. According to previous theoretical study using Burton–Cabrera–Frank (BCF) theory, the step-flow growth occurs if there is an



**Figure 6.** Schematics of the adsorption behavior of Ga adatoms near the single step edges of reconstructed vicinal GaN(0001) surfaces with (a)  $N_{ad}\text{-H}+\text{Ga-H}$  and (b)  $N_{ad}\text{-H}+\text{Ga-NH}_2$  obtained from Figure 4(a) and Figure 5(a), respectively, which correspond to low and high temperatures under a  $\text{H}_2$  carrier gas in MOVPE, and with (c) Ga atoms corresponding to a  $\text{N}_2$  carrier gas obtained by our previous study.<sup>19</sup> Stepwise lines indicate the step and terrace regions along the  $[\bar{1}\bar{1}00]$  direction. Calculated adsorption energies of the Ga adatom at terraces are obtained using the  $(2 \times 2)$  slab models.

inverse ESB and adatoms are incorporated into the step edges that are only from the upper terrace.<sup>40</sup> Therefore, the presence of the inverse ESB and the adsorption of Ga adatoms into the step edges could lead to step-flow growth. For the surface with  $N_{ad}\text{-H}+\text{Ga-NH}_2$  shown in Figure 6(b), the value of the ESB is positive but negligible at step B. If the contribution of step B is ignored, the situation on the surface with  $N_{ad}\text{-H}+\text{Ga-NH}_2$  shown in Figure 6(b) is similar to that on the surface with  $N_{ad}\text{-H}+\text{Ga-H}$  shown in Figure 6(a). Consequently, the presence of the inverse ESB at step A and the adsorption of Ga adatoms into the step edges could lead to step-flow growth irrespective of the growth temperature of MOVPE when using a  $\text{H}_2$  carrier gas. This is qualitatively consistent with the AFM observation of smooth GaN layers with steps and terraces obtained by the MOVPE using a  $\text{H}_2$  carrier gas.<sup>2</sup>

In contrast, the calculated results for MOVPE using a  $\text{N}_2$  carrier gas are different from those using a  $\text{H}_2$  carrier gas. Figure 6(c) show the results corresponding to the surface with Ga atoms obtained in our previous study,<sup>19</sup> which correspond to the surface under MOVPE using a  $\text{N}_2$  carrier gas. On the

surface with Ga atoms, the values of the ESB are 1.0 and  $-1.2$  eV for step A and step B, respectively, and the Ga adatom is preferentially incorporated into step B with a low adsorption energy. According to the BCF-based theoretical study,<sup>40</sup> step-meandering occurs when there is an ESB and when adatoms are incorporated into the step edges that are only from the lower terrace. Thus, the presence of the large ESB at step A in Figure 6(c) could result in step-meandering. This conclusion is also consistent with the AFM observation during MOVPE using a  $\text{N}_2$  carrier gas.<sup>2</sup>

## CONCLUSION

The adsorption behavior of adatoms on stepped GaN(0001) surfaces during MOVPE growth has been investigated on the basis of *ab initio* calculations. The calculations using vicinal surfaces consisting of single layer step edges along the  $[\bar{1}\bar{1}00]$  direction have revealed that the structure of step edges depends on the growth condition. It has been revealed that the surface with  $N_{ad}\text{-H}+\text{Ga-H}$  is stabilized under moderate N-rich conditions, while the surface with  $N_{ad}\text{-H}+\text{Ga-NH}_2$  is stabilized under a N-rich limit. Furthermore, we have found that the adsorption behavior of Ga and N adatoms close to the step edges depends on these structures. The Ga adatom that is preferentially incorporated at step A with a low adsorption energy and an inverse ESB is recognized. On the other hand, the N adatom is preferentially incorporated in the terrace, and  $\text{N}_2$  molecules are formed when the N adatom adsorbs on the step edges. On the basis of the calculated results of the Ga adatom on the vicinal surfaces, differences of the surface morphology that depend on the growth condition of MOVPE have been verified. These calculated results suggest the possibility of step-flow growth in MOVPE under a  $\text{H}_2$  carrier gas condition, which is reasonably consistent with the AFM observation of smooth GaN layers on a GaN(0001) surface. Although the effects of N adsorption should be carefully examined, our results would be helpful in understanding and controlling the growth morphology of group-III nitride surfaces.

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### Notes

The authors declare no competing financial interest.

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