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Modified approach for calculating individual energies of polar and semipolar surfaces of group-III nitrides

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Abstract

We propose an approach for simultaneously calculating absolute surface energies of polar and semipolar planes without invoking the similarity between hexagonal and cubic structures. Our approach is based on the calculations of total energy differences between two identical wedge-shape geometries with ideal surfaces using density functional calculations in conjunction with the evaluations of surface dangling bonds for various orientations. The calculations demonstrate characteristic features of the surface stability depending on the crystal orientation: For both GaN and AlN, the surface energy of semipolar (1122) plane under H-rich condition is lower than that of nonpolar (1120) plane. The lower surface energy on the (1122) plane compared with the (1120) plane implies that the semipolar (1122) surface is preferentially formed for high H₂ pressures during the metal-organic vapor phase epitaxy, consistent with the experimental results of selective-area growth of GaN. Similar trends can also be found in the surface energies of semipolar (1101) plane in both GaN and AlN, and the absolute surface energy on the (1101) plane is found to be lower than that on the (1122) plane. These calculated results suggest that all of phenomena related to the stability of polar and semipolar planes of group-III nitrides would benefit from these accurate values of surface energies.
I. INTRODUCTION

Group-III nitrides have attracted much attention for use in power devices as well as optoelectronic devices such as laser diodes and light-emitting diodes. Surfaces of group-III nitrides are of importance for their epitaxial growth and causes different surface morphologies, chemical properties, and growth kinetics depending on the orientation of surfaces. For instance, processes such as selective area growth (SAG) are usually used to improve the quality of heteroepitaxial films, and result in the formation of semipolar and nonpolar planes. [1–7] Self-assembled low dimensional nanostructures in group-III nitrides form various types facets consisting of semipolar planes. [8–11] Moreover, it has been reported that the growth of nonpolar AlN(1100) films on SiC substrates obtained by conventional metal-organic chemical vapor deposition exhibits rough surfaces with deep trenches consisting of (0001) and (1101) microfacets. [12] Therefore, surface stability for different planes is a key concept to understand and optimize these growth processes, and knowledge of surface energies of various crystal planes is one of important physical quantities.

Furthermore, in the field of bright green-light emitting diode development, the epitaxial growth of group-III nitrides on nonpolar and semipolar surfaces is attracting attention. Since the polar [0001] direction has large polarization related electric field inside the multiquantum wells, the radiative efficiency within the quantum wells is reduced by the quantum-confined Stark effect. [13] To overcome the polarization effects, there is an increasing interest in crystal growth and device fabrication in semipolar orientations due to their reduced and even negligible electric field. [14–21] Despite the experimental studies, little is known about the surface reconstructions depending on growth conditions and the growth kinetics on semipolar surfaces in group-III nitrides. This is because polar and semipolar surfaces for low symmetry crystalline materials including wurtzite (WZ) structure cannot be individually treated in conventional electronic structure calculations using slab geometries. [22, 23]

To calculate individual polar surface energies a local energy density approach have been applied, [23, 24] but the method suffers from nontrivial calculations of the local energy density. For accurately calculating individual energy for polar semiconductor surfaces, a direct approach using total energy difference between two identical wedge structures of different size has been proposed, [25] and applied to absolute surface energies of GaN polar planes by invoking the similarity between polar (0001)/(0001) surface in WZ structure and (111)/(111) surface in zinc blende (ZB) structure. [26, 27] Although this approach is successful to calculate polar surface energies of group-III nitrides and ZnO, [26, 31] a direct approach to
calculate individual semipolar surface energies are still lacking. Li et al. have recently attempted to understand GaN crystal shapes with semipolar planes by using various wedges with WZ structure. However, the results of surface energies seem to be rather averaged and no absolute surface energies are obtained: The contributions from ridges of wedges are not completely eliminated.

In fact, there are two drawbacks in the approach using ZB structured wedges passivated by artificial hydrogen atoms. The effect of different layer stacking sequence along the [0001] direction in WZ structure is neglected in the wedges with ZB structure. Although the error caused by invoking the similarity between ZB and WZ structures has been estimated to be negligibly small for GaN and InN, the error might be severe for other materials with large ionicity, in which the energy difference between ZB and WZ structures is quite large. Another problematic deficiency is the treatment of passivated surfaces: The bond length between cation and artificial H atom with a charge of 1.25 becomes too long to form tetrahedrally coordinated atomic configuration. The ideal tetrahedrally coordinated bond angle (θ=109.471°) cannot be obtained for group-III nitrides with small lattice constant such as BN and AlN due to the presence of steric barriers of artificial H atoms. It is thus expected that unphysical electronic states appear due to the atomic configurations different from tetrahedrally coordinated ones, and crucially affect to total energies especially for semipolar surfaces, which can be regarded as a combination of stepped surfaces. Most recently, Zhang et al. have proposed a calculation scheme to the absolute formation energies of wurtzite semipolar surfaces using slab models consisting of polar and nonpolar bottom surfaces. Although the scheme successfully obtained the absolute surface energies of semipolar GaN surfaces, effects of H atoms on the reconstructions, which are crucial for the growth conditions of metal-organic vapor phase epitaxy (MOVPE), are not taken into account. In order to overcome these problems, developing a new approach to calculate absolute surface energies of not only polar but also semipolar planes considering surface reconstructions under epitaxial growth condition should be a challenging issue.

In this paper, we propose a modified approach to calculate absolute surface energies of polar and semipolar planes simultaneously without invoking the similarity between ZB and WZ structures. This approach is based on the calculations of total energy differences between two identical wurtzite wedge-shape geometries without passivating H atoms using density functional calculations in conjunction with the evaluations of surface dangling bonds for various orientations. This approach is successfully applied to clarify the stability of
polar and semipolar surfaces of GaN and AlN and to connect to a variety of conditions representing experimental growth conditions. The calculated surface energies for various atomic configurations with different planes are related to each other by considering the formation of stable bonds and the geometries of surface atoms depending on the surface orientation.

II. COMPUTATIONAL DETAILS

We perform total-energy calculations within the density functional theory (DFT) are performed using the plane-wave pseudopotential approach with the generalized gradient approximation (GGA). The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 30.25 Ry. We use norm-conserving pseudopotentials for Ga, Al and H atoms and ultrasoft pseudopotentials for N atoms. $3d$ electrons of Ga atoms are treated by partial core corrections. The conjugate gradient technique is utilized for both electronic structure calculation and geometry optimization. The optimization of geometry is performed until the remaining forces acting on the atoms are less than $5.0 \times 10^{-3}$ Ry/Å. We use the $k$-point sampling corresponding to 36 points in the irreducible part of the $1 \times 1$ surface Brillouin zone, which provides sufficient accuracy in the total energies. The computations are carried out using Tokyo Ab initio Program Package.

The present approach to calculate polar and semipolar surface energies is based on an effective approach using both slabs and wedges. In order to avoid the passivation of artificial H atoms different from those of tetrahedrally coordinated configuration, we use ideal pristine slabs and wedges without artificial H atoms. These models are used to calculate the energies of ideal cleavage surfaces as a reference for each orientation. In the case of reconstructed GaN($hkle$) surface using Miller-Bravais indexing, for instance, the surface energy for a certain atomic configuration including H atoms, is given by using its total energy $E_{tot}^{(hkle)}$ written as

$$\sigma^{(hkle)}_{\mu_Ga, \mu_H} = \frac{1}{A_{hkle}} \left\{ E_{tot}^{(hkle)} - E_{ideal}^{(hkle)} - (\Delta n_{Ga} - \Delta n_{N}) \mu_{Ga} - \Delta n_{N} E_{bulk}^{GaN} - n_H \mu_H \right\} + \sigma_{ideal}^{(hkle)},$$

where $A_{hkle}$ is the area of $(hkle)$-1×1 surface, $E_{ideal}^{(hkle)}$ is the total energy of ideal surface using conventional slab model whose bottom surface is passivated by artificial H atoms with a charge of $0.75e$ and $1.25e$, $\Delta n_{Ga}$ ($\Delta n_{N}$) is the the number of Ga (N) atoms added or removed to form the reconstructed surface, $n_H$ is the number of H atoms, $\mu_{Ga}$ ($\mu_{H}$) is Ga (H) chemical potential, $E_{bulk}^{GaN}$ is the total energy of bulk GaN, and $\sigma_{ideal}^{(hkle)}$ is the absolute surface energy.
of the ideal \((hkil)\) surface. Here, we employ the relationship between \(\mu_{Ga}\) and \(N\) chemical potential \(\mu_N\) expressed as \(\mu_{Ga} + \mu_N = E_{GaN}^{bulk}\) as an equilibrium condition. The surface energies are thus evaluated as a function of \(\mu_{Ga}\), which can vary in the thermodynamically allowed range. This range corresponds to the heat of formation (formation enthalpy), and the calculated values for GaN and AlN are \(-1.23\) and \(-2.90\) eV, respectively. Therefore, the ranges for \(\mu_{Ga}\) and \(\mu_{Al}\) are \(\mu_{Ga}^{bulk} - 1.23\) eV \(\leq \mu_{Ga} \leq \mu_{Ga}^{bulk}\), and \(\mu_{Al}^{bulk} - 2.90\) eV \(\leq \mu_{Al} \leq \mu_{Al}^{bulk}\), where \(\mu_{Ga}^{bulk}\) and \(\mu_{Al}^{bulk}\) are the chemical potentials of bulk Ga and Al, respectively. If the value of \(\sigma_{ideal}^{hkil}\) is known in advance, the absolute surface energies for reconstructed surfaces can be determined straightforwardly by the conventional slab models.

In this study, the absolute surface energies of ideal surfaces of polar and semipolar planes are determined by considering various combination slabs and wedges. For each polar and semipolar orientation, we can straightforwardly construct the equations from the sum of polar and semipolar planes using the total energies of slab models, and another equation describing the relationship between polar and semipolar planes from the total energies of wedge models. However, the surface energies cannot be sufficiently solved using these equations because the number of equations is still missing. To solve these equations, we focus on the relationship between two different semipolar planes each of which has different number of dangling bonds in the unit cell. On the basis of the energy deficit of dangling bonds, we obtain a hypothetical equation for the surface energies of semipolar planes, which is described later. First of all, the sum of the absolute surface energies of ideal \((0001)\) and \((000\overline{1})\) surfaces, \(\sigma_{0001}^{ideal} + \sigma_{000\overline{1}}^{ideal}\), is calculated as

\[
\sigma_{0001}^{ideal} + \sigma_{000\overline{1}}^{ideal} = \frac{1}{A_{0001}} \left( E_{slab0001}^{(0001)/(000\overline{1})} - n_{GaN} E_{GaN}^{bulk} \right), \tag{2}
\]

where \(E_{slab0001}^{(0001)/(000\overline{1})}\) is total energy of pristine \((0001)/(000\overline{1})\) slab, and \(n_{GaN}\) is the number of formula units in the slab model. By considering semipolar orientations, such as \((11\overline{2}2)/(11\overline{2}\overline{2})\) surface with twofold and threefold coordinated atoms, we can also obtain the relationship between the sum of surface energies. In the case of the slab (labeled slab1 henceforth) consisting of \((11\overline{2}2)\) and \((11\overline{2}\overline{2})\) surfaces shown in Fig. 1(a), the sum of surface energies, \(\sigma_{11\overline{2}2}^{ideal} + \sigma_{11\overline{2}\overline{2}}^{ideal}\), is calculated as

\[
\sigma_{11\overline{2}2}^{ideal} + \sigma_{11\overline{2}\overline{2}}^{ideal} = \frac{1}{A_{11\overline{2}2}} \left( E_{slab1}^{(11\overline{2}2)/(11\overline{2}\overline{2})} - n_{GaN} E_{GaN}^{bulk} \right), \tag{3}
\]

where \(A_{11\overline{2}2}\) is the area of \((11\overline{2}2)-1\times1\) surface, \(E_{slab1}^{(11\overline{2}2)/(11\overline{2}\overline{2})}\) is total energy of slab1. In addition, another relationship in the surface energies can be derived from the slab (labeled slab2
FIG. 1. (Color online) Schematics of 1×1 slab models to calculate the sum of surface energies of (a) ideal (11\text{22}) and (11\text{22}) surfaces with both Ga (Al) and N dangling bonds in Eq. (3) labeled as slab1 and (b) ideal (11\text{22}) surface with only N dangling bonds and (11\text{22}) surface with only Ga (Al) dangling bonds in Eq. (4) labeled as slab2. Large and small circles correspond to cations (Al or Ga) and anions (N), respectively. Twofold and threefold coordinated cations (anions) are indicated by solid and dashed gray (purple) arrows, respectively. The unit cell of slabs is shown by rectangles. Note that the vacuum region is truncated for visual understanding.

henceforth) with different atomic configurations shown in Fig. (b), in which only Ga and N dangling bonds appear on (11\text{22}) and (11\text{22}) surfaces, respectively. The sum of surface energies for this configuration, \(\tilde{\sigma}_{\text{ideal}}^{11\text{22}} + \tilde{\sigma}_{\text{ideal}}^{11\text{22}}\), is written as,

\[
\tilde{\sigma}_{\text{ideal}}^{11\text{22}} + \tilde{\sigma}_{\text{ideal}}^{11\text{22}} = \frac{1}{A_{11\text{22}}} \left[ E_{\text{slab2}}^{11\text{22}/11\text{22}} - (n_{\text{GaN}} + 2) E_{\text{GaN bulk}} \right],
\]

where \(E_{\text{slab2}}^{11\text{22}/11\text{22}}\) is total energy of slab2. Since the thickness of slab in Figs. (a) is the same that in Figs. (b), the effect of different atomic configurations between slab1 and slab2 on the surface energies are expressed using Eqs. (3) and (4) as \((\tilde{\sigma}_{\text{ideal}}^{11\text{22}} + \tilde{\sigma}_{\text{ideal}}^{11\text{22}}) - (\sigma_{\text{ideal}}^{11\text{22}} + \sigma_{\text{ideal}}^{11\text{22}})\).

Indeed, this effect originates from the interactions among dangling bonds depending on the atomic configurations and is a key quantity to solve the absolute surface energies.

From the total energies of periodic triangular wedges along the [11\overline{2}0] direction, whose facets consist of one polar \{00\overline{1}1\} bottom surface and two semipolar \{11\text{22}\} planes shown in Figs. 2(a) and 2(b), the difference in surface energies are calculated by taking an energy difference between structures of the same size in which cations and anions are interchanged.
FIG. 2. (Color online) Cross sectional views of triangular wedge consisting of (a) 97 fomura units (wedge1), (b) 97 formula units with 14 adatoms (wedge2) to calculate the energy differences between (11\underline{2}2) and (11\underline{2}2) surfaces, and (c) 64 formula units (wedge3), (d) 64 fomula units with 9 desorbed atoms (wedge4) to calculate the energy differences between (1\underline{1}01) and (\underline{1}101) surfaces. Large and small circles correspond to cation (Al or Ga) and anion (N), respectively. The wedges consisting with smaller formula units (78 and 43 formula units for (a, b) and (c, d), respectively) are constructed by removing the atoms enclosed by dashed lines.

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configurations of (11\overline{2}2) and (11\overline{2}\overline{2}) surfaces shown in Fig. 1(b), the energy difference is given by

\[ 2A_{0001}\{\sigma^{\text{ideal}}_{0001} - \sigma^{\text{ideal}}_{0001}\} + A_{11\overline{2}2}\{\tilde{\sigma}^{\text{ideal}}_{11\overline{2}2} - \tilde{\sigma}^{\text{ideal}}_{11\overline{2}2}\} = \left\{E^{(11\overline{2}2)}_{\text{wedge}2}(97) - E^{(11\overline{2}2)}_{\text{wedge}2}(97)\right\} - \left\{E^{(11\overline{2}2)}_{\text{wedge}2}(78) - E^{(11\overline{2}2)}_{\text{wedge}2}(78)\right\} + 4\mu_{\text{Ga}} - 2E_{\text{GaN}}^{\text{bulk}}, \quad (6) \]

where \( E^{(11\overline{2}2)}_{\text{wedge}2}(n) \) and \( E^{(11\overline{2}2)}_{\text{wedge}2}(n) \) are the total energies of the wedges [Fig. 2(b)] containing \( n (=97, 78) \) formula units with (0001) and (0001) bottom surfaces, respectively.

Although the relative stability between different orientations can be obtained from Eqs. (2), (3), and (5), the absolute surface energies cannot be solved because another independent equation connecting the surface energies is required. However, by constructing similar types of equations using the slabs with (1\overline{1}01) and (1\overline{1}0\overline{1}) surfaces and the wedges along the [11\overline{2}0] direction shown in Figs. 2(c) and 2(d), and considering the orientation dependence of atomic configurations, we can derive another relationship derived from physical insights of the orientation dependence. For the (1\overline{1}01)/(1\overline{1}0\overline{1}) slab model (labeled slab3 henceforth) with both Ga and N dangling bonds on each of (1\overline{1}01) and (1\overline{1}0\overline{1}) surfaces, the sum of surface energies is given by

\[ \sigma^{\text{ideal}}_{1\overline{1}01} + \sigma^{\text{ideal}}_{1\overline{1}0\overline{1}} = \frac{1}{A_{1\overline{1}01}}\{E^{(1\overline{1}01)/(1\overline{1}0\overline{1})}_{\text{slab}3} - n_{\text{GaN}}E_{\text{GaN}}^{\text{bulk}}\}, \quad (7) \]

where \( A_{1\overline{1}01} \) is the area of (1\overline{1}01)-1\times1 surface, and \( E^{(1\overline{1}01)/(1\overline{1}0\overline{1})}_{\text{slab}3} \) is the total energy of slab3. \[42\] For the (1\overline{1}01)/(1\overline{1}0\overline{1}) slab model (labeled slab4 henceforth) with only N and Ga dangling bonds on (1\overline{1}01) and (1\overline{1}0\overline{1}) surfaces, respectively, the sum of these surface energies is given by

\[ \tilde{\sigma}^{\text{ideal}}_{1\overline{1}01} + \tilde{\sigma}^{\text{ideal}}_{1\overline{1}0\overline{1}} = \frac{1}{A_{1\overline{1}01}}\{E^{(1\overline{1}01)/(1\overline{1}0\overline{1})}_{\text{slab}4} - (n_{\text{GaN}} - 1)E_{\text{GaN}}^{\text{bulk}}\}, \quad (8) \]

where \( E^{(1\overline{1}01)/(1\overline{1}0\overline{1})}_{\text{slab}4} \) is the total energy of slab4. \[42\] Note that the number of surface atoms in the unit cell of slab1 and slab2 is twice as much as that of slab3 and slab4. In the case of the wedge (labeled wedge3 henceforth) shown in Fig. 2(c), the difference in surface energies is given by

\[ A_{0001}\{\sigma^{\text{ideal}}_{0001} - \sigma^{\text{ideal}}_{0001}\} + A_{1\overline{1}01}\{\sigma^{\text{ideal}}_{1\overline{1}01} - \sigma^{\text{ideal}}_{1\overline{1}01}\} = \left\{E^{(1\overline{1}01)}_{\text{wedge}3}(64) - E^{(1\overline{1}01)}_{\text{wedge}3}(43)\right\} - \left\{E^{(1\overline{1}01)}_{\text{wedge}3}(64) - E^{(1\overline{1}01)}_{\text{wedge}1}(43)\right\}/2, \quad (9) \]

where \( E^{(1\overline{1}01)}_{\text{wedge}3}(n) \) and \( E^{(1\overline{1}01)}_{\text{wedge}3}(n) \) are the total energies of the wedges [Fig. 2(c)] containing \( n (=64, 43) \) formula units with (000\overline{1}) and (0001) bottom surfaces, respectively. For the
wedge (labeled wedge4 henceforth) shown in Fig. [2d], which corresponds to the atomic configurations of the slab4, the difference is given by

\[
A_{0001}\{\sigma^{\text{ideal}}_{0001} - \sigma^{\text{ideal}}_{0001}\} + A_{11\bar{1}0}\{\sigma^{\text{ideal}}_{11\bar{1}0} - \sigma^{\text{ideal}}_{11\bar{1}0}\} = \left\{E^{(1\bar{1}0)}_{\text{wedge4}}(64) - E^{(1\bar{1}0)}_{\text{wedge4}}(64)\right\} - \left\{E^{(1\bar{1}0)}_{\text{wedge4}}(43) - E^{(1\bar{1}0)}_{\text{wedge4}}(43)\right\} + 4\mu_{\text{Ga}} - 2E_{\text{bulk}}^{\text{GaN}}/2, (10)
\]

where \(E^{(1\bar{1}0)}_{\text{wedge4}}(n)\) and \(E^{(1\bar{1}0)}_{\text{wedge4}}(n)\) are the total energies of the wedges [Fig. 2(d)] containing \(n\) (=64, 43) formula units with (000\(\bar{1}\)) and (0001) bottom surfaces, respectively.

Another relationship can be derived from the orientation dependence of surface energy difference for different atomic configurations. This is based on the assumption for the energy deficit of surface dangling bonds, which depends on their geometric configurations as well as their numbers. As shown in Fig. 11, the total number of Ga and N dangling bonds and its content in slab1 (two twofold-coordinated Ga and N atoms and two threefold-coordinated Ga and N atoms) in the unit cell is exactly the same as that in slab2. For the slabs with semipolar (1\(\bar{1}\)01) and (1\(\bar{1}\)01) surfaces, the total number of Ga and N dangling bonds and its content in slab3 is also exactly the same as those in slab4, and the ratio of twofold coordinated atoms with respect to threefold coordinated ones in slab3 and slab4 is the same as those in slab1 and slab2. Therefore, the energy difference between slab1 and slab2 (slab3 and slab4) originates from the geometric configuration of dangling bonds i.e., the energy difference is caused by transfer of electrons among neighboring dangling bonds. By comparing the surface energy difference \((\sigma^{\text{ideal}}_{11\bar{1}0} + \sigma^{\text{ideal}}_{1\bar{1}0}) - (\sigma^{\text{ideal}}_{11\bar{1}0} + \sigma^{\text{ideal}}_{1\bar{1}0})\) with \((\sigma^{\text{ideal}}_{11\bar{2}2} + \sigma^{\text{ideal}}_{1\bar{1}22}) - (\sigma^{\text{ideal}}_{11\bar{2}2} + \sigma^{\text{ideal}}_{1\bar{1}22})\), contribution of different atomic configurations including charge transfer and electrostatic interaction for Ga and N dangling bonds, we can evaluate the orientation dependence of the effects of atomic configurations. Here, \((\sigma^{\text{ideal}}_{11\bar{1}0} + \sigma^{\text{ideal}}_{1\bar{1}0}) - (\sigma^{\text{ideal}}_{11\bar{1}0} + \sigma^{\text{ideal}}_{1\bar{1}0})\) and \((\sigma^{\text{ideal}}_{11\bar{2}2} + \sigma^{\text{ideal}}_{1\bar{1}22}) - (\sigma^{\text{ideal}}_{11\bar{2}2} + \sigma^{\text{ideal}}_{1\bar{1}22})\) come from the differences in the charge transfer among dangling bonds between slab1 and slab2 for (11\(\bar{2}2)/(11\bar{2}2) and between slab3 and slab4 for (1\(\bar{1}\)01)/(1\(\bar{1}\)01) planes, respectively. Furthermore, the orientation dependence can also be applied for both the sum of Eqs. [6] and [8] for (11\(\bar{2}2) and (11\(\bar{2}2) surfaces, \((\sigma^{\text{ideal}}_{11\bar{2}2} - \sigma^{\text{ideal}}_{1\bar{1}22}) + (\sigma^{\text{ideal}}_{11\bar{2}2} - \sigma^{\text{ideal}}_{1\bar{1}22})\), and the sum of Eqs. [9] and [10] for (1\(\bar{1}\)01) and (1\(\bar{1}\)01) surfaces, \((\sigma^{\text{ideal}}_{11\bar{1}0} - \sigma^{\text{ideal}}_{1\bar{1}10}) + (\sigma^{\text{ideal}}_{11\bar{1}0} - \sigma^{\text{ideal}}_{1\bar{1}10})\). If we assume that the orientation dependence in the contribution of atomic configurations between (1\(\bar{1}\)01) and (11\(\bar{2}2) surfaces is comparable to that between (1\(\bar{1}\)01) and (11\(\bar{2}2) surfaces, the relationship between surface energies between (1\(\bar{1}\)01)/(1\(\bar{1}\)01) and (11\(\bar{2}2)/(11\bar{2}2) planes [42] is written as

\[
\frac{(\sigma^{\text{ideal}}_{11\bar{1}0} + \sigma^{\text{ideal}}_{1\bar{1}10}) - (\sigma^{\text{ideal}}_{11\bar{1}0} + \sigma^{\text{ideal}}_{1\bar{1}10})}{(\sigma^{\text{ideal}}_{11\bar{2}2} + \sigma^{\text{ideal}}_{1\bar{1}22}) - (\sigma^{\text{ideal}}_{11\bar{2}2} + \sigma^{\text{ideal}}_{1\bar{1}22})} = \frac{(\sigma^{\text{ideal}}_{11\bar{1}0} - \sigma^{\text{ideal}}_{1\bar{1}10}) + (\sigma^{\text{ideal}}_{11\bar{1}0} - \sigma^{\text{ideal}}_{1\bar{1}10})}{(\sigma^{\text{ideal}}_{11\bar{2}2} - \sigma^{\text{ideal}}_{1\bar{1}22}) + (\sigma^{\text{ideal}}_{11\bar{2}2} - \sigma^{\text{ideal}}_{1\bar{1}22})}. \quad (11)
\]
Combining ten equations described in Eqs. (2) − (11), these surface energies can be analytically solved. It should be noted that the relationship described in Eq. (11) is fulfilled only for surface planes containing same number of twofold and three coordinated cations and anions in the unit cells: This condition should be satisfied between (110l)-2×1 and (112l′)-1×1 surfaces with l′ = 2l.

As shown in Fig. 2, the calculations of wedges are performed using the unit cells consisting of 97 and 78 formula units for wedge1, and of 97 and 78 formula units with 14 and 12 adatoms for wedge2, respectively. For the (110l) and (110l̅) surfaces, we employ the unit cells consisting of 64 and 43 formula units for wedge3, and of 64 and 43 formula units with 9 and 7 desorbed atoms for wedge4, respectively. The wedge is placed with its facets being separated by approximately 10 Å from those of adjacent wedges. For the calculations of reconstructed (0001) and (000l̅) surfaces, we adopt slab models with 2×2 and √3×√3 unit cells consisting of six bilayers of GaN and AlN along the [0001] direction and approximately 13 Å of vacuum region. For the calculations of reconstructed (11̅22) and (110l) surfaces, we adopt c(2×2) and 2×2 slab models consisting of ten bilayers of GaN and AlN and approximately 10 Å vacuum region. Furthermore, calculations for 1×1 nonpolar (11̅20) and (1̅100) surfaces are performed using 12 bilayers of GaN and AlN and approximately 13 Å of vacuum region for comparison. For each surface orientation, we consider several models for the reconstructions of AlN and GaN surfaces, 29−31, 44−55, which are stabilized under the growth conditions of MOVPE: Various hydrogen terminated surfaces are taken into account. Most of stable surface structures satisfy the electron counting (EC) rule. 56 To calculate the absolute surface energies in Eqs. (2) − (11), (7), and (8), for each orientation we employ the 1×1 slabs with the same number of bilayers as those of above mentioned reconstructed surfaces. The calculations using slab models with large numbers of bilayers and vacuum region thickness are also performed. The difference of surface energies depending on the number of layers is found to be less than 0.005 eV/Å. This small energy difference reflects the absence of a macroscopic field in the slab models passivated by artificial H atoms. 57

III. RESULTS AND DISCUSSION

A. Absolute energies of ideal surfaces

Table II shows the calculated surface energy of ideal AlN and GaN surfaces with polar and semipolar orientations under N-rich limit, along with those of nonpolar orientations. Even in ideal surface, it depends on μGaN owing to the definition of surface energies in Eqs. (6) and
TABLE I. Calculated 1×1 surface area $A_{hkil}$ and surface energy of ideal AlN and GaN surfaces $\sigma_{hkil}^\text{ideal}$ with polar and semipolar orientations obtained using Eqs. (2)–(11) under N-rich limit. Calculated surface energy for nonpolar (1100) and (1120) surfaces are also shown. For semipolar orientations, the surface energies described in Eqs. (3) and (7) are shown. The numbers of dangling bonds in the 2×1 surfaces on (1100) and (1101) planes are the same as those in the 1×1 surfaces on (1120) and (1122) planes, respectively. Note that relaxation of atoms is not taken into account.

<table>
<thead>
<tr>
<th>Material</th>
<th>Orientation</th>
<th>$A_{hkil}$ ($\text{Å}^2$)</th>
<th>$\sigma_{hkil}^\text{ideal}$ (eV/$\text{Å}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN</td>
<td>(0001)</td>
<td>8.95</td>
<td>0.185</td>
</tr>
<tr>
<td></td>
<td>(0001)</td>
<td>8.95</td>
<td>0.228</td>
</tr>
<tr>
<td></td>
<td>(1100)</td>
<td>16.80</td>
<td>0.141</td>
</tr>
<tr>
<td></td>
<td>(1120)</td>
<td>28.69</td>
<td>0.141</td>
</tr>
<tr>
<td></td>
<td>(1101)</td>
<td>19.03</td>
<td>0.158</td>
</tr>
<tr>
<td></td>
<td>(1122)</td>
<td>34.17</td>
<td>0.194</td>
</tr>
<tr>
<td>AlN</td>
<td>(0001)</td>
<td>8.38</td>
<td>0.250</td>
</tr>
<tr>
<td></td>
<td>(0001)</td>
<td>8.38</td>
<td>0.255</td>
</tr>
<tr>
<td></td>
<td>(1100)</td>
<td>15.51</td>
<td>0.173</td>
</tr>
<tr>
<td></td>
<td>(1101)</td>
<td>17.63</td>
<td>0.261</td>
</tr>
<tr>
<td></td>
<td>(1122)</td>
<td>31.66</td>
<td>0.259</td>
</tr>
</tbody>
</table>

The surface energy decreases with $\mu_{\text{Ga}}$ for (0001) surface, while increases for (0001), (1122), and (1101) surfaces. For both GaN and AlN, it is found that the surface energies of nonpolar (1100) and (1120) planes are the lowest among various orientations. This is because these surfaces satisfy the EC rule [56] even in ideal cleavage atomic configurations. For each orientation, the surface energy of GaN is found to be lower than that of AlN. Although lower surface energy in GaN compared with AlN is consistent with the difference in surface area depending on the atom species, surface energy ratio on nonpolar planes between GaN and AlN (0.82~0.83) is much lower than the inverse of surface area ratio of 0.92~0.94. This indicates that the difference of electronic interactions among dangling bonds as well as surface area difference depending on the orientation affects the surface energy.

Since the surface energies shown in Table I are obtained from the slab models each of
bottom and top surface does not satisfies the EC rule, one of concerns in the present approach is taking pristine surfaces as references of absolute surface energies. It is likely that the contributions of charge transfer between bottom and top surface and the formation of dipole field in the vacuum region affect the energies of ideal surfaces. To check the validity of the ideal surfaces for slabs and wedges, we also perform the calculations of slabs and wedges using pristine surfaces only for semipolar (1\bar{1}01) and (1\bar{1}22) planes: Twofold coordinated anions and threefold cations in the slabs and wedges are passivated by artificial H atoms for the other polar and semipolar planes. In these models, charge transfer between surfaces hardly occurs, and tetrahedrally coordinated atoms are appropriately maintained owing to the absence of twofold coordinated Al and Ga atoms terminated by artificial H atoms with a charge of 1.25e on semipolar planes. The differences in the absolute surface energy depending on the scheme of passivation are found to be less than 0.002 and 0.009 eV/\AA^2 for GaN and AlN, respectively, which are much smaller than the values of absolute surface energies shown in Table I. It is thus concluded the contribution of charge transfer has a minor effect on the surface energy for group-III nitrides.

It has been suggested that the exchange correlation functional affects the absolute surface energy using the wedge-shape geometries. Although the effects of functional on the absolute surface energies should be carefully examined, we could not find sizable differences in the absolute surface energies. The calculated absolute surface energies of GaAs polar surfaces with ZB structure using GGA is only \(\sim 0.009\) eV/\AA^2 lower than those using local density approximation in Ref. [25]. The calculated absolute surface energies for nonpolar GaN(1\bar{1}00) and AlN(1\bar{1}00) surfaces using the GGA are found to be lower than those using the hybrid functional [58] by 0.007 eV/\AA^2.

B. GaN surfaces

Figure 3 shows the calculated absolute surface energy of reconstructed semipolar (1\bar{1}22) planes of GaN as a function of \(\mu_{\text{Ga}}\) by using Eq. 11 with \(\sigma_{\text{ideal}}^{1\bar{1}22}\) in Table I along with those of polar (0001) and (000\bar{1}) planes. The calculated surface energy of nonpolar (1\bar{1}20) plane is also shown for comparison. Here, we assume the value of hydrogen chemical potential \(\mu_H - \mu_{H_2}/2 = -0.75\) and \(-1.1\) eV, which corresponds to low and high H\(_2\) pressures \((p=40\) and 760 Torr) at 1270 K \((\mu_{H_2} = \text{the chemical potential of single H}_2\) molecule at 0 K\) for the MOVPE, respectively. The calculated absolute surface energy of GaN(0001) surface is ranging from 0.075 to 0.15 eV/\AA^2 while that of GaN(000\bar{1}) surface takes smaller values less
FIG. 3. (Color online) Absolute surface energies of semipolar (1122) and nonpolar (1120) planes of GaN as a function of Ga chemical potential $\mu_{\text{Ga}}$, under (a) H-poor and (b) H-rich conditions, along with those of polar (0001) and (000$\bar{1}$) planes. Solid blue and red lines denote surface energies of (1120) and (1122) planes, respectively. Surface energies of polar (0001) and (000$\bar{1}$) planes are represented by dashed black and purple lines, respectively. Surface reconstructions are also labeled. The values of hydrogen chemical potential $\mu_{\text{H}} - \mu_{\text{H}_2} = -1.1$ and $-0.75$ eV, which correspond to low and high H$_2$ pressure (40 and 760 Torr) at 1270 K ($\mu_{\text{H}_2}$ is the chemical potential of single H$_2$ molecule at 0 K) are considered for H-poor and H-rich conditions, respectively.

The structures and energies on polar (0001) and (000$\bar{1}$) planes under H-poor condition shown in Fig. 3(a) are fairly consistent with those in previous calculations using passivated wedges with ZB structure. When we use $\mu_{\text{H}} - \mu_{\text{H}_2}=1.1$ eV using passivated wedges with ZB structure, the differences in absolute surface energies for (0001) and (000$\bar{1}$) planes depending on the calculations scheme are less than 0.001 and 0.006 eV/Å$^2$, respectively.
respectively. For GaN(1122) surface, the stable surface structure depends on $\mu_{\text{Ga}}$: The $c(2 \times 2)$ surface with Ga monolayer is stabilized under Ga-rich conditions. On the other hand, the $1 \times 1$ surface terminated by H atom (3N-H+NH$_2$) is favorable under N-rich condition, and the surface with Ga adatom (Ga$_{\text{ad}}$) appears under intermediate condition with low H$_2$ pressures, consistent with previous calculations. $^{47}$ Under high H$_2$ pressures, this is structure is metastable and the surface with H atoms (3N-H+NH$_2$) are stabilized over the wide range of $\mu_{\text{Ga}}$.

One of important features of absolute surface energies found in Fig. 3 is that the H chemical potential crucially affects the orientation dependence of surface stability. In particular, the absolute surface energies of polar (0001) and semipolar (1122) planes drastically decrease with $\mu_{\text{H}}$. This is quite different from nonpolar (1120) surface without H atoms, which does not show H$_2$ pressure dependence. The calculated absolute surface energy on Ga-polar GaN(0001) shown in Fig. 3(a) is lower than those on GaN(1122) surface for $-0.85 \leq \mu_{\text{Ga}} \leq -0.40$ eV and $\mu_{\text{Ga}} \geq -0.11$ eV under low H$_2$ pressure, while the energy of GaN(1122) surface under high H$_2$ pressure shown in Fig. 3(b) is lower than that on GaN(0001) surface over wide range of $\mu_{\text{Ga}}$. Furthermore, under high H$_2$ pressure the absolute surface energy of GaN(1122) surface becomes lower than that of nonpolar GaN(1120) surface over the wide range of $\mu_{\text{Ga}}$. These results suggest that semipolar (1122) facets can be formed on GaN(0001) substrate under high H$_2$ pressure condition during the MOVPE.

Although more elaborate analysis of equilibrium crystal morphology on the basis of the Wulff construction $^{59-61}$ and growth kinetics such as adsorption, desorption, and migration behavior $^{31}$ should be necessary, the trend of stable surface orientation depending of H$_2$ pressure is consistent with the epitaxial lateral over growth in SAG of GaN along the $\langle 11 \bar{2} 2 \rangle$ direction. $^{4,5}$ The stabilization of (0001) and semipolar (1122) planes originates from their atomic arrangements which exhibit N-polar behavior. Since most of the topmost N atoms are terminated by H atoms, the density of stable N-H bonds on (0001) and (1122) planes are much larger than those of the other orientations, resulting in the low surface energies.

The results of the most stable polar GaN(0001) surface can also explain the experimental results of slower growth of the (0001) plane compared with the (0001) plane in the SAG of GaN. $^{7}$ Since GaN(0001) surface is sufficiently stabilized with low absolute surface energy, it is expected that the adsorption energy is too high to stabilize the additional atoms. Indeed, the calculated adsorption energy of Ga atom at the most stable adsorption site on the H-terminated (0001) surface (3N-H in Fig. 3) is only $-0.93$ eV, which is higher than
that on H-terminated (0001) surface. Therefore, in the case of GaN(000\bar{1}) plane Ga atoms easily desorb from the surface during its migration processes at high temperature around 1300 K, indicating the low growth rate compared with (0001) plane. Furthermore, the results of stable (000\bar{1}) plane is consistent with the formation of GaN nanopillars with (000\bar{1}) top plane instead of semipolar facets grown on N-polar GaN templates.

Figure 4 shows the calculated absolute surface energy of reconstructed semipolar (1\bar{1}01) plane of GaN as a function of \( \mu_{\text{Ga}} \) by using Eq. (1) with \( \sigma_{1\bar{1}01}^{\text{ideal}} \) in Table I, along with those of (1\bar{1}00), (0001), and (000\bar{1}) planes. We find that the stable surface structures on GaN(1\bar{1}01) surface depends on \( \mu_{\text{Ga}} \): The surface with Ga bilayer is stabilized under Ga-rich condition. On the other hand, the 2\times2 surfaces terminated by H atom (2NH\textsubscript{2}+5N-H and Ga-H+4N-H) is favorable under N-rich condition. Trends in the stabilization of the surfaces with Ga bilayer and those with H atoms under Ga-rich and N-rich conditions, respectively, are reasonably consistent with those in previous calculations. In contrast to (1\bar{1}22) surface, the absolute surface energy of semipolar (1\bar{1}01) plane is lower than that of Ga-polar (0001) plane over the entire range of \( \mu_{\text{Ga}} \). The difference in the absolute surface energy between (1\bar{1}22) and (1\bar{1}01) planes is due to the difference in dangling bonds density, which is extracted from the 1\times1 surface area shown in Table I.

Similar to the case of (1\bar{1}22) surface shown in Fig. 3, the absolute surface energy of semipolar (1\bar{1}01) plane shown in Fig. 4 drastically decreases with H\textsubscript{2} pressure. The calculated absolute surface energy on GaN(000\bar{1}) shown in Fig. 4(a) is lower than those on GaN(1\bar{1}01) surface for \( \mu_{\text{Ga}} \leq -0.09 \text{ eV} \) under low H\textsubscript{2} pressure, while the energy of GaN(1\bar{1}01) surface under high H\textsubscript{2} pressure shown in Fig. 4(b) is lower than that on GaN(000\bar{1}) surface for \( \mu_{\text{Ga}} \leq -0.74 \text{ eV} \). It should be noted that the absolute surface energy of semipolar (1\bar{1}01) plane under N-rich limit (0.064 eV/Å\textsuperscript{2}) is comparable to that of (000\bar{1}) plane and lower than (1\bar{1}00) plane (0.108 eV/Å\textsuperscript{2}) even under H-poor condition, as shown in Fig. 4(a). Therefore, it is highly likely that the facets consisting of (1\bar{1}01) plane are dominantly formed during the MOVPE-SAG. This conclusion is consistent with the formation of (1\bar{1}01) facets in the SAG of GaN \cite{3,5,10} and in the MOVPE growth of GaN nanopillars with (1\bar{1}00) and (1\bar{1}01) facets on Ga-polar GaN films.

We also note that it is difficult to directly compare the absolute surface energies of GaN shown in Figs. 3 and 4 with those of recent calculated results by Zhang et al., \cite{34}, where the effect of H atoms are not included. However, if we focus on only Ga-rich condition, the results of (1\bar{1}22), (1\bar{1}20), (000\bar{1}), (1\bar{1}00), and (1\bar{1}01) surfaces can be evaluated. The
FIG. 4. (Color online) Absolute surface energies of semipolar (1¯101) and nonpolar (1¯100) planes of GaN as a function of Ga chemical potential $\mu_{\text{Ga}}$, under (a) H-poor and (b) H-rich conditions, along with those of polar (0001) and (000¯1) planes. Solid blue and red lines denote surface energies of (1¯100) and (1¯101) planes, respectively. Surface energies of polar (0001) and (000¯1) planes are represented by dashed black and purple lines, respectively. Surface reconstructions are also labeled. For hydrogen chemical potential, the values described in the caption of Fig. 2 are used.

Absolute surface energies on (000¯1) and (11¯22) surfaces under Ga-rich limit (0.098 and 0.093 eV/Å², respectively) obtained in this study are almost the same and the value of (11¯20) of 0.12 eV/Å² is comparable to previous calculations. On the other hand, the absolute surface energies of (1¯101) and (1¯100) surfaces under Ga-rich limit (0.068 and 0.058 eV/Å², respectively) are lower than those of previous calculations. Although these values obtained in this study are underestimated, the relative stability between (1¯101) and (1¯100) surfaces under Ga-rich limit can be reproduced even in our calculations.
FIG. 5. (Color online) Absolute surface energies of semipolar (11¯22) and nonpolar (11¯20) planes of AlN as a function of Al chemical potential $\mu_{\text{Al}}$, under (a) H-poor and (b) H-rich conditions, along with those of polar (0001) and (000¯1) planes. Solid blue and red lines denote surface energies of (11¯20) and (11¯22) planes, respectively. Surface energies of polar (0001) and (000¯1) planes are represented by dashed black and purple lines, respectively. Surface reconstructions are also labeled. For hydrogen chemical potential, the values described in the caption of Fig. 2 are used.

C. AlN surfaces

Figure 5 shows the calculated absolute surface energy of reconstructed semipolar (11¯22) planes of AlN as a function of $\mu_{\text{Al}}$ by using Eq. (11) with $\sigma_{\text{ideal}}^{\text{11\bar{2}2}}$ in Table II along with those of polar (0001) and (000¯1) planes. The calculated surface energy of nonpolar (11¯20) plane is also shown for comparison. The calculated absolute surface energy of AlN(0001) surface is ranging from 0.11 to 0.17 eV/Å$^2$ while that of AlN(000¯1) surface takes smaller values less than 0.16 eV/Å$^2$. The trend of stable surface structures on polar AlN planes are similar to
that on polar GaN planes. The structures and energies on polar (0001) and (000\bar{1}) planes under H-poor condition shown in Fig. 5(a) are not only qualitatively but also quantitatively consistent with those in previous calculations using passivated wedges with ZB structure. The chemical potential ranges for the stabilization of each surface structure are the same as those in Ref. [31] within the error of 0.15 eV. The difference in absolute surface energies for (0001) and (000\bar{1}) planes between the present scheme and the method using passivated ZB structure in Ref. [31] are within 0.005 eV/Å². For AlN(11\bar{2}2) surface, the stable surface structure depends on \(\mu_{\text{Al}}\): The surface with Al monolayer is stabilized under Ga-rich conditions. On the other hand, the surfaces terminated by H atom (3N-H+NH\textsubscript{2} and Al\textsubscript{ad}-H+N\textsubscript{ad}-H) are favorable under N-rich condition, and the surface with Al adatom (Al\textsubscript{ad}) appears under relatively Al-rich conditions. For H-rich condition, the surface with H atoms are stabilized over the wide range of \(\mu_{\text{Al}}\). Furthermore, the absolute surface energies of polar AlN(000\bar{1}) and semipolar AlN(11\bar{2}2) planes drastically decrease with H\textsubscript{2} pressure.

The calculated absolute surface energy on AlN(11\bar{2}2) surface shown in Fig. 5(a) is higher than that on AlN(0001) surface under low H\textsubscript{2} pressure, but the energy of AlN(11\bar{2}2) surface under high H\textsubscript{2} pressure shown in Fig. 5(b) is lower than those on AlN(0001) and (11\bar{2}0) surface for N-rich condition. These results suggest that semipolar (11\bar{2}2) facets can be formed on AlN(0001) substrate under high H\textsubscript{2} pressure condition during the MOVPE.

Owing to the stabilization of AlN(0001) surface with low absolute surface energy, it is also expected that the adsorption on the (000\bar{1}) surface is suppressed. The calculated adsorption energy of an Al atom on the H-terminated (000\bar{1}) surface (3N-H in Fig. 5) of −1.17 eV is higher than those on the H-terminated (0001) surface (−1.89 eV). Therefore, Al atoms easily desorb from AlN(000\bar{1}) surface during its migration processes at high temperature around 1300 K, indicating low growth rate of AlN(000\bar{1}) surface compared with AlN(0001) surface.

Figure 6 shows the calculated absolute surface energy of reconstructed semipolar (1\bar{1}01) planes of AlN as a function of \(\mu_{\text{Al}}\) by using Eq. (1) with \(\sigma_{\text{ideal}}^{1\bar{1}01}\) in Table I along with those of (1\bar{1}00), (0001), and (000\bar{1}) planes. It is found that the stable surface structures on AlN(1\bar{1}01) surface depends on \(\mu_{\text{Al}}\): The surface with Al bilayer is stabilized under Al-rich conditions. On the other hand, the 2\times2 surfaces terminated by H atoms (2NH\textsubscript{2}+5N-H and N\textsubscript{de}+3Al-H) are favorable under N-rich condition. The stabilization of Al bilayer and N\textsubscript{de}+3Al-H shown in Fig. 6(a) is qualitatively consistent with previous calculations. In contrast to the (11\bar{2}2) plane, the absolute surface energy of (1\bar{1}01) plane is lower than that of (0001) plane.
FIG. 6. (Color online) Absolute surface energies of semipolar (1101) and nonpolar (1100) planes of AlN as a function of Al chemical potential $\mu_{\text{Al}}$, under (a) H-poor and (b) H-rich conditions, along with those of polar (0001) and (000$\bar{1}$) planes. Solid blue and red lines denote surface energies of (1100) and (1101) planes, respectively. Surface energies of polar (0001) and (000$\bar{1}$) planes are represented by dashed black and purple lines, respectively. Surface reconstructions are also labeled. For hydrogen chemical potential, the values described in the caption of Fig. 2 are used.

Over the wide range of $\mu_{\text{Al}}$, as explained in Sec. III B, the difference in the absolute surface energies between (1122) and (1101) planes is due to the difference in dangling bonds density, which is extracted from the $1 \times 1$ surface area shown in Table I.

Similar to the case of (1122) plane shown in Fig. 5, the absolute surface energy of (1101) plane shown in Fig. 6 drastically decrease with $H_2$ pressure. Under high $H_2$ pressure shown in Fig. 6(b), the energy of AlN(1101) surface is comparable to that on AlN(000$\bar{1}$) surface for N-rich limit. Therefore, it is likely that the facets consisting of (1101) and (000$\bar{1}$) planes...
can be formed. Indeed, the growth of AlN(1̅100) films using MOVPE exhibit rough surfaces with deep trenches consisting of (1̅101) and (000̅1) N-face microfacets. Furthermore, the stabilization of ideal (11̅00) surface under Al-rich condition with the absolute surface energy less than 0.139 eV/Å² shown in Fig. 6 is consistent with the experimental results of the formation of AlN(1̅100) films with good crystallinity and smooth surfaces under Al-rich condition. [12]

IV. SUMMARY

We have proposed an approach to calculate individual energy of polar and semipolar surfaces and applied to various surfaces of GaN and AlN. This approach has resolved some deficiencies in the conventional approach using the wedge models with ZB structure. We have found that characteristic features of the surface stability depending on the crystal orientation. For GaN, the surface energy of semipolar (11̅22) plane under high H₂ pressure condition is lower than that of nonpolar (1̅120) plane. The lower surface energy on the (11̅22) planes compared with the (1̅120) plane implies that the semipolar (11̅22) surface is preferentially formed for high H₂ pressures during the MOVPE, consistent with the experimental results of SAG of GaN. Similar trends can also be seen in the surface energy of semipolar (1̅101) plane, and its absolute surface energy is found to be lower than that of (11̅22) plane. For AlN, we have found that the absolute surface energy of semipolar (1̅101) plane under high H₂ pressure condition is comparable to that of polar (000̅1) plane, which is the most stable among various orientations. This implies that both semipolar (1̅101) and polar (000̅1) surfaces can be formed under high H₂ pressures during the MOVPE, consistent with the growth of AlN(1̅100) films on SiC substrates. These calculated results suggest that our approach is versatile for clarifying various phenomena related to the stability of polar and semipolar planes such as maximum temperature for crystal growth and equilibrium crystal shape for the class of wurtzite materials. For instance, according to recent thermodynamic analysis method that incorporates surface energies, the epitaxial growth at higher temperature is possible for the surface orientation with lower surface energy. [29, 30] Our results can be used such kind of thermodynamic analysis to predict the growth condition of group-III nitrides along various orientations. In addition, equilibrium crystal morphologies of nanostructures depending on the growth condition can be tailored on the basis of absolute surface energies using Wulff’s theorem, such as γ- and v-plots. [59, 61] Since the absolute surface energy depends on the growth condition, we can predict the growth condition for a
desired crystal morphology. By comparing the calculated crystal shapes according to $\gamma$- and $\nu$-plots with experiments, we can also clarify the effects of kinetics on the crystal morphologies of nanostructures: if the crystal shapes using the calculated absolute surface energies can reproduce those in experiments, the main contribution for the crystal shape is statically determined on the basis of absolute surface energies. Furthermore, this approach can be applicable for not only the SAG but also self-assembled systems such as quantum dots (QDs). We are now applying the approach for investigating the formation of GaN three-dimensional islands (a sort of QDs) on AlN(0001) substrates. Our approach provide a firm theoretical framework to clarify the growth mechanisms of wurtzite materials.

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[39] M. Tsukada et al., Computer program package TAPP (The University of Tokyo, Tokyo, Japan, 1983-2016).
[42] See Supplemental Material at http://link.aps.org/ for the slab models of (1¯101)/(1¯10¯1) surfaces, wedge models in which all cations and anions in Fig. 2 are interchanged, and detailed description to obtain Eq. (11).


[62] The calculated adsorption energy of Ga adatom on GaN(0001) surface with H atoms (\(\sim -2.3\) eV) is found to be smaller than that on GaN(0001) surface.

[63] The surface with NH\(_2\) (2NH\(_2\)+5N-H) is not taken into account in Ref. [46]. The difference in chemical potential range for the stabilization of Ga-H+4N-H between Fig. 4(a) and Fig. 1 in Ref. [46] is due to the difference in hydrogen chemical potential.