Domain boundaries on {11$\bar{2}$0} planes in GaN: A theoretical study

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Local-density-functional methods are used to examine the atomic geometries, energetics, and electrical properties of different models for domain boundaries on {11$\bar{2}$0} planes in wurtzite GaN. In agreement with recent experiments, we find that the energetically most favorable model is characterized by a displacement of 1/2⟨10$\bar{1}$1⟩ and has no inversion of polarity. In this model all atoms at the boundary are fourfold coordinated and form strong Ga-N bonds, which results in a band gap free from deep states. However, our calculations also suggest that electrically active point defects, in particular gallium vacancies, may segregate to the boundary and thus introduce deep acceptor states. [S0163-1829(98)04048-X]

GaN has recently been the subject of considerable interest due to its optoelectronic properties. In particular, the wide band gap (3.4 eV for wurtzite GaN) makes blue light applications feasible. Defect-induced electronic states in the band gap can significantly alter the optical performance. This fact becomes extremely important in laser devices, where parasitic components in the emission spectrum are highly undesirable. Therefore, there is considerable interest in understanding the defect microstructure of GaN.

Epitaxial GaN layers used for device fabrication are usually highly faulted wurtzite single crystals and typically adopt a mosaic structure with subgrain boundaries delineated by threading dislocations.[1] The atomic structures and electrical properties of the most common types of threading dislocations have been studied theoretically[2] and experimentally.[3] Also, the effects on the electrical properties caused by the segregation of common point defects to dislocations have been investigated.[4]

In addition to dislocations, two kinds of domain boundaries have also been observed.[5–10] They lay on {11$\bar{2}$0} and {10$\bar{1}$0} planes and following Xin *et al.*[10] are denoted by DB-I and DB-II, respectively. Domain boundaries are either described in terms of a double-position boundary (DPB) (otherwise termed a stacking mismatch boundary) consisting of a different stacking sequence across the boundary, or an inversion domain boundary (IDB), which is characterized by a polarity inversion across the boundary. Domain boundaries of type DB-II have been explored extensively using transmission electron microscopy (TEM).[5–8] Northrup *et al.*[11] performed total energy calculations for several possible models and concluded that an inversion-domain boundary involving a $c/2$ translation along the ⟨0001⟩ direction has a very low domain-wall energy and is thus a suitable candidate for many of the vertical defects observed on {10$\bar{1}$0} planes. At this shifted inversion-domain boundary denoted by IDB*-II all atoms remain fourfold coordinated with Ga-N bonds across the boundary and therefore do not induce electronic states in the band gap. Furthermore, Northrup *et al.*[11] investigated a double-position boundary (DPB-II). DPB-II could account for those domain boundaries on {10$\bar{1}$0} planes for which no inversion of polarity across the boundary is observed.[10] Across the boundary DPB-II would have threefold coordinated Ga and N atoms both in sp^2 hybridizations, which gives rise to a deep-acceptor state localized at the lone pair of the sp^2 hybridized N atoms.

For domain boundaries of the DB-I type, structural models have been proposed based on high resolution transmission electron microscopy studies by Xin *et al.*[10] and Rouvière *et al.*.[9] However, no theoretical investigations for the energetics and electrical properties of these models have been reported, presumably because of the larger supercells required to model domain boundaries terminating in {11$\bar{2}$0} planes.

In this paper, we explore the geometries, energetics, and electrical properties of several models proposed for domain boundaries on {11$\bar{2}$0} planes using a charge self-consistent density-functional based tight-binding method (SCC-DFTB). For a description of the SCC-DFTB method and applications to GaN see Refs. 12, 13, 2, 14, and 4. In the current application, the Ga $3d$ electrons are included as valence states to obtain accurate formation energies,[15] since the Ga $3d$ and N $2s$ levels hybridize. As an illustrative benchmark of the

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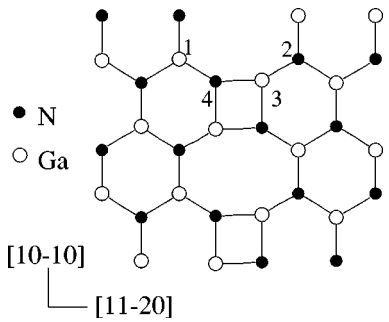

FIG. 1. Top view along [0001] of a domain boundary of DB-I type, i.e., on $\{11\bar{2}0\}$ planes. From TEM experiments the *horizontal* shift across the boundary is found to be $1/2\langle 10\bar{1}0\rangle$. All models discussed below (DPB-I, DPB*-I and IDB-I) agree with this top view. (Of course, in this figure the bonding across the boundary is arbitrary and varies with the different models.) Here and in the following figures atom numbers 1 (2) refer to Ga (N) atoms in eightfold rings close to the boundary, whereas atom numbers 3 (4) refer to Ga (N) atoms in fourfold rings with bonds across the boundary.

SCC-DFTB method, we choose quantitative calculations for the nonpolar GaN $(10\bar{1}0)$ and $(11\bar{2}0)$ surfaces, since domain boundaries are formed by bringing these surfaces together. For both surfaces we find geometries very similar to those derived from first-principles calculations by Northrup and Neugebauer.[15] Moreover, the calculated absolute surface energies of 121 meV/Å^2 (128 meV/Å^2) for the $(10\bar{1}0)$ $[(11\bar{2}0)]$ surfaces agree very well with the 118 meV/Å^2 (123 meV/Å^2) reported in Ref. 15.

The DB-I domain boundaries considered in this work are modeled within 64-atom supercells containing two boundaries and eight layers of atoms between the boundaries. Four k points are used to sample the Brillouin zone. Following Northrup *et al.*[11] we define the formation energy for the domain boundary as $E_{\mathrm{form}}=\frac{1}{2}(E-E_{\mathrm{bulk}})$, where E is the total energy of a cell containing two boundaries and E_{bulk} is the energy of a bulk system with an equivalent number of atoms. The domain-wall energy σ_{wall} is then given by E_{form}/A, where $A=28.64$ Å^2 is the area of the periodic unit cell of the boundary in the $(11\bar{2}0)$ plane.

In contrast to DB-II type boundaries, which originate at the epilayer substrate interface the DB-I type boundaries found in a GaN sample grown by molecular-beam epitaxy on GaP extend only a short distance along the c axis.[10] A high-resolution Z-contrast image down [0001] reported by Xin *et al.*[16] shows clearly that DB-I has a *horizontal* displacement of $R_h=1/2\langle 10\bar{1}0\rangle$. This configuration which is also called prismatic stacking fault is composed of fourfold and eightfold rings along the fault. For an illustration see Fig. 1.

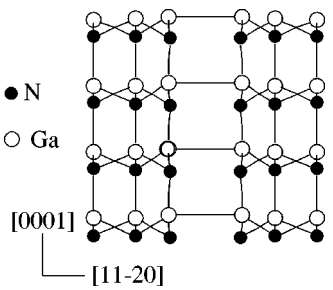

FIG. 2. Side view along $[10\bar{1}0]$ of the DPB-I structure. Wrong bonds yield a high energy, which is only slightly less than that of two free $(11\bar{2}0)$ surfaces.

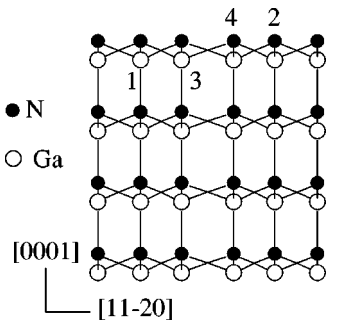

FIG. 3. Side view along $[10\bar{1}0]$ of the DPB* structure, which has a total displacement of $1/2\langle 10\bar{1}1\rangle$. All atoms are fourfold coordinated and exhibit strong Ga-N bonds across the boundary. Although the bond angles are considerably distorted (see Table I) the structure induces no deep electronic states in the band gap. DPB*-I has the lowest wall energy among all domain boundaries of type DB-I.

Assuming no additional displacement in the *vertical*, i.e., $\langle 0001\rangle$ direction gives a model for a double position boundary denoted by DPB-I. As can be seen in the side view in Fig. 2, DPB-I contains wrong, i.e., Ga-Ga and N-N bonds. Due to the very different bond lengths of both species (~2.7 Å in Ga bulk and ~1.5 Å in the N_2 molecule) wrong bonds give rise to a high energy and thus reduce the stability of the system. The lowest energy configuration is achieved for a spacing of 2.8 Å between the boundary planes (in the ideal lattice the corresponding distance would be ~1.6 Å) which is comparable with the bond length in bulk Ga. Our calculations find a high domain-wall energy $\sigma_{\mathrm{wall}}=246$ meV/Å^2, which is only slightly less than the energy of two free surfaces (256 meV/Å^2). This suggests, that DPB-I should not occur frequently and if it occurs it should exist with different spacings. Indeed, we find that varying the spacing between the boundaries changes the wall energy only slightly since the wrong bonds across the boundary are very weak. We note that at the equilibrium distance of 2.8 Å the structure has shallow occupied N-derived states at ~0.2 eV above the valence-band maximum (VBM) and unoccupied states at ~0.4 eV below the conduction-band minimum. At larger distances the influence of the Ga-Ga bonds across the boundary should vanish so that the electrical properties correspond to free $(11\bar{2}0)$ surfaces that we found to be electrically inactive.

TABLE I. Bond lengths in Å and bond angles in degree at the DPB*-I domain boundary. Atom numbers refer to Figs. 1 and 3.

Atom	Bond lengths (min, max)	Bond angles (min, max)
1 (Ga)	1.86, 1.95	107.0, 112.6
2 (N)	1.88, 1.96	106.1, 111.5
3 (Ga)	1.86, 2.11	80.6, 130.2
4 (N)	1.88, 2.11	86.3, 127.8

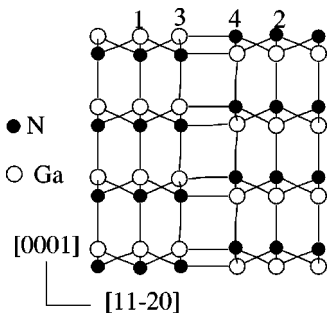

FIG. 4. Side view along $[10\bar{1}0]$ of the IDB-I structure. In analogy to DPB*-I all atoms are fourfold coordinated and exhibit strong Ga-N bonds across the boundary, which makes the structure electrically inactive. The wall energy is slightly higher than for DPB*-I.

We now examine the structure with an additional vertical displacement of $1/2\langle 0001\rangle$ giving a total displacement of $1/2\langle 10\bar{1}1\rangle$ as derived from TEM by Xin *et al.*[10] In this double-position boundary denoted by DPB*-I all atoms along the boundary are fourfold coordinated and form Ga-N bonds across the boundary (see Fig. 3). Since Ga-N bonds are very strong, DPB*-I has a clearly defined spacing of ~ 1.90 Å between the $\{11\bar{2}0\}$ planes at the boundary. The calculated domain-wall energy of 99 meV/Å^2 is significantly lower than the energy of the unshifted DPB-I model suggesting that DPB*-I is a promising candidate for domain boundaries in $\{11\bar{2}0\}$ planes for which no polarity inversion across the boundary has been observed.[10] DPB*-I are thought to be associated with single growth faults in the basal plane:[17,10] DPB*-I starts and ends with a basal plane stacking fault. Since these basal plane stacking faults have a low energy and thus are easily formed during growth, there are many possibilities for DPB*-I to nucleate but also to be overgrown. This explains why DPB*-I are observed throughout the whole epilayer but extend only over a short distance along the c axis.[10]

Details of the geometry of DPB*-I can be found in Table I. As can be seen, some of the bonds are quite distorted, which makes that DPB*-I induces shallow electronic states ~ 0.35 eV above VBM in the band gap. However, these states are not deep enough to be responsible for the yellow luminescence, which is centered at ≈ 2.2 eV and observed in n-type GaN. On the other hand, point defects may segregate to the DPB*-I boundary and change the electrical properties. A particularly important point defect are gallium vacancies (V_{Ga}) which have been detected by positron annihilation studies in bulk GaN and their concentration was found to be related to the intensity of the yellow luminescence (YL).[18] Indeed also theoretical calculations[19,20] show that in its triple negative charge state V_{Ga} possesses a low formation energy in n-type material and a transition level at the center of the YL spectrum [$E^{2-/3-}$ referenced to the valence band maximum (VBM) was calculated to be ≈ 1.1 eV in Ref. 19 and ≈ 1.5 eV in Ref. 20]. We therefore evaluated the formation energy of V_{Ga}^{3-} at the domain boundary and found it to be lower by 1.1 eV at position 3 with respect to a position in a bulklike environment. The electronic properties of V_{Ga} at the DPB*-I were found to be similar to V_{Ga} at a perfect lattice position with deep-acceptor states ≈ 1.1 eV above VBM and $E^{2-/3-} \approx 1.6$ eV with respect to VBM (in a bulklike position we found $E^{2-/3-} \approx 1.4$ eV). This suggests that if Ga vacancies diffuse easily in GaN a lot of them will be trapped at DPB*-I where they would introduce deep-acceptor states and can act as electron traps, in agreement with recent electron-energy loss spectroscopy measurements by Natusch *et al.*.[21]

TABLE II. Bond lengths in Å and bond angles in degree at the IDB-I domain boundary. Atom numbers refer to Figs. 1 and 4.

Atom	Bond lengths (min, max)	Bond angles (min, max)
1 (Ga)	1.88, 1.95	105.4, 112.4
2 (N)	1.87, 1.95	103.9, 111.7
3 (Ga)	1.87, 2.04	87.6, 142.3
4 (N)	1.87, 2.04	91.6, 141.0

A model for an inversion-domain boundary on $\{11\bar{2}0\}$ planes (IDB-I) has been suggested by Rouvière *et al.*.[9] It has a total displacement of $1/2\langle 10\bar{1}0\rangle$ (see Fig. 4) and again fourfold coordinated atoms with Ga-N bonds across the boundary yielding a spacing of ~ 2.0 Å between the boundary planes. Features of the geometry are listed in Table II. The domain-wall energy for IDB-I of 122 meV/Å^2 is slightly above the wall energy for DPB*-I. This can be understood by analyzing the structural properties. At DPB*-I each of the boundary atoms (No. 3 and 4 in Fig. 1) has four bond angles near to the ideal sp^3 value of 109.3°. Only two angles at each atom deviate considerably ($\sim 80°$ and $\sim 130°$). At IDB-I only three angles at each boundary atom are near to the ideal value whereas each atom has two angles of $\sim 90°$ and one angle as large as $\sim 140°$. The bond angles are significantly more distorted at IDB-I compared to DPB*-I. This explains the higher domain-wall energy found for IDB-I. Also, in spite of the considerable distortion IDB-I has only shallow gap states ~ 0.3 eV above VBM. It is worth noting that in contrast to DPB*-I, which can be terminated by a low-energy basal plane stacking fault, a mechanism to end IDB-I will be energetically much more costly. Therefore, domain boundaries of type IDB-I should thread over a long distance along the c axis.

In summary, total energy calculations for structural models of domain boundaries in $\{11\bar{2}0\}$ planes reveal that only boundaries that have Ga-N bonds across the boundary have low formation energies. The model with the lowest domain-wall energy has a total displacement of $1/2\langle 10\bar{1}1\rangle$, which is in agreement with recent transmission electron experiments.[10] This boundary does not induce deep states in the band gap. However, gallium vacancies, which are a common point defect in GaN could segregate to the domain boundary and adversely influence the electrical properties.

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