Ab initio prediction of GaN (10$\bar{1}$0) and (110) anomalous surface relaxation

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The results of a study of the surface relaxation of GaN in the framework of the *ab initio* (all-electron) Hartree-Fock method are presented. We perform total-energy calculations using a two-dimensionally periodic slab model for the most stable nonpolar cleavage faces, namely, the (10$\bar{1}$0) and (110) surfaces of the wurtzite and zinc-blende phases, respectively. For both surfaces, when the energy is minimized the Ga-N surface bonds show a very small rotation angle of about 6° accompanied by a reduction in surface bond length of about 7%. This result differs from the well-accepted model of the GaP (110) and GaAs (110) surfaces, where there is a large rotational angle in the range of 27°–31° and little change in surface bond length. The structure dependence of the calculated density of states suggests that this difference is at least partly due to interaction of the Ga $3d$ states with N $2s$-derived states in GaN. Partial double-bond character in the surface bond may also be important.

There has been considerable interest in gallium nitride (GaN) due to its potential device applications in high-temperature electronics and near-ultraviolet electro-optics.[1] GaN usually crystallizes at ambient conditions in the wurtzite structure, but thin films of GaN grown epitaxially on various substrates have also been reported to have the zinc-blende structure.[2] A complete understanding of surface reconstruction is a prerequisite for better epitaxial growth of thin films for the development of GaN-based devices. However, such an understanding has not yet been achieved, as both experimental and theoretical surface scientists have paid relatively less attention to GaN than to, for example, GaP or GaAs. In this paper, we aim to enhance the understanding of the main nonpolar cleavage faces of GaN by describing a calculation of their atomic structures and electronic properties.

Our approach is based on the *ab initio* periodic Hartree-Fock approximation as implemented in the CRYSTAL92 program, which has been successful in describing bulk and surface structural properties of many materials.[3] We have performed all-electron total-energy calculations using linear combinations of Gaussian orbitals to construct a localized atomic basis from which Bloch functions are constructed by a further linear combination. These Bloch functions are the basis in which the Fock operator is diagonalized.[4] In the present case, the LCAO basis set was taken from an earlier study[5] of structural and electronic properties of bulk GaN. The basis set[6] consists of four shells of s-type and three shells of p-type functions for N (a 7311/311 set) and six s-, five p-, and two d-type shells for Ga (an 864111/64111/41 set). The bulk lattice constants calculated[5] with this basis[6] for the wurtzite phase, $a=3.201$ Å and $c=5.169$ Å, agreed with experiment to within 1%. For the zinc-blende phase the calculated lattice constant[5] was 4.510 Å. These same calculated lattice constants were used in setting up our two-dimensional slab model in which the two terminating surfaces are both taken to be the physical surface under study. The slab consists of a finite number of layers and is periodic in two dimensions. For the wurtzite phase, the translational lattice constants of the slab are the uniaxial c and the basal plane a of the bulk structure, while they are a and $a/\sqrt{2}$ for the zinc-blende phase. Each layer in the slab is neutral, consisting of equal numbers of Ga and N atoms. We began by testing the convergence of our slab model with respect to the slab's thickness. We performed total-energy calculations on two-, four-, and six-layer slabs of the wurtzite phase terminated by ideal (unreconstructed) (10$\bar{1}$0) surfaces. The calculated results yielded surface energies [defined as $S=(nE_{\text{bulk}} - E_{n\text{-layer slab}})/2$] of 1.31, 1.58, and 1.55 eV per surface atom for the $n=2$, 4, and 6 slabs, respectively. This rapid convergence[7] to the thick-slab limit indicates the adequacy of a four-layer slab for further calculations. As an additional test we fully relaxed the GaN zinc-blende (110) top surface layers with both three- and four-layer slab models (see below) and obtained nearly the same geometry with either thickness.

Symmetry-conserving reconstruction (relaxation) of nonpolar semiconductor surfaces is generally described by the bond rotation model in which anions move outward and cations move inward with respect to the unrelaxed surface plane. This model is referred to as the rigid rotation model when the lengths of both surface and back bonds do not change with the displacement of surface atoms.[8] In our calculations, we allow a general, non-bond-length-conserving relaxation of the surface atoms starting from the bulk (i.e., unrelaxed) geometry and ending when total energy is minimized to within approximately 1 meV per atom. The interior atoms are kept unrelaxed to maintain the correct bulk periodicity in the directions parallel to the slab. Experimental and theoretical studies agree that nonpolar surface relaxation of the tetrahedrally coordinated semiconductors is mainly confined to the surface layer, with atoms of the second layer typically displaced by 0.05 Å or less.[8,9] Hence it is not a

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TABLE I. Calculated structural parameters of GaN surfaces from the four-layer slab model.

	Wurtzite ($10\overline{1}0$)	Zinc blende (110)
Bulk lattice constants		
c	5.169Å	
a	3.201Å	4.510Å
$\Delta_{1\perp}$	0.046Å	0.032Å
$d_{12\perp}$	0.671Å	1.560Å
Δ_{1y}	3.350Å	3.622Å
Δ_{12y}	2.703Å	2.450Å
ΔR (Ga-N)	−7.4%	−6.5%
Layer rotation angle ω	1.45°	2.06°
Bond rotation angle θ	1.45°	1.00°

severe approximation to relax only the outside layer, and the computational cost is reduced since otherwise a thicker slab would have had to be used. We describe below a test of this approximation for one case.

The calculated minimum-energy structural parameters for the wurtzite ($10\overline{1}0$) and zinc-blende (110) surfaces of GaN are given in Table I and the structures are illustrated in Fig. 1, parts (a) and (b). (Definitions of the surface structural parameters are discussed in Ref. 8.) For both surfaces we found a relaxation characterized mainly by surface bond-length changes [ΔR(Ga-N)] of approximately −7% together

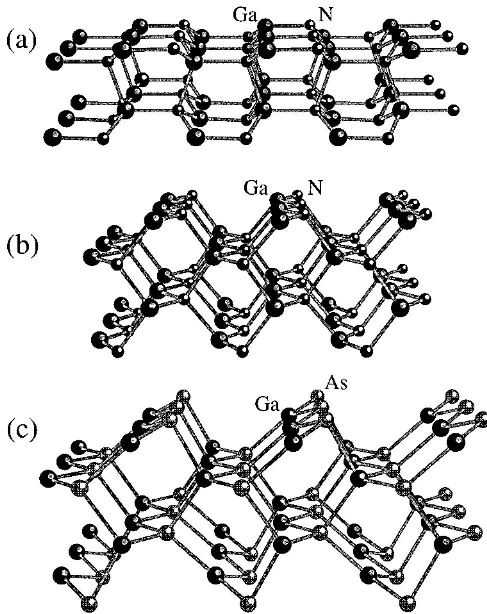

FIG. 1. Slab structures computed in the present work with fully relaxed outer layers: (a) ($10\overline{1}0$) surface of wurtzite GaN; (b) (110) surface of zinc-blende GaN; (c) (110) surface of zinc-blende GaAs. Note the much larger rotation of the double rows of surface atoms in (c). Note also that the surface bonds are perpendicular to the rows in (a), so that the bond and layer rotation angles are the same; this is not the case in (b) and (c).

with very small surface bond rotations on the order of 1°. This is in contrast to the surface relaxation of GaP and GaAs, where large rotation angles on the order of $\omega=30°$ are observed with small (~2%) contractions of the surface bond lengths. Our results thus contradict claims[8] of universal behavior of surface relaxation among III-V semiconductors. On the other hand, our predictions are very similar to those made for the ZnO ($10\overline{1}0$) surface by the same method[7] and also by a recent density-functional calculation.[10]

Before considering possible explanations for this prediction of anomalous relaxation, let us review the existing literature on GaN surfaces. We know of no experimental surface structure measurements on any surface of GaN to date, nor of any theoretical work on the GaN wurtzite ($10\overline{1}0$) surface. The polar surfaces of GaN have attracted some recent theoretical attention[11] but the only theoretical work on any nonpolar surface of GaN is an early small-cluster Hartree-Fock pseudopotential calculation by Swarts and co-workers[12] on the zinc-blende (110) surface. They found a surface bond rotation of 19.4° for GaN, considerably smaller than for GaAs but still much larger than what we found. Thus our results disagree with the only other theoretical prediction as well as with the general trend for binary semiconductors with non-first-row anions. We must therefore investigate the reasons for this apparent discrepancy.

One possibility is that there is some inherent pathology in our method which causes it to always predict very small rotation angles. To eliminate this possibility we have performed calculations on the GaAs (110) surface by exactly the same methods as we used for GaN. The Ga basis was the same as before and an As basis of the same type was constructed and optimized for the solid. We obtained a cubic lattice constant for bulk GaAs of 5.750 Å as compared to the experimental value of 5.653 Å, and a bulk modulus of 70 GPa versus 75 GPa experimentally. We then set up and relaxed the same type of four-layer slab as before and found the geometry shown in Table II and Fig. 1(c), characterized by a surface bond rotation angle of 24.3° and a decrease in surface bond length of about 1.3%. Though the angle is somewhat too small, our result is in reasonable agreement with theoretical calculations[13] and experimental studies[14] on the GaAs (110) surface, which have reported a rotation angle of about 27°–32° and a 1–2 % decrease in surface bond length. The discrepancy would have been even less if we had included second-layer relaxation in our test calculation on GaAs. Thus our theoretical approach has no intrinsic bias towards extremely small surface rotations or excessive bond contraction.

The only other obvious source of possible error in our calculation is the neglect of second-layer relaxation. We have addressed this concern by setting up a five-layer GaN zinc-blende (110) slab which allowed us to relax the second and fourth (i.e., second from the bottom) layers; the unrelaxed center layer maintained the bulk periodicity. When the atomic coordinates were reoptimized the second-layer Ga and N atoms moved outwards from the center of the slab by 0.027 and 0.052 Å, respectively, the surface dimer tilt angle increased to $\omega=6.1°$, and the surface bond length was almost unchanged at 6.6% less than the bulk value. Computational limits prevented us from doing a similar recalculation for the wurtzite phase, but we expect that the changes would have

TABLE II. Calculated configurational parameters of the (110) surface of GaAs compared with typical results of other theoretical and experimental work.

	Hartree-Fock[a]	Pseudopotential local-density approximation[b]	Expt.– low-energy-electron-diffraction[c]
Lattice constant	5.750Å	5.559Å	5.654Å
$\Delta_{1\perp}$	0.568Å	0.67 Å	0.69 Å
$d_{12\perp}$	1.618Å	1.415Å	1.442Å
Δ_{1y}	4.491Å	4.407Å	4.518Å
Δ_{12y}	3.256Å	3.339Å	3.190Å
ΔR(Ga-As)	−1.3%	−1.4%	−2.0%
Rotation angle ω	24.3°	30.2°	31.1°
Rotation angle θ	13.4°	16.4°	16.7°

[a]Present work.
[b]Alves, Hebenstreit, and Scheffler, Ref. 13.
[c]Mailhiot, Duke, and Chadi, Ref. 14.

been similarly small in that case. Thus while the tilt angle increases slightly with second-layer relaxation, it remains far smaller than in GaAs.

Let us therefore assume that our prediction of small surface rotations and relatively large bond contractions in GaN is correct, and consider possible reasons why GaN might behave differently from, say, GaAs in regard to nonpolar surface relaxation. Since GaN is much more ionic than any of the non-nitride III-V compounds, one might attribute its anomalous surface relaxation to electrostatic effects, as has been suggested to occur in some II-VI semiconductors.[15] However, the I-VII noble-metal halides (e.g., CuCl), which are the most ionic group of tetrahedrally coordinated compounds, have very *large* (110) surface rotation angles (~41°–44°).[16] Thus ionicity cannot be a general case of small surface rotations, though it does appear to be important[16] for surface bond contraction. Another possibility would be the large size mismatch between the Ga and N atoms, e.g., the difference of 0.56 Å in their Pauling[17] covalent radii. However, there is no strong trend among the non-nitride III-V compounds related to size mismatch. For example, the Pauling covalent radii of In and P differ by 0.34 Å while those of Ga and As differ by only 0.08 Å, yet the surface rotation angle ω is approximately 30° and 31° for InP and GaAs, respectively,[14] a very small difference. Thus, atomic size effects also do not explain the small surface rotation in GaN.

Next let us consider how the electronic structure GaN differs from GaAs and other III-V's. The core of the N atom consists of the $1s$ shell only, and thus has a very small radius (compared to P, As, etc.) and contains no p-type orbitals. In consequence, the valence orbitals associated with the N atom occur lower relative to the Fermi energy than in the heavier column V atoms. As noted by several authors[5,18] this causes a near degeneracy of the N $2s$-derived bands with the Ga $3d$ levels, which needs to be taken into account for accurate

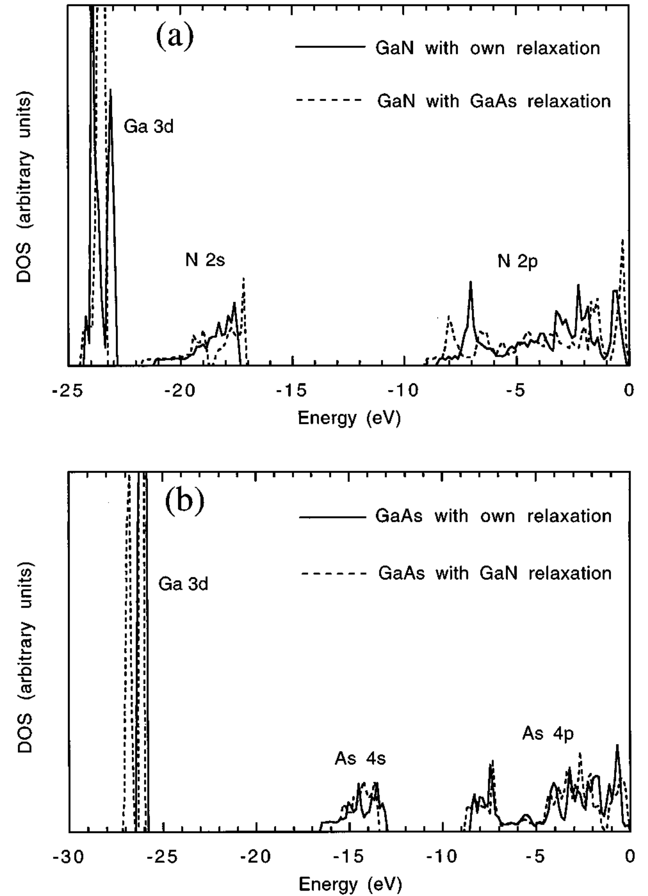

FIG. 2. Total valence DOS for (a) GaN and (b) GaAs (110) four-layer slabs. In both cases the solid curves gives the DOS for the compound at the surface geometry calculated for it in this work, and the dashed curve gives the DOS for the two compounds with their surface structures (rotation angles and fractional bond contractions) interchanged.

geometry calculations. (An analogous interaction of oxygen $2p$-derived bands was previously suggested[10] to play a role in the nonpolar surface relaxation of ZnO.) To explore the interplay of the surface relaxation with s-d hybridization effects we have plotted in Fig. 2 the total density of states (DOS) for four-layer zinc-blende (110) slabs for the following cases: (a) GaN with its calculated relaxed geometry (Table I), and with the bond rotation and fractional contraction calculated for GaAs (Table II); (b) GaAs in its calculated relaxed geometry (Table II), and with the bond rotation and fractional contraction calculated for GaN (Table I). We see that the GaN geometry leads to a splitting of the Ga $3d$ states, indicative of hybridization with other orbitals, and that this effect is more pronounced in GaN than it would be if it occurred in GaAs. Hence, we find that hybridization effects of cation d states with anion-derived valence states are correlated with the small surface rotation and relatively large surface bond contraction in GaN, much as in ZnO.[10]

Another important difference between the first-row atoms C, N, O and their heavier counterparts is the ability to participate in double or triple bonds. If the N-Ga surface bond has a partial double-bond character then some of the electronic charge associated with the occupied lone pair orbital on the anion would instead be found in the surface bond

region, making that bond shorter and stronger in GaN than in, say, GaAs. One would then expect *both* surface atoms in GaN to seek an approximately planar sp^2 coordination to the extent permitted by the back bond geometry, resulting in a more symmetric (less tilted) surface dimer displaced downwards towards the interior of the solid. All these effects are present in our results, suggesting that the surface bonds in GaN can indeed be characterized as having some multiple-bond character.

In summary, we have calculated the equilibrium geometries for the principal nonpolar cleavage faces of GaN. We find that the surface relaxation is characterized by very small surface bond rotations and relatively large surface and back bond contractions. In contrast, the non-nitride III-V semiconductors (and nonoxide II-VI semiconductors) have large surface rotations with small bond contractions. Of all binary semiconductors only ZnO seems to behave similarly to GaN in terms of nonpolar surface reconstruction. Interactions of cation d electrons with anion valence electrons appear to be important in this unusual surface behavior, and the surface bond may also have some double-bond character. An experimental test of these predictions is called for. Also, theoretical study of the nonpolar surfaces of BeO, AlN, and cubic BN (Ref. 19) would be useful in sorting out the various electronic effects.

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