Theory of GaN($10\bar{1}0$) and ($11\bar{2}0$) surfaces

John E. Northrup and J. Neugebauer
Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304
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The surface energies and atomic structures for two nonpolar surfaces of GaN have been calculated within the local-density approximation. For the ($10\bar{1}0$) surface, which has Ga-N dimers in the surface layer, the calculated surface energy is 118 meV/Å^2, and for the ($11\bar{2}0$) surface, which has Ga-N chains in the topmost layer, the energy is 123 meV/Å^2. The relaxation mechanisms on both surfaces are a Ga-N bond contraction and a $\sim 7°$ buckling rehybridization in the surface layer. For the ($10\bar{1}0$) surface we find that under Ga-rich conditions a nonstoichiometric surface having Ga-Ga dimers is stable with respect to the ideal Ga-N dimer-terminated surface.

GaN crystallizes in the wurtzite structure and exhibits a direct energy band gap of approximately 3.4 eV at room temperature. Interest in characterizing the properties of GaN is partly driven by the fact that blue light-emitting diodes have been fabricated in GaN-based materials,[1] and the possibility exists that laser diode technology will be developed. Despite the fact that the epitaxially grown material is highly defective, the luminescence efficiency is high.[2] This has led to the suggestion that the threading defects in these films are electrically inert. Although the precise structure of the threading defects in GaN films and their electronic properties are not known, one type of defect appears to be a stacking mismatch boundary[3] in which the local atomic structure could be similar to that expected on the ($10\bar{1}0$) surface. Therefore, studies of the atomic and electronic structure of the GaN($10\bar{1}0$) surface may provide information on the electronic properties of the defects.

Because of the high density of threading defects in GaN grown on *c*-plane sapphire, there is considerable interest in exploring alternative growth techniques, including other substrates. At present most growth has involved the polar (0001) surface of GaN.[4] However, it is possible that growth on the nonpolar ($10\bar{1}0$) or ($11\bar{2}0$) surfaces could have some advantages. In this work, we present a theoretical study of two nonpolar surfaces: the ($10\bar{1}0$) and the ($11\bar{2}0$). We present results for the surface energies and atomic structures as well as a discussion of the surface state electronic properties.

The ($10\bar{1}0$) and the ($11\bar{2}0$) surfaces are nonpolar and could result from cleaving. On each surface there are equal numbers of threefold-coordinated Ga and N in the surface layer of atoms, thus allowing charge neutrality to be obtained without changes in stoichiometry or reconstruction. Schematic models of these surfaces are shown in Figs. 1 and 2. The truncated bulk structure represents a reasonable starting point to determine the structure by performing an energy minimization, and we have performed such calculations within the local-density-functional approximation. The two main relaxation mechanisms are a contraction of the GaN bond in the surface layer and a slight buckling rehybridization with N atoms tending to adopt p^3 coordination and Ga atoms adopting an sp^2 configuration. The calculations indicate that the ($10\bar{1}0$) and ($11\bar{2}0$) surfaces have very similar surface energies. Since it is possible in principle to prepare the ($10\bar{1}0$) or ($11\bar{2}0$) surface by an epitaxial growth process rather than by cleaving, we also consider the possibility of nonstoichiometric surfaces. We have investigated structures in which Ga replaces N and vice versa and find that a ($10\bar{1}0$) surface having Ga-Ga dimers instead of Ga-N dimers in the surface layer may be stable under very Ga-rich conditions. Such a surface should be more reactive than the Ga-N dimer-terminated surface, and could be a useful intermediate stage in atomic layer epitaxial growth processes.

The surfaces of GaN were modeled in the supercell approach with each cell consisting of eight layers of GaN. Tests preformed with slabs containing 12 layers indicated that the eight layer slabs are adequate. The atoms in the top two layers of each side of the slabs were allowed to relax. Total energy and force calculations were performed within density-functional theory using the first-principles pseudopotential method. The Perdew and Zunger[5] exchange and correlation energy function derived from the Ceperley and Alder electron-gas data was employed. Forces and total energies were determined using a highly optimized planewave code similar to that described by Stumpf and Scheffler,[6] supplemented by an efficient tight-binding scheme to generate the starting wave functions.[7] The pseudo-

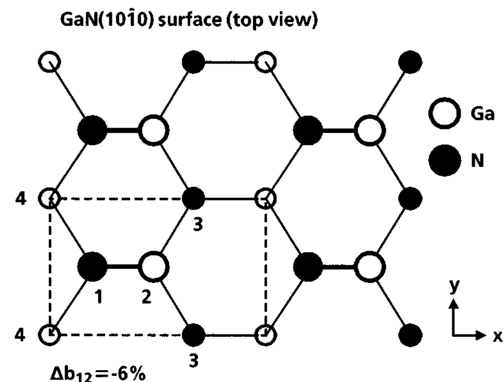

FIG. 1. Schematic top view of the ($10\bar{1}0$) surface of wurtzite GaN. The dashed lines outline the boundary of a unit cell (5.179 Å by 3.171 Å). Atoms 1 and 2 form a dimer in the surface layer. Atoms 3 and 4 form the second layer.

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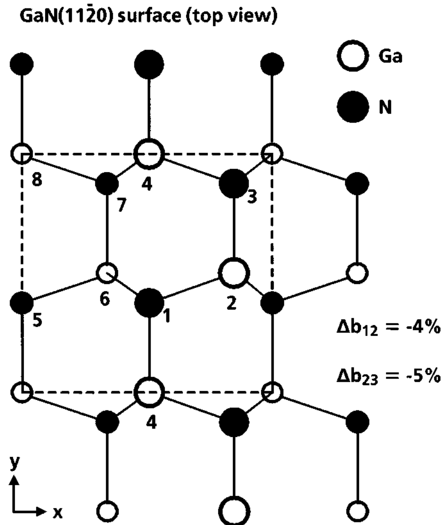

FIG. 2. Schematic top view of the (11$\bar{2}$0) surface of wurtzite GaN. The dashed lines outline the boundary of a unit cell (5.493 Å by 5.179 Å). Atoms 1–4 form the Ga-N chain in the surface layer, while atoms 5–8 comprise the second layer.

potentials are expressed in the Kleinman and Bylander form,[8] with the 3*d* electrons of Ga included in the valence band. The plane-wave cutoff was 60 Ry and four *k* points were used to sample the Brillouin zone. Soft pseudopotentials have been generated in the Troullier and Martins[9] approach and have been tested in calculations for bulk Ga, N_2 molecules, and bulk GaN.[10] The calculated heat of formation of GaN is 0.90 eV, which is in good agreement with the experimental value, 1.14 eV.[11]

On the (10$\bar{1}$0) surface the Ga and N atoms form an array of GaN dimers as indicated schematically in Fig. 1. The bond length of the GaN dimers on the (10$\bar{1}$0) surface is 1.82 Å. This corresponds to a 6% contraction with respect to the bond length calculated for the bulk (1.94 Å). The vertical displacement between N and Ga atoms in the surface dimer is 0.22 Å and corresponds to a buckling angle of 7°. The bond angles around the Ga atom become 118°, 118°, and 113°, while those around the N atom are 105°, 105°, and 114°. Thus the Ga atom moves closer to the sp^2 configuration and N remains close, on average, to its original configuration. In a recent Hartree-Fock calculation,[12] the GaN dimer bond is found to be contracted by 7% and the buckling angle was found to be only about 1°. To our knowledge, there have been no experimental studies of the GaN(10$\bar{1}$0) surface structure. The calculated atomic displacements for the (10$\bar{1}$0) surface are listed in Table I.

The structure of the (11$\bar{2}$0) surface corresponds to a chain of threefold-coordinated Ga and N atoms, as indicated in Fig. 2. In each unit cell there are four surface atoms: two Ga and two N atoms. The calculated Ga-N bond lengths in the surface chain are 1.85 Å (*cis*) and 1.87 Å (*trans*), corresponding to contractions of 4%–5% compared to the bulk value. The vertical separation between the N and Ga atoms in the surface layer is 0.22 Å, the same as found for the (10$\bar{1}$0) surface. In this case, the N atoms exhibit bond angles of 107°, 106°, and 101°. The Ga atoms again relax towards a

TABLE I. Atomic displacements in Å for the top two layers of atoms at the GaN(10$\bar{1}$0) surface. Atom numbers refer to Fig. 1.

Atom	Δx	Δy	Δz
1 (N)	0.01	0.0	0.02
2 (Ga)	−0.11	0.0	−0.20
3 (N)	0.05	0.0	0.05
4 (Ga)	0.05	0.0	0.05

sp^2 configuration with bond angles of 119°, 116°, and 115°. Calculated atomic displacements are listed in Table II.

The surface energy for the (10$\bar{1}$0) surface is found to be 1.95 eV (two-atom cell) corresponding to 118 meV/Å^2. For the (11$\bar{2}$0) surface the surface energy is 3.50 eV/(four-atom cell) which corresponds to 123 meV/Å^2. It is important to note also that although the energy per surface atom is higher on the (10$\bar{1}$0) surface, the density of surface atoms is higher on the (11$\bar{2}$0) surface. The result is that the surface energy/(unit area) is slightly lower on the (10$\bar{1}$0) surface. The calculated surface energies for GaN may be compared with that of GaAs(110) which is 1.20 eV/(two-atom cell) corresponding to 54 meV/Å^2.[13] The larger cleavage energy for GaN results from two effects: the density of bonds that are broken to create the surface is larger in the case of GaN, and the energy required to break each bond is greater.

The energy required to rupture a bond may be estimated from the cohesive energy of the solid, which is 8.7 eV for GaN. Since there are four bonds per GaN pair we arrive at a bond energy of 2.17 eV/bond. In forming a GaN(10$\bar{1}$0) surface one must break one bond per cell; thus the estimated surface energy is 2.17 eV/(two-atom cell). This estimate is in rough agreement with our calculated value, 1.95 eV/(two-atom cell). For the (11$\bar{2}$0) surface the estimated surface energy is 4.35 eV/(four-atom cell), compared to the calculated value of 3.50 eV. For GaAs the cohesive energy is 6.6 eV, and therefore the estimated surface energy for a GaAs(110) surface is 1.65 eV/(two-atom cell), which may be compared to the value calculated by Qian, Martin, and Chadi, which is 1.2 eV/(two-atom cell).

We have also explored the possibility of nonstoichiometric surfaces which could occur in the process of epitaxial growth. To do this we have calculated the formation energy for several possible nonstoichiometric surfaces as a function of the atomic chemical potential of Ga.[14,15] The results are shown in Fig. 3. We considered structures in which the surface Ga (N) was replaced with N (Ga). Under N-rich growth conditions we might imagine that the structure in which the

TABLE II. Atomic displacements in Å for the top two layers of atoms at the GaN(11$\bar{2}$0) surface. Atom numbers refer to Fig. 2.

Atom	Δx	Δy	Δz
1 (N)	−0.02	−0.02	0.05
2 (Ga)	−0.16	0.10	−0.17
3 (N)	0.02	−0.02	0.05
4 (Ga)	0.16	0.10	−0.17
5 (N)	0.01	−0.01	0.02
6 (Ga)	0.00	−0.02	0.05
7 (N)	−0.01	−0.01	0.02
8 (Ga)	0.00	−0.02	0.05

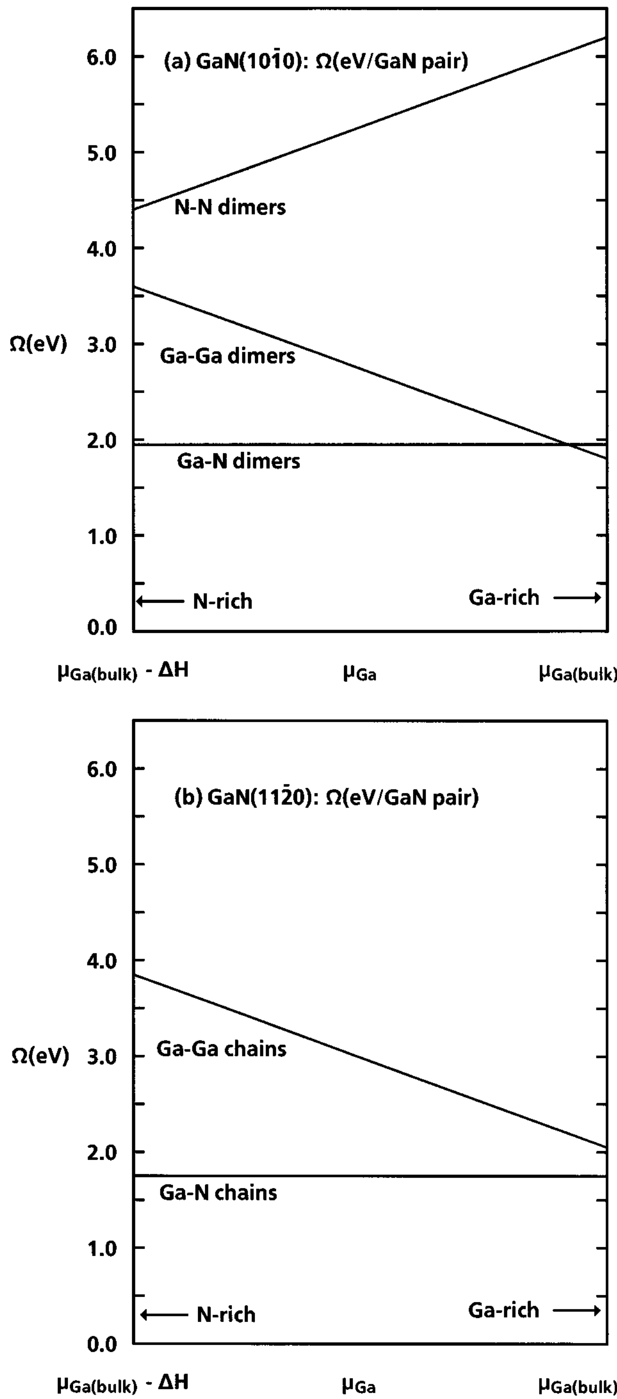

FIG. 3. (a) Formation energy vs Ga chemical potential for the (10$\bar{1}$0) surface. (b) Formation energy vs Ga chemical potential for the (11$\bar{2}$0) surface. The maximum chemical potential for Ga is equal to the energy per atom calculated for bulk Ga.

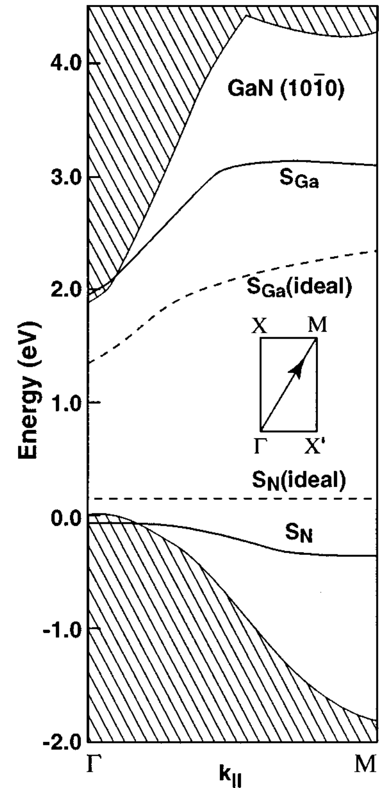

FIG. 4. Band structure calculated within the local-density approximation for both the ideal and relaxed (10$\bar{1}$0) surfaces of GaN. The shaded region corresponds to the bulk projected band structure. The dashed lines indicate the dispersion of the surface states calculated for the surface without structural relaxation.

surface Ga atoms are replaced by N atoms would be stable. In that case we would have N-N dimers on the (10$\bar{1}$0) surface and chains of N atoms on the (11$\bar{2}$0) surface. However, our calculations indicate that the formation energy of the N-N dimer surface is very high, even under N-rich growth conditions. This is because the N atoms are simply too small to establish both strong back bonds and strong N-N bonds in the surface layer. On the other hand, the structure obtained by replacing N with Ga, resulting in Ga-Ga dimers, is found to be energetically favorable under Ga-rich conditions. Therefore, we suggest that a (10$\bar{1}$0) surface with Ga-Ga dimers could be formed under Ga-rich growth conditions. Such a Ga-rich surface should have a higher sticking coefficient for N, and so it may be advantageous to employ such a surface as an intermediate stage in atomic layer epitaxy. For the (11$\bar{2}$0) surface, the structure formed by replacing surface N atoms with Ga is not energetically favorable, even under Ga-rich conditions.

An important issue confronting theoretical studies of energetics and structure of GaN systems is the potentially important role of the Ga $3d$ electrons in obtaining accurate results. For very large-scale calculations it is desirable to treat the $3d$ electrons within the nonlinear core (NLC) approximation.[16] It is therefore of interest to quantify the differences between NLC calculations and those which include the Ga $3d$ electrons in the valence bands. In the NLC approximation, we find the surface energy of the (10$\bar{1}$0) surface to be 1.45 eV/cell, a 25% reduction in energy compared to our full calculations (1.95 eV/cell). For the (11$\bar{2}$0) surface, we obtain 2.59 eV/cell compared to 3.50 eV/cell in the full calculation. Thus, the NLC approximation underestimates the surface energy by roughly 0.5 eV per GaN pair. This level of accuracy may be acceptable in some cases. In general, though, one should be cautious in reaching conclusions based on NLC calculations for GaN. In the NLC calculations we find the surface GaN dimer bond length to be 1.76 Å, a 7% contraction with respect to the bulk bond length calculated in the same approximation (1.89 Å); the

buckling angle is 5°. Thus, the atomic structure obtained in the NLC approximation is qualitatively the same as that obtained in the calculations with the Ga $3d$ electrons in the valence band.

Finally, we discuss the electronic structure for the $(10\bar{1}0)$ surface calculated within the local-density approximation (LDA). In such calculations for bulk GaN we obtain a band gap of about 1.9 eV compared to the experimental gap of 3.4 eV. This difference is typical of LDA calculations for semiconductors. Previous quasiparticle calculations for bulk GaN (Ref. 17) yield gaps which are typically 1.2 to 1.6 eV larger than the LDA gaps, and with this correction our LDA result is in good agreement with experiment. The calculated LDA electronic structure for both the ideal and the relaxed $(10\bar{1}0)$ surface is shown in Fig. 4. The occupied surface state (S_N) is p like with respect to the N atoms while the unoccupied surface state (S_{Ga}) is a dangling bond localized on the Ga atoms. The effect of atomic relaxation is to increase the gap between the S_N and S_{Ga} bands by more than 1 eV. A similar mechanism is operative for other wurtzite materials.[18] For the fully relaxed structure, the N-derived band lies just below the valence-band maximum, while the Ga-derived band lies just above the conduction-band minimum. Thus, if the quasiparticle self-energy corrections correspond primarily to a rigid shift of the unoccupied states relative to the occupied states, then there should be no surface states in the gap on GaN$(10\bar{1}0)$. Clearly, both experimental studies of the electronic structure and quasiparticle calculations are in order to test this conjecture. In any case, the qualitative picture that emerges for GaN is that doubly occupied N p-like states lie near the valence-band maximum, while the empty Ga-derived dangling bonds are close in energy to the conduction-band minimum. If the threading defects in thin GaN epitaxial films contain nearest-neighbor pairs of Ga and N dangling bonds, as on the $(10\bar{1}0)$ surface, then the electronic levels associated with these defects may lie outside the fundamental energy band gap. In this case the defects may be electrically inactive.

In conclusion, we have calculated the atomic structure and surface energetics for cleaved GaN$(10\bar{1}0)$ and $(11\bar{2}0)$ surfaces. For both surfaces we find a rehybridization of the Ga atoms towards an sp^2 configuration. The surface energies for these two surfaces are similar in value (~120 meV/Å^2) and are more than a factor of 2 larger than for the GaAs surface. Under Ga-rich conditions we find that a $(10\bar{1}0)$ surface terminated by Ga-Ga dimers may be stable. The occupied N-derived surface state on $(10\bar{1}0)$ lies just below the valence-band maximum and the empty Ga-derived state lies above the conduction-band minimum.

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