Inversion Domain and Stacking Mismatch Boundaries in GaN

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We present first-principles calculations of domain wall energies for inversion domain boundaries and stacking mismatch boundaries in GaN. We find a low-energy inversion domain boundary in which each atom remains fourfold coordinated without the formation of Ga-Ga or N-N bonds. This boundary, denoted IDB*, *does not induce electronic states in the band gap* and would therefore not adversely impact photoluminescence efficiency. The stacking mismatch boundary has a higher formation energy than IDB*, and gives rise to occupied N-derived interface states in the band gap. [S0031-9007(96)00522-4]

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Because of their increasing importance as optoelectronic materials employed in the fabrication of blue light-emitting diodes [1] and lasers [2] there is significant interest in understanding the properties of the group-III nitrides (AlGaInN). GaN adopts the wurtzite crystal structure when grown on hexagonal substrates such as the basal planes of Al_2O_3 or SiC. One of the most interesting experimental observations [3] is that GaN exhibits high efficiency luminescence even when containing a high density ($\sim 10^{10}/\mathrm{cm}^2$) of extended defects which could give rise to electron hole traps. This defect density is $\sim$6 orders of magnitude larger than what is usually required for acceptable performance in GaAs optoelectronic devices. This raises the possibility that many of the defects may be electronically inert, i.e., they do not induce electronic levels in the gap. Despite their potential importance in governing the electronic properties of GaN epitaxial films, very little is known about the atomic or electronic structure of the extended defects. In this Letter we present the first calculations of extended defect energetics for GaN.

Transmission electron microscopy (TEM) experiments [4–10] have revealed that epitaxial films of GaN grown on Al_2O_3 or SiC appear to contain planar defects in the (10-10) planes. The planes are very flat and remain parallel to the [0001] growth direction. Typically these planar defects begin at the substrate and run throughout the entire thickness of the epilayer. Based on TEM observations, two types of models for these defects have been considered: double positioning boundaries [4,5], also referred to as stacking mismatch boundaries [6,7], and inversion domain boundaries [10]. At a stacking mismatch boundary (SMB) the stacking sequence of the wurtzite material is altered across the boundary. For the inversion domain boundary (IDB) the occupation of the Ga and N sublattices is reversed. On the basis of convergent beam electron diffraction experiments for metalorganic chemical vapor deposition (MOCVD) grown films of GaN on Al_2O_3, Rouviere *et al.* [10] have proposed that the planar defects are inversion domain boundaries which enclose columns (up to 75 nm in width) in which the GaN polarity is reversed. Moreover, they have related these columns to the formation of hexagonal shaped hillocks on the surface of the GaN epilayer. Because the atomic structure and the corresponding electronic structure are still unclear, we have performed total energy and electronic structure calculations for possible models of both inversion domain and stacking mismatch boundaries.

At an inversion domain boundary occurring in the wurtzite structure, the identity of the atoms occupying the two sublattices is interchanged. This is illustrated in Fig. 1(a), where the Ga and N atoms are interchanged as one crosses the (10-10) plane. Without any other changes in structure, this interchange leads to both Ga-Ga and N-N bonds at the boundary. Such bonds are commonly termed wrong bonds, and their presence increases the total energy and thereby reduces the stability of the system. We will see that such a boundary structure is quite unstable in GaN, and would transform via a translation along the [0001] direction into a structure having no wrong bonds. The structure obtained by the translation is illustrated in Fig. 1(b). We refer to it as IDB*. Although it contains a four-membered ring of bonds, each atom is fourfold coordinated and the equilibrium bond lengths are close to the bulk bond length of GaN.

At a stacking mismatch boundary the stacking sequence of the atomic layers is reversed, but the Ga and N atoms are not interchanged. The stacking sequence of wurtzite along the [0001] direction may be described as $ABAB\ldots$, where the letters denote a GaN double layer. The letters A, B, and C indicate the three different atomic positions projected onto the (0001) plane as shown in Fig. 2. On one side of a stacking mismatch boundary the sequence switches from $ABABABA\ldots$ to $ABCBCBC\ldots$ and this leads to a significant disruption in the bonding at the boundary as shown in Fig. 3. One may easily construct a model without wrong bonds, but both the Ga and N atoms at the boundary are threefold coordinated. Our calculations indicate that this leads to both a higher formation energy than the IDB* structure, and also to the presence of electronic states in the band gap of GaN.

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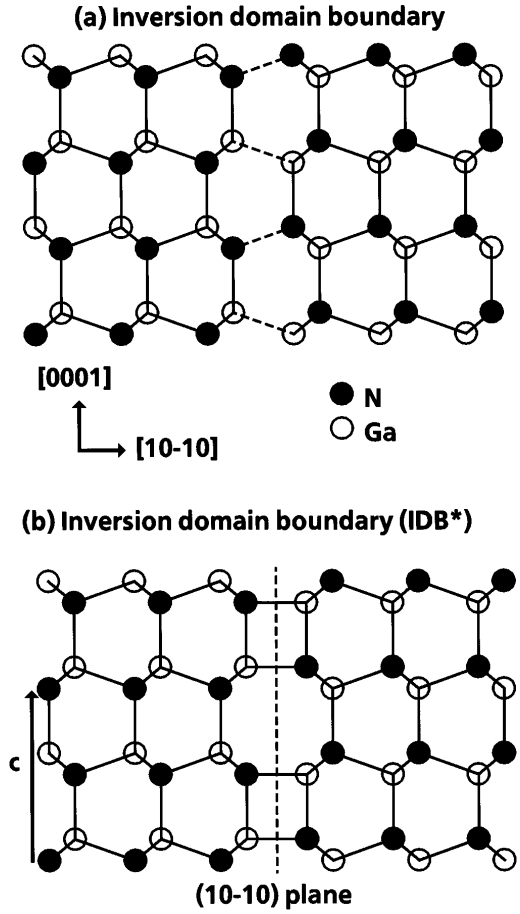

FIG. 1. (a) Schematic representation of a simple inversion domain boundary in wurtzite. The dashed lines denote wrong bonds between like atoms. Atom positions are projected onto the (1-210) plane. (b) Schematic representation of IDB*. This structure can be formed by translating one side of an IDB by $c/2$ along the [0001] direction. The IDB* structure contains fourfold and eightfold rings of bonds, but there are no Ga-Ga or N-N bonds.

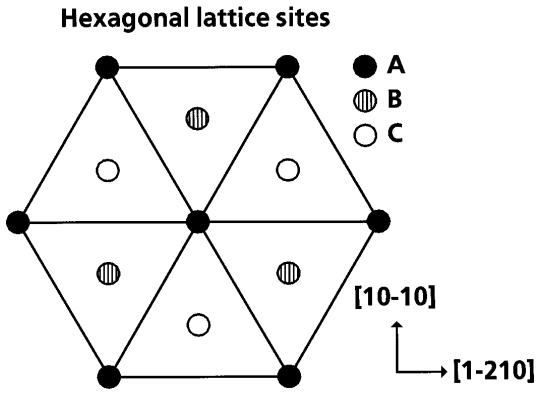

FIG. 2. Projection of three possible hexagonal lattice sites onto the (0001) plane.

We have performed calculations of the total energy and atomic structure within the local density approximation and the first-principles pseudopotential approach. Forces and total energies were calculated in an iterative procedure similar to that described by Stumpf and Scheffler [11], but with a local orbital scheme employed to generate the initial approximation to the wave functions [12]. As in previous calculations [13,14], soft Troullier-Martins [15] pseudopotentials are employed for Ga and N, and the Ga $3d$ electrons are treated as part of the valence band. The domain boundaries are modeled with a supercell having two boundaries in each cell and 8 layers of atoms between each boundary. For the inversion domain boundaries this results in cells having 32 atoms. The forces and resulting displacements calculated for the atoms in the regions between the boundaries remain negligible as the geometry is optimized. Thus the cells are large enough to model isolated boundaries. The plane wave cutoff is taken to be 60 Ry and 2 k points are included in the sum over the Brillouin zone. Calculations were also performed with the Ga $3d$ electrons treated as part of the core, but with the nonlinear core correction [16] included in the pseudopotential for Ga. In these calculations we increased the k-point sampling from 2 to 8 k points and found differences in formation energies of less than 0.02 eV/cell. Thus the 2 k point set is adequate for the calculations. We define the formation energy for the boundary as $E_{\text{form}} = \frac{1}{2}(E - E_{\text{bulk}})$, 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 $A = 16.424$ Å^2 is the area of the periodic unit cell of the boundary in the (10-10) plane.

The formation energy of the simple IDB structure is calculated to be 2.73 eV, and from this we obtain a domain wall energy of 167 meV/Å^2. Since the IDB can be formed by bringing together two (10-10) surfaces, it is instructive to compare the formation energy of the boundary with that of two free (10-10) surfaces: $2\sigma_{\text{surf}} = 236$ meV/Å^2 [14]. The IDB is only slightly more energetically favorable than the two free surfaces, indicating that the wrong bonds formed across the boundary are very weak. The high formation energy of the IDB is consistent with results for other GaN structures which contain wrong bonds: e.g., nonstoichiometric GaN(10-10) surfaces [14] and antisite defects in bulk GaN [13]. In the relaxed structure the Ga-Ga bonds are 2.28 Å and the N-N bonds are 1.51 Å. The Ga-Ga distance is compressed and the N-N distance is expanded compared to values exhibited in bulk Ga (2.7 Å) and N_2 molecules (1.1 Å).

The formation energy of IDB* is calculated to be 0.41 eV, which corresponds to a domain wall energy of only 25 meV/Å^2. In the fully relaxed structure the Ga-N bond lengths in the fourfold ring of bonds are found to be approximately equal to the bulk value (1.94 Å). The IDB* structure can be obtained from the simple IDB by a translation of the material on one side of the boundary through a distance of $c/2 = 2.6$ Å along the

[0001] direction. Given the huge energy difference and the simple pathway by which an IDB may transform into IDB*, we think it unlikely that the simple IDB structure will be found in GaN. On the other hand, the IDB* appears to be a promising candidate for many of the vertical defects observed in TEM experiments [4,6–10]. In addition to its low energy, the IDB* model provides a natural explanation for the small shift in the image intensity along the [0001] direction which is observed across some boundaries in TEM [4,6–9]. In the IDB* structure, as one crosses the boundary the atomic planes containing a particular species are shifted along the [0001] direction by ± 0.64 Å (approximately $\pm c/8$). This is consistent with the lattice displacements observed in the TEM images. A precise determination of the magnitude of the lattice displacement indicated by the TEM images requires simulations involving the scattering potentials of the N and Ga atoms and the film thickness [9].

Calculations of the electronic structure revealed *no interface states in the energy region between the valence band maximum and the conduction band minimum for the IDB* structure*. This is understandable since gap states typically arise from reduced coordination, and in the IDB* structure all atoms remain properly coordinated. Such a boundary should not adversely impact the optoelectronic properties of the GaN epilayer, unless electrically active vacancies or impurities become bound to the lattice sites comprising the fourfold rings.

In the model for the SMB (shown in Fig. 3) there exist threefold coordinated Ga and N atoms in sp^2 bonded configurations. This structure was found to be stable with respect to dimerization of the atoms along the [1-210] direction. The equilibrium bond length between the threefold coordinated Ga and N atoms in the boundary is found to be 1.81 Å, a contraction of 7% with respect to the bulk bond length. A similar contraction occurs for the Ga-N dimers on the (10-10) surface [14]. The formation energy for the SMB is found to be 1.73 eV, and the corresponding domain wall energy is 105 meV/Å^2. This energy is comparable to the surface energy of the (10-10) surface [14], 118 meV/Å^2. The similarity arises from the fact that each system contains one threefold Ga and one threefold N atom in each 1×1 unit cell of the (10-10) plane. While the nonbonding Ga *p* orbital is empty and does not give rise to states in the gap, the nonbonding N *p* orbital does induce occupied interface states in the band gap. This N-derived band has its maximum energy at the Γ point, where it is about 1.1 eV above the bulk valence band maximum [17]. Such a stacking mismatch boundary would therefore be expected to give rise to electron-hole recombination between the conduction band minimum and the top of the N-derived interface band. The energy of the transition should be roughly $E_{\text{gap}} - 1.1$ eV $= 2.3$ eV. We note that this is approximately equal to the energy ($\sim$2.2 eV) of the spatially inhomogeneous yellow luminescence observed in GaN [18].

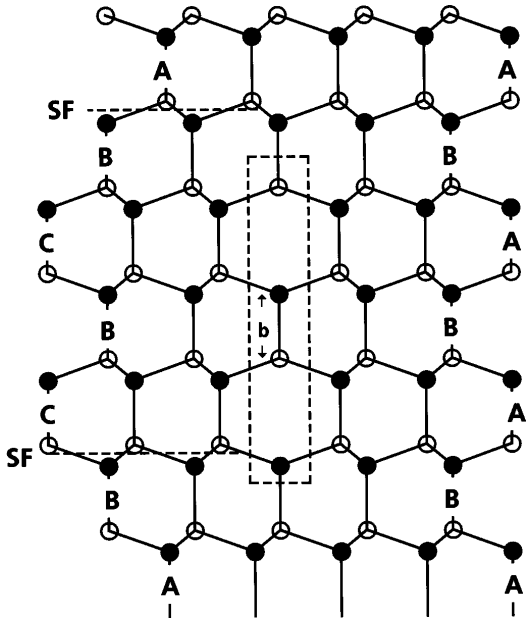

FIG. 3. Schematic representation of a stacking mismatch or double positioning boundary. Atom positions are projected onto the (1-210) plane. The filled (open) circles denote N (Ga) atoms. The boundary lies in the (10-10) plane and connects two stacking faults on the left side of the boundary. The dashed lines enclose the threefold coordinated atoms which comprise the boundary. The distance between threefold coordinated Ga and N atoms in the boundary is $b = 1.81$ Å. The boundary begins when a stacking fault occurs on the left side, and ends when a second stacking fault occurs.

Stacking mismatch boundaries are closely associated with stacking faults. In Fig. 3 we illustrate how the SMB begins when a faulted bilayer (on the left) meets the correctly stacked bilayer (on the right). The SMB terminates when a second stacking fault occurs on the left side of the boundary. Since the stacking fault is a rather low energy defect, the SMB can be terminated by overgrowth of the correctly stacked bilayer on the right, without a significant energy cost. Of course, it is also possible to terminate the SMB by creating a second stacking fault on the *right* side of the boundary. In either case we expect the SMB to extend for only short distances in the [0001] direction before it is terminated by a fault. On the other hand, it is difficult to see how the IDB* structure can be terminated without the introduction of an inversion domain boundary in the (0001) plane. We expect such a boundary to have a large formation energy. Thus, once formed at the interface, an inversion domain column is expected to extend throughout the epilayer and terminate at the surface. The nucleation of inversion domains in GaN grown on Al_2O_3 (sapphire) could be related to the inhomogeneous nature of the interface, which can arise from both the in-plane lattice mismatch (13%) and the mismatch in the repeat distance of the structures in the [0001] growth direction. The minimum step height in sapphire corresponds to the spacing between adjacent O layers: approximately $c_{\text{sapphire}}/6 = 2.17$ Å. This

TABLE I. Formation energies calculated for inversion domain boundaries in GaN, GaAs, and Si. The energies are given in eV for a unit area of boundary. The unit areas are 16.42 Å^2 for GaN, 26.03 Å^2 for GaAs, and 23.82 Å^2 for Si.

Material	Boundary	E_{form} (eV)
GaN	IDB*	0.41
	IDB	2.73
	SMB	1.73
GaAs (wurtzite)	IDB*	0.39
	IDB	0.63
Si (wurtzite)	IDB*	0.48
	IDB (= bulk)	0.0

is significantly less than the spacing between adjacent N layers in GaN (2.59 Å). This vertical mismatch comes into play at steps and provides a possible driving force for polarity reversal at the interface.

The surprisingly low formation energy for the IDB* structure prompted an investigation of the formation energies for IDB and IDB* in other materials, such as GaAs and Si. This allows us to better understand two features which make bonding in GaN different from that in GaAs: the larger ionicity and the larger size mismatch. For consistency we calculated the formation energies of IDB and IDB* for Si and GaAs in the wurtzite structure rather than diamond and zinc blende. The results are shown in Table I, together with the results already discussed for GaN. For Si, the IDB structure is simply "bulk wurtzite" and the formation energy is, by definition, zero. Remarkably we find that the formation energy of IDB* is not very dependent on the material; it is approximately 0.4 to 0.5 eV in each instance. We learn from this comparison that the energy cost incurred by distorting the bonds to form fourfold rings is not very dependent on the ionicity and size mismatch. On the other hand, the formation energy of the simple inversion domain boundary IDB, which contains wrong bonds for GaAs and GaN, is quite different for the three materials: It is 0.0 for Si, 0.63 eV for GaAs, and 2.7 eV for GaN. As the ionicity and the size mismatch increase, the cost of forming wrong bonds increases dramatically. Thus domain boundaries and dislocations which minimize the number of wrong bonds are expected to be the most energetically favorable in group-III nitrides.

In summary, we have calculated the energy for possible structures occurring at an inversion domain boundary and a stacking mismatch boundary in GaN. The stacking mismatch boundary has a domain wall energy of 105 meV/Å^2 and exhibits N-derived interface states above the bulk valence band maximum. We find that the domain wall energy for the IDB* model ($\sigma_{\text{wall}} = 25$ meV/Å^2) is much less than for the other structures considered and that the IDB* boundary does not give rise to gap states. We propose that many, if not all, of the planar vertical defects [4,6,8–10] occurring in epitaxial GaN films correspond to IDB* structures. Finally, our calculations strongly suggest that models for domain boundaries and dislocations which minimize the number of wrong bonds are likely to be the most energetically favorable in group-III nitrides.

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