Absolute surface energies of polar and nonpolar planes of GaN

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Accurate values for absolute surface energies are required to understand bulk and thin-film growth. Using first-principles calculations based on hybrid density functional theory we determine energies for bare and hydrogenated surfaces of wurtzite GaN in polar and nonpolar orientations. We find that the energies of the nonpolar m and a planes are similar and constant over the range of Ga, N, and H chemical potentials studied. In contrast, the energies of the polar planes are strongly condition dependent. We find that the $+c$ polar plane is systematically lower in energy than the $-c$ plane.

The surface energies of different planes in a crystal determine the equilibrium morphology [1,2] and equilibrium growth rate in the direction normal to each plane [3]. Absolute surface energies are, therefore, key to understanding and optimizing growth processes of bulk or epitaxial films. In the case of III-nitrides, the lack of availability of bulk substrates currently requires performing heteroepitaxial growth, affecting the crystal quality and sometimes leading to facet formation or to the presence of residual strains that cause cracking, another effect which is closely related to surface energies. Processes such as selective area growth (SAG) are used to improve the quality of heteroepitaxial films [4], hydride vapor phase epitaxy (HVPE) is employed to produce thick substratelike films [5], and actual bulk growth is being explored using techniques such as ammonothermal growth [6] or Na flux [7]. All of these would benefit from having accurate values for surface energies.

The fact that accurate values for nitride surface energies are not yet available is due to two issues: (1) absolute energies for polar or semipolar planes are fundamentally ill-defined for a crystal with low symmetry such as wurtzite (wz), as shown rigorously in Ref. [8], and further discussed in Ref. [9]; and (2) uncertainties in previously calculated results due to limitations in the computational techniques. In this work, we have overcome these problems and calculated the absolute surface energies of the polar and nonpolar planes in GaN from first principles; we have investigated a large number of reconstructions for bare as well as hydrogen-covered surfaces to connect to a variety of conditions representing experimental growth by molecular beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD), and HVPE.

The indeterminacy of the individual surface energies for the polar surfaces is a fundamental problem that is intrinsic to the wurtzite crystal structure. Here, we approach the issue pragmatically by invoking the similarity between polar $(0001)/(000\bar{1})$ planes in wz and $(111)/(\bar{1}\bar{1}\bar{1})$ planes in zinc blende (zb), for which absolute surface energies *can* be determined due to the higher symmetry of the zb crystal structure (see Fig. 1) [8,10]. Such an approach was previously applied to CdSe [11,12]. The second issue, accuracy of the computational results, is addressed by our use of a hybrid functional in the first-principles calculations based on density functional theory (DFT). This approach overcomes the deficiencies of traditional functionals such as the local density approximation (LDA) or generalized gradient approximation

(GGA), which severely underestimate the band gap (by as much as 50% in GaN). The band-gap error also affects the energies of surface states within the gap [13], and when these states are occupied with electrons (which is invariably the case for all relevant surface reconstructions) the calculated surface energy is also affected.

Absolute surface energies of the nonpolar $\{10\bar{1}0\}$ m and $\{11\bar{2}0\}$ a planes are rigorously defined and accessible from slab calculations that can be performed within the supercell approach [14]. For a supercell containing a slab with n formula units, separated by an appropriate amount of vacuum, the surface energy is obtained by subtracting the total energy of n formula units of bulk GaN from the total energy of the slab and dividing by twice the total surface area (since the cell contains two identical surfaces).

GaN slabs terminated by polar planes inevitably exhibit inequivalent surfaces; a surface energy obtained from a slab calculation therefore yields the *average* surface energy of the (0001) $(+c)$ and $(000\bar{1})$ $(-c)$ planes. In addition, spurious charge transfer from the Ga dangling bonds on the $+c$ to the N dangling bonds on the $-c$ surface is likely to occur; this problem can be avoided by passivating the bottom surface of the slab with fractionally charged hydrogen. By keeping the structure of the bottom surface fixed, energy differences can be determined between various reconstructions of the top surface for a particular polar plane [14–18]. This procedure yields relative energies; the absolute surface energy of the top surface can still not be determined without knowledge of the absolute surface energy of the passivated bottom surface.

In this work, we assume the energies of the wz passivated bottom surfaces are equal to the energies of passivated zb (111) or $(\bar{1}\bar{1}\bar{1})$ planes. The zb phase of GaN is energetically similar to wz (we calculate an energy difference of 26 meV per formula unit), and the atoms on the zb $(111)/(\bar{1}\bar{1}\bar{1})$ planes have the same coordination and structure up to the next-nearest neighbors of the surface atoms as the wz polar planes. In addition, the calculated sum of the surface energies of the passivated (0001) and $(000\bar{1})$ planes (a well defined quantity) differs from the sum of the (111) and $(\bar{1}\bar{1}\bar{1})$ surface energies by less than 2%. At first sight, the zb $(111)/(\bar{1}\bar{1}\bar{1})$ planes may seem to suffer from the same problem as wz polar surfaces in that a slab oriented along the [111] direction exhibits inequivalent top and bottom surfaces. However, the higher symmetry of the zb phase (in particular, the existence of two rotation axes [8]) ensures that a rigorous definition of the absolute $(111)/(\bar{1}\bar{1}\bar{1})$ surface energy
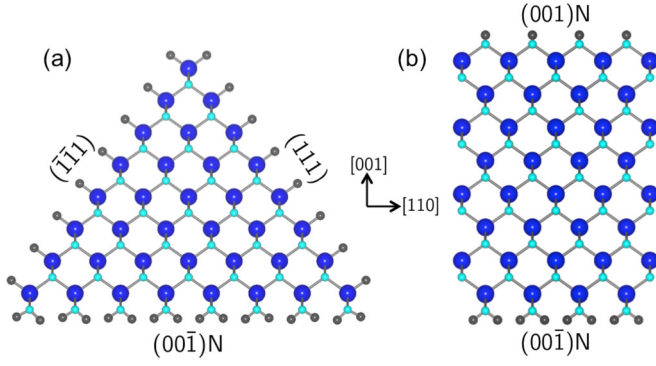
FIG. 1. (Color online) (a) Cross section of a zb-GaN triangular wedge used to determine the energy of the (111) surface. The bottom surface is a N-terminated (001)N surface, the other surfaces are symmetrically equivalent (111) and ($\bar{1}\bar{1}1$) surfaces. All surfaces are passivated with fractional H atoms. (b) Cross section of the zb-GaN slab used to determine the energy of the passivated {001} surface.

is possible [9], and a practical method was proposed by Zhang and Wei [10] based on calculations for an infinitely long wedge with triangular cross section [Fig. 1(a)].

The wedge surfaces are all passivated with fractional hydrogen atoms (i.e., hydrogen-like atoms with an electron/proton charge of $0.75e$ for the N-terminated face and $1.25e$ for the Ga-terminated face). A similar wedge can be constructed with ($\bar{1}\bar{1}\bar{1}$) surfaces and a Ga-terminated (001) surface.

The contribution to the total energy from the {001} surface can be determined straightforwardly by using a slab with two equivalent (either Ga- or N-terminated) surfaces [Fig. 1(b)]. Such cells are not stoichiometric, and the additional energy required to add an extra Ga or N surface atom must be accounted for by reference to the species' chemical potentials [15]. In equilibrium, these chemical potentials are related through the equation $\mu_{Ga} + \mu_N = \mu_{GaN}$; we present our surface energies as a function of μ_{Ga}, which is referenced to the energy of bulk Ga. μ_{Ga} ranges from 0 under Ga-rich conditions to a minimum value set by the enthalpy of formation of GaN (calculated to be -1.35 eV) under N-rich conditions.

Contributions from ridges of the wedge can be removed by subtracting energies for different wedge sizes [10] (here $n = 28, 36$). Rempel *et al.* [12] subsequently showed that better convergence can be obtained if an energy difference is considered between structures of the same size in which cations and anions are interchanged, i.e., wedges terminated by (111) planes versus ($\bar{1}\bar{1}\bar{1}$) planes. Altogether, the difference in surface energy $\sigma_{pass}^{(111)} - \sigma_{pass}^{(\bar{1}\bar{1}\bar{1})}$ is given by

$$\sigma_{pass}^{(111)} - \sigma_{pass}^{(\bar{1}\bar{1}\bar{1})} = \frac{1}{2A^{(111)}}\Bigg\{ \big[E_{wedge}^{(111)}(36) - E_{wedge}^{(\bar{1}\bar{1}\bar{1})}(36)\big] - \big[E_{wedge}^{(111)}(28) - E_{wedge}^{(\bar{1}\bar{1}\bar{1})}(28)\big] - \frac{1}{2}\big[E_{slab}^{(001)N} - E_{slab}^{(001)Ga}\big] + \frac{1}{2}[\mu_N - \mu_{Ga}]\Bigg\},$$

(1)

where $E_{wedge}^{(111)}(n)$ is the total energy of the wedge [Fig. 1(a)] with passivated (111) surfaces containing n GaN formula units

and $E_{slab}^{(001)Ga/N}$ is the total energy of a slab with (001)Ga/N surfaces [Fig. 1(b)]. As noted above, the *sum* of the polar surface energies, $\sigma_{pass}^{(111)} + \sigma_{pass}^{(\bar{1}\bar{1}1)}$ is easily obtained from a slab calculation, and combining that value with Eq. (1) then gives the individual absolute energies for the passivated surfaces.

The absolute surface energy for a reconstructed wz polar surface is then given by

$$\sigma^{(0001)} = \frac{1}{A^{(0001)}}\big[E^{(0001)}(n) - E_{bulk}(n) - n_{Ga}\mu_{Ga} - n_N\mu_N - A^{(0001)}\sigma_{pass}^{(\bar{1}\bar{1}\bar{1})}\big],$$

(2)

where $E^{(0001)}$ is the total energy of a slab with the $-c$ face passivated and the $+c$ face reconstructed and n_{Ga}/n_N is the number of atoms added or removed to form the reconstructed surface.

The total energy calculations were performed using the hybrid functional of Heyd, Scuseria, and Ernzerhof [19] with 31% mixing of Hartree-Fock exchange, and projector-augmented-wave [20] pseudopotentials as implemented in the Vienna *Ab Initio* Simulation Package (VASP) [21] code. This functional has been shown to provide a good description of the electronic structure of GaN, including the band gap and defect levels within the gap [22]. The energy cutoff of the plane-wave basis set was set to 300 eV, with convergence checks up to 400 eV.

The wedge cells [Fig. 1(a)] contained 28 or 36 formula units of zb-GaN separated by at least 15 Å of vacuum. A $1 \times 1 \times 4$ Monkhorst-Pack [23] k-point mesh was used for integrating over the Brillouin zone (four k points in the direction along the wedge axis). Keeping the geometry of the passivated (111)/($\bar{1}\bar{1}\bar{1}$) surfaces identical between the wedge and slab cells is essential for consistency. The fractional hydrogen atoms on the wedge surfaces were first allowed to relax with the Ga and N atomic positions fixed. The H atoms along with the surface layer of GaN were then fixed, and the bulk-coordinated GaN atoms were allowed to relax. These fixed surface geometries were used for the first layer of the wz-GaN passivated bottom surfaces for the calculation of the reconstructions on the $+c$ and $-c$ planes.

The zb {001} surface energy slab cells contained 8 bilayers of GaN, and 18 Å of vacuum; the reconstructed wz slabs were 2×2 or $\sqrt{3} \times \sqrt{3}$ unit cells by 12 bilayers of GaN and 18 Å of vacuum; the *a* plane slab cells contained 14 bilayers of GaN and 12 Å of vacuum; the *m* plane slab cells contained 12 bilayers of GaN and 12 Å of vacuum. A $4 \times 4 \times 1$ k-point mesh was used for all slab calculations. We estimate the numerical convergence of surface energies to be within 0.02 eV/Å².

The results for bare surfaces are presented in Fig. 2. For clarity, only the lowest-energy reconstruction for a specific surface plane at each value of $\mu_{Ga} - \mu_{Ga(bulk)}$ is plotted in Fig. 2. Those lowest-energy reconstructions for given planes are the same as those found in previous calculations [15,16], but our results now allow comparing *absolute* energies for different planes. Our calculated surface energies for the unreconstructed (but of course relaxed) nonpolar planes agree within 9% with values obtained using DFT LDA [24]. For polar surfaces, we have found sizable differences between absolute surface energies calculated with HSE and less accurate functionals
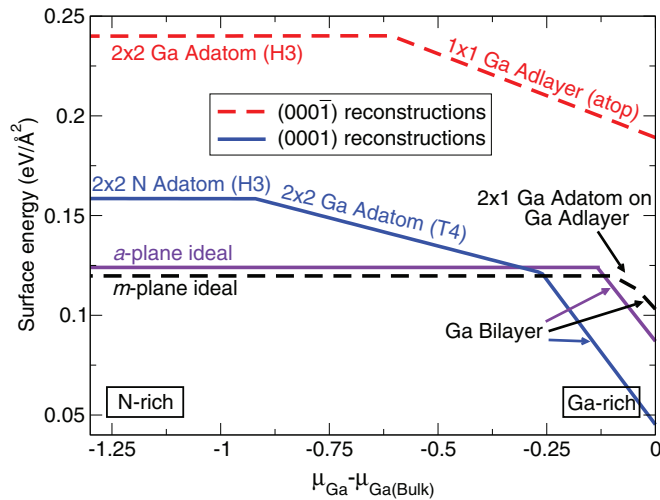
FIG. 2. (Color online) Absolute surface energies of GaN nonpolar and polar planes as a function of Ga chemical potential.

such as GGA, confirming the importance of the use of a hybrid functional.

In order to address MOCVD, HVPE, or ammonia MBE growth, we need to study reconstructions involving hydrogen and explicitly consider *free* energies, both because of the temperature and pressure dependence of the chemical potential of gaseous sources and because of entropy contributions from vibrational modes of adsorbates, which can be sizable due to the small atomic mass of hydrogen [25,26]; the latter have been determined as in Ref. [26].

Figure 3 shows the lowest-energy hydrogenated polar surface reconstructions for $T = 1300$ K, $p = 1$ atm, representative of MOCVD growth conditions, and $T = 1000$ K, $p = 10^{-12}$ atm, representative of MBE growth [27]. The effects of temperature and pressure conditions that differ from
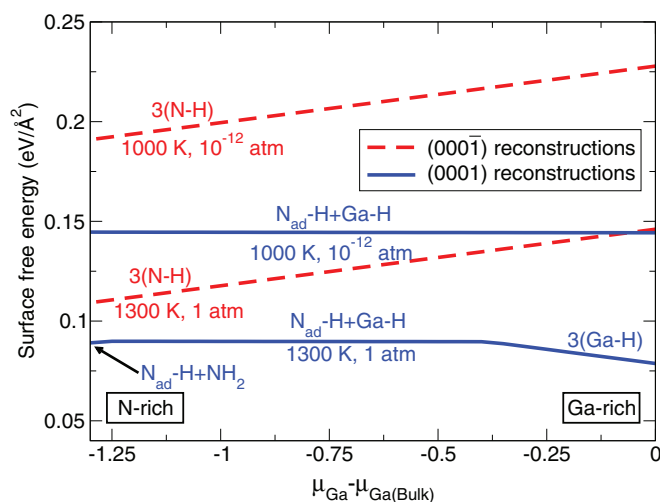

FIG. 3. (Color online) Absolute surface free energies of hydrogenated GaN polar planes for different temperature and pressure conditions, as a function of Ga chemical potential. Hydrogenation of nonpolar surfaces does not lower the surface energy at these T and p conditions.

these specific choices can be estimated by considering that increasing T increases the surface energy of the hydrogenated reconstructions (mainly due to a decrease in μ_H), while increasing p (increasing μ_H) decreases the surface energy.

The energies in Fig. 3 can be compared with those of the bare surfaces in Fig. 2 (free-energy contributions have only minor effects on the latter). We find that hydrogenated reconstructions significantly decrease the surface energies of the $+c$ and $-c$ planes, except under very Ga-rich conditions; reconstructions are designated by the same labels as in Refs. [26] and [27]. On the other hand, reconstructing the nonpolar surfaces with hydrogen did not lower the surface energy [25]. The similarity in surface energies between the m and a planes over a wide range of conditions is consistent with observations of similar growth rates of the planes in MOCVD and HVPE SAG [4,5,28–30].

Even when considering H-containing reconstructions, the $+c$ surface remains lower in energy than the $-c$ over the whole Ga chemical potential range, though this difference is significantly reduced under N-rich conditions at 1300 K, 1 atm. On the other hand, hydrogenation of the polar planes significantly alters their relative stability with respect to the nonpolar planes (which remain bare). For MOCVD conditions, the hydrogenated $+c$ surface is lower in energy than the nonpolar planes over the entire chemical potential range, and the $-c$ plane is more stable than the nonpolar planes under N-rich conditions.

In SAG experiments, the $-c$ plane is observed to grow much more slowly than the $+c$ [4,5,28], contrary to the equilibrium growth we would expect from our surface energies. The difference could be due to kinetic factors, or possibly due to a lower-energy surface reconstruction on the $-c$ surface that has not yet been considered.

In summary, we have calculated absolute surface energies for nonpolar and polar orientations of GaN, for bare and hydrogenated surfaces. The nonpolar a and m planes are similar in energy, and their energies do not depend on the growth conditions over a wide range of temperatures, pressures, and chemical potentials. The $+c$ face is lower in energy than the $-c$ face for all conditions considered. Hydrogenation of the polar surfaces under relevant growth conditions significantly reduces their energy, rendering them more stable than the nonpolar planes. These results will form a sound basis for analyzing and guiding growth of GaN with a variety of techniques, as well as providing a framework to determine surface energies of other technologically relevant wurtzite materials such as InN, AlN and ZnO.

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