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Energetics and electronic structure of stacking faults in AlN, GaN, and InN

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Basal-plane stacking faults in wurtzite AlN, GaN, and InN are studied using density-functional-pseudopotential calculations. The formation energies follow the trend exhibited for the zinc-blende/wurtzite energy differences in the bulk materials, namely, lowest energy for GaN and highest for AlN. Type-I stacking faults have the lowest energy, followed by type-II stacking faults, and finally extrinsic stacking faults. We also examine a type of intrinsic stacking fault that has not, to the best of our knowledge, been previously discussed; its energy is slightly lower than the type-II faults. Investigations of the electronic structure reveal that there are no localized states in the band gap. However, stacking faults can bound a quantum-well-like region of zinc-blende material surrounded by the wurtzite host, giving rise to a luminescence line below the wurtzite band gap. [S0163-1829(98)50224-X]

The III-nitrides have great potential for technological applications in the area of optoelectronic devices operating in the green, blue, and ultraviolet region of the spectrum, as well as for high-power and high-temperature electronics. A number of materials problems still exist, however, many of which are related to the lack of suitable substrates. Growth on mismatched substrates causes the epilayers to contain a very high concentration of extended defects, up to five orders of magnitude higher than in other materials used for optoelectronic devices.[1] Light-emitting diodes and lasers can be fabricated in this material in spite of the high defect concentrations. However, the extent to which the extended defects affect quantum efficiencies and device lifetime is still unknown. Fundamental studies of the effect of extended defects on the electronic and optical properties of the material are necessary to address these issues. In particular, it is essential to know whether the defects give rise to electrically active levels in the band gap.

Stacking faults are one of the main types of extended defects occurring in epitaxial III-V nitrides. Typically they are terminated at each end by partial dislocations, and transmission electron microscopy studies have reported a higher density of stacking faults near the film/substrate interface.[2–5] In this paper we use first-principles calculations to investigate the atomic and electronic structure and the formation energy of stacking faults along the [0001] direction in wurtzite (WZ) AlN, GaN, and InN. Our main conclusions are that (1) type-I stacking faults always have the lowest energies; (2) the formation energy increases going from GaN to InN to AlN; and (3) stacking faults introduce no localized states in the band gap, although they can give rise to a zinc-blende-like region that can trap electrons, as suggested by Albrecht *et al.*[6] We also introduce a type of intrinsic stacking fault, which has an energy higher than type-I faults but lower than the other types. Estimates of stacking-fault energies based on bulk calculations for polytypes were recently derived by Wright;[7] to our knowledge, however, ours are the first *ab initio* calculations of stacking faults in the III-nitride semiconductors that allow explicit investigation of the electronic structure.

The stacking faults considered in the present study are depicted in Fig. 1. In the WZ structure, along the [0001] direction, the atoms follow the stacking sequence . . . AaBbAaBb . . . , while in the zinc-blende (ZB) structure, along the [111] direction, the sequence is . . . AaBbCcAaBbCc . . . . Capital letters correspond to group-III atoms (Al, Ga, and In) and lowercase letters to N atoms. We study four types of stacking faults (Fig. 1).

(a) Type-I stacking faults (also called I_1). These contain

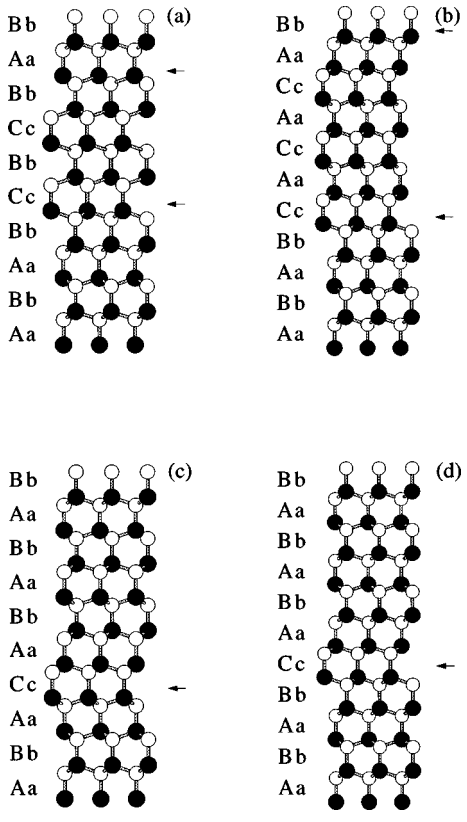

FIG. 1. Stacking faults considered in this work: (a) type I, (b) type II, (c) type III, and (d) extrinsic. The arrows indicate the position of the stacking faults and the black and white circles denote cations and anions, respectively.

one violation of the stacking rule.[8,9] This fault is commonly expected to have the lowest formation energy. For type-I faults (as for all of the stacking faults), two stacking sequences can be considered: the first where the fault starts on a Bb layer, shown in Fig. 1(a) (. . . AaBbCcBb . . .), and the second (not shown) where the fault starts on the Aa layer (. . . AaBbAaCcAaCc . . .). The two are, of course, equivalent, and they have the same energy.

(b) Type-II stacking faults (also called I_2). These contain *two* violations of the stacking rule,[8] and are commonly expected to have the next lowest formation energy. The stacking sequence depicted in Fig. 1(b) has the fault starting on a Bb layer (. . . AaBbCcAaCc . . .).

(c) Type-III stacking faults. These are intrinsic stacking faults in which one of the Aa or Bb layers occupies the ''wrong'' Cc position, e.g., . . . AaBbAaCcAaBb . . . . To our knowledge this type of fault has not been discussed in the literature, although it has the second-lowest formation energy. We will discuss under what conditions it might be observed.

(d) Extrinsic stacking faults. These stacking faults have an additional Cc layer inserted in the midst of the normal stacking sequence: . . . AaBbCcAaBb . . . .

Our calculations are based on density-functional theory in the local-density approximation (LDA),[10] *ab initio* pseudopotentials,[11] a supercell geometry, and a plane-wave basis set.[12] We tested the accuracy of the LDA by carrying out extensive test calculations using the generalized-gradient approximation[13] (GGA) for the exchange-correlation functional. Use of the GGA affected stacking-fault formation energies by only a few meV, and had no effect on the calculated electronic structure. Details of these calculations will be reported elsewhere.[14]

Since the energy differences involved in calculating stacking faults are extremely small, care must be taken to maximize the accuracy. We treated the *d* electrons of the Ga and In atoms as valence electrons, and exercised particular caution concerning the **k**-point sampling, as discussed below. Extensive convergence tests for bulk properties of the III-V nitrides[14] led to the following choice of energy cutoffs: 70 Ry for GaN, and 60 Ry for AlN and InN. The higher plane-wave cutoff required for GaN is related to the stronger Ga 3*d* potential. All our calculations were carried out with the lattice constants and structural parameters that were optimized at the relevant cutoffs; this is important so as to not introduce artificial strain in the material.

Use of the supercell method implies that the stacking faults are repeated in the [0001] *z* direction after a certain number of atomic layers, and represent infinite planar defects in the (0001) *xy* plane. We used either eight or nine double layers (16 or 18 atoms) to model the stacking faults, depending on the defect under consideration. Convergence checks for type-I faults using 12-double-layer (24-atom) supercells produced exactly the same results as eight-double-layer cells in GaN and AlN; in InN, the formation energy was lower by 4 meV.

The formation energy per unit cell of a stacking fault E^f is obtained as

$$E^f = E_{\rm tot}^{\rm defect} - E_{\rm tot}^{\rm ref}, \qquad (1)$$

where $E_{\rm tot}^{\rm defect}$ is the total energy of a supercell containing the stacking fault, and $E_{\rm tot}^{\rm ref}$ is a reference energy corresponding to a bulk structure of equivalent size. The total-energy calculation for this bulk structure should be carried out at the same level of convergence as the defect supercell; in particular, the **k**-point grid has to be equivalent. The grid in the *xy* plane is always the same, namely six **k**-points in the irreducible part of the Brillouin zone.[15] For the eight-double-layer supercells, the reference structure is an identically sized supercell containing the WZ structure, or equivalently, a two-double-layer (four-atom) WZ cell with the same six **k**-points but ''folded'' four times along the *z* direction, yielding an equivalent **k**-point grid.

For the nine-double-layer supercell, an identically sized reference supercell (or a smaller cell) containing the WZ structure cannot be constructed. We therefore calculate the energy of an identically sized nine-double-layer *zinc-blende* supercell, or equivalently a three-double-layer (six-atom) ZB cell with the six **k**-points folded three times in the *z* direction. $E_{\rm tot}^{\rm ref}$ is then obtained by adding the calculated energy difference between the WZ and ZB phases to the energy of the ZB supercell. The energy difference between these phases is, again, obtained in a consistent fashion, using a two-double-layer (four-atom) WZ cell with the six **k**-points folded *six* times in the *z* direction, and a three-double-layer (six-atom) ZB cell with the six **k**-points folded *four* times in the *z* direction.

Our supercells impose periodicity in the *z* direction and hence there are two type-I stacking faults per cell [see Fig. 1(a)]; this is taken into account when evaluating the formation energy. Similarly, the structure shown in Fig. 1(b) contains not only a type-II fault, but also a type-I fault. We therefore use the formation energy obtained for the type-I stacking fault in determining that of the type-II defect. The periodicity in the *z* direction for the faults shown in Figs. 1(c) and 1(d) introduces no additional faults in the supercell.

Structural optimization was investigated in detail for type-I faults. The calculated equilibrium structures for the ZB and WZ phases differ only very slightly with respect to volume and in-plane lattice constant [''in-plane'' referring to the (0001) plane for WZ, and the (111) plane for ZB]. In our supercells the in-plane and perpendicular lattice constants were fixed to those of the WZ structure. We checked that optimizing the dimension along the *c* axis of our supercell (to allow for volume changes in the region of the stacking fault) did not lead to any significant change in the results. Atomic relaxations introduced only very small decreases in formation energies: the maximum change was about 2 meV, in the case of type-I faults in AlN, and the corresponding atomic displacements were less than 0.003 Å. Based on our extensive investigations of structural optimizations for the type-I faults, we concluded that calculations for the other types of stacking faults could be carried out allowing no relaxation of atomic positions or change in volume of the supercell.

Our calculated stacking fault formation energies are given in Table I. For all faults considered, those in GaN have the lowest formation energy, followed by InN and then AlN. This trend is the same as that which we found for the ZB/WZ energy difference of the bulk materials.[14] Indeed, the formation energy of the stacking faults roughly scales with the

TABLE I. Stacking-fault formation energies per unit cell area (in meV). The conversion factors from meV/(unit cell area) to erg/cm^2 (using our theoretical lattice constants) are 1.81 for GaN, 1.47 for InN, and 1.98 for AlN. The conversion factor from erg/cm^2 to J/m^2 is 10^{-3}.

	Type I	Type II	Type III	Extrinsic
GaN	10	24	19	38
InN	19	44	36	65
AlN	49	103	97	150

number of ''zinc-blende units'' contained in the structure (one for type I, two for types II and III, and three for the extrinsic fault). Table I shows that the type-I fault always has the lowest energy, as is commonly expected. Stacking faults of type II are slightly more than twice as high in energy. The type-III stacking faults have a formation energy slightly *less* than twice the formation energy of the type-I defect. Figure 1(c) shows that the type-III stacking fault can be regarded as consisting of two neighboring type-I faults. The slight reduction in energy compared to two type-I defects may be indicative of an attractive interaction between type-I stacking faults. Similarly, we see that the extrinsic fault has a formation energy very similar to the sum of the type-I and type-II stacking faults. The geometry can indeed be thought of as a type-II neighboring a type-I stacking fault [see Fig. 1(d)].

These correlations suggest that the energetics of stacking faults are governed by local effects. Some years ago Denteneer and van Haeringen[16] proposed a scheme for calculating stacking-fault energies based on a one-dimensional Ising-type model, with interaction parameters determined from bulk calculations for various polytypes (2H, 3C, 4H, and 6H in the case of SiC). Wright[7] recently applied this approach to the nitrides; for AlN and GaN his values are within 10% of the present results, confirming the validity of the Ising-model approach. The agreement is not as good for InN, where Wright's values are significantly larger. Combined with our finding that the stacking-fault energies in InN exhibited sensitivity to the supercell size, this indicates that longer-range interactions play a role in InN.

The low energy of the type-I stacking fault is consistent with experimental observations. In AlN, stacking faults observed with high-resolution microscopy were identified to be of type I.[9] Since type-I stacking faults cannot be generated as a result of strain relaxation, they must be growth related.[8] Type-II stacking faults were observed by Suzuki *et al.*,[17] who estimated the formation energy based on the width of 60° dislocations; they found 115 ± 37 meV in AlN and 28 ± 6 meV in InN. The AlN value agrees with our result, but the InN value is significantly smaller than our calculated energy. An older estimate for the formation energy of the type-II stacking fault in AlN, 2 meV,[18] is clearly much too small.

The type-III fault proposed here has energies that are higher than those of type I, but lower than the type-II or extrinsic faults. To our knowledge there is no mention in the literature of this type of fault. As pointed out above, the type-III fault can be thought of as a combination of two type-I faults. Experimental observations of type-I faults generated during growth usually display a stacking fault followed by a certain number of layers in the new stacking sequence, and then another type-I fault reverting the stacking sequence to the original order.[19] Our type-III fault is essentially a limiting case of this structure, in which the thickness of the layer with alternate stacking is reduced to one atomic layer. Whether such a structure is stable is still an open question; examination of high-resolution micrographs for evidence of such a defect may shed light on the issue.

We have also investigated stacking-fault electronic structure. A detailed investigation of the band structure revealed no defect-induced localized states in the band gap. A slight narrowing of the band gap was observed, consistent with the presence of a zinc-blende-like region (see below); for the type-I fault this narrowing was less than 0.02 eV. Our results differ from the conclusions of Bandic *et al.*,[20] who investigated stacking faults in GaN using local empirical pseudopotentials and identified an interface state within the band gap about 0.13 eV above the valence-band maximum. In the theoretical approach of Ref. 20 the electronic structure was not evaluated self-consistently.

The stacking faults considered here can be thought of as a thin layer of ZB material embedded in the WZ lattice. Albrecht *et al.*[6] recently observed that GaN samples that contain a high concentration of stacking faults exhibit a luminescence line at 364 nm (3.40 eV). They proposed that the luminescence orginates from excitons bound to stacking faults that form a quantum well of ZB material surrounded by the WZ structure. In order to understand the electronic behavior of such a structure it is essential to know the band lineup between the ZB and the WZ phase. To extract this lineup we have investigated the electronic structure of a system consisting of six double layers of ZB material alternating with equally thick regions of the WZ phase. Full atomic relaxation was allowed. The two interfaces contained in the supercell are inequivalent, but with band lineups that are expected to be very similar.

Once again, the electronic structure revealed no evidence of any interface states in the band gap. An examination of charge densities and potentials shows that an electric field is set up in the layers, due to the spontaneous polarization of GaN in the WZ phase; the magnitude of this field is in good agreement with the results reported in Refs. 21 and 22. The valence-band offset ΔE_v at the ZB/WZ interface consists of two contributions: one is the lineup in electrostatic potentials across the interface ΔV_c; the other, $\Delta E_v^{\rm bulk}$, is the difference in the calculated valence-band positions between the bulk WZ and ZB materials. These quantities are taken as positive if the value in the WZ structure is higher than the value in the ZB structure. Our bulk calculations yield $\Delta E_v^{\rm bulk} = 0.06$ eV. The lineup of electrostatic potentials ΔV_c was obtained following the procedure in Ref. 21, resulting in $\Delta V_c \approx 0.01$ eV. The valence-band offset is then $\Delta E_v = \Delta V_c + \Delta E_v^{\rm bulk} \approx 0.07$ eV. Using an experimental band-gap difference of 0.20 eV,[23] a conduction-band offset of 0.27 eV is obtained.

These offsets correspond to a so-called type-II lineup: the electronic states at the conduction-band minimum are localized mainly in the ZB region, while those at the valence-band maximum are preferentially localized in the WZ region. Indeed, this is what we find when examining the spatial distribution of the states at the band extrema, although the lo-

calization of the valence-band states is weak, due to the small valence-band offset. The band lineup obtained here is qualitatively consistent with the estimate of Ref. 6. We thus support the suggestion by Albrecht *et al.* that stacking faults can give rise to a quantum-well-like region that can lead to luminescence transitions.[6]

In summary, we have investigated the atomic and electronic structure of [0001] stacking faults in WZ AlN, GaN, and InN using first-principles calculations. We find that type-I stacking faults, which contain one violation of the stacking rule, have the lowest formation energy in each material. The stacking-fault formation energies are lowest in GaN followed by InN and then AlN, thus exhibiting the same trend as the energy difference of the bulk ZB/WZ structures. An investigation of the electronic structure of stacking faults in GaN indicates that there are no defect-induced states in the band gap. The ZB/WZ interface exhibits a type-II lineup with $\Delta E_v \approx 0.07$ eV and $\Delta E_c \approx 0.27$ eV, supporting the suggestion that stacking faults can give rise to quantum-well-like regions of ZB material embedded in the WZ lattice that can bind excitons.

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