Small valence-band offsets at GaN/InGaN heterojunctions

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The band discontinuities between GaN and InN, as well as InGaN alloys, are key parameters for the design of nitride-based light emitters. Values reported to date are subject to large uncertainties due to strain effects at this highly mismatched interface. We have investigated the band lineups using first-principles calculations with explicit inclusion of strains and atomic relaxations at the interface. We find that the ''natural'' valence-band offset between unstrained InN and GaN is 0.3 eV. Prescriptions are given, including the band shifts, due to strains at a pseudomorphic interface. © *1997 American Institute of Physics.* [S0003-6951(97)03319-6]

GaN and its alloys with AlN and InN are successfully being used for optoelectronic devices in the green, blue, and UV regions of the spectrum. All of these devices rely on band-gap engineering to provide carrier confinement or optical confinement; knowledge of the offsets in conduction and valence bands is therefore crucial for device design. This issue is complicated in the nitride system by the large lattice mismatch between the compounds: 3% between AlN and GaN, and 11% between GaN and InN (see Table I). The band offsets are only well defined when the materials are in registry at the interface, requiring a so-called pseudomorphic interface, in which at least one of the materials is strained in order to match the in-plane lattice constant across the interface. The large mismatch between InN and GaN complicates experimental measurements of the band offsets in two ways: first, it may be difficult (or even impossible) to obtain a pseudomorphic interface between the binary compounds; and second, one needs to have information about the strains in the heterojunction and their effect on the bands in order to extract reliable information about the band offsets.[1]

We report first-principles calculations for band discontinuities between the III-nitride semiconductors based on the pseudopotential-density-functional method. This approach has been successfully applied to a wide variety of heterojunctions, including systems with large lattice mismatch.[2] We are able to separate the effects of strain, which can be expressed through deformation potentials, from the ''natural'' band lineup between the unstrained materials. Our main conclusion is that the natural band lineup between GaN and InN leads to a rather small value of the valence-band offset (0.3 eV). Valence-band offsets for InGaN alloys can be obtained by linear interpolation. Effects of strain in the InGaN tend to increase the valence-band offset, but the resulting discontinuity is still quite small, and smaller than reported values.[3,4]

Details about our calculations for AlN/GaN interfaces, in which strains play a less important role, will be published elsewhere.[5] Our calculated valence-band offset between unstrained AlN and GaN is 0.7 eV,[6] consistent with other experimental and theoretical determinations.[3,7–10]

In this letter we will first outline the theoretical approach, list some of the computational details, and describe how we proceed from a calculation for a strained system to the extraction of an unstrained lineup. We will then focus on our calculations for GaN/InN heterojunctions, where the presence of large strains leads to sizeable atomic relaxations at the interface, which in turn significantly affect the band offsets. We also give values for the deformation potentials that describe the changes in the band structure due to strain. Finally, we discuss our results in light of the ''common anion rule,'' taking the effects of *d* electrons into account.

For concreteness' sake, we consider a heterojunction between unstrained GaN and InN strained to match the in-plane lattice constant of GaN, i.e., $a_{\parallel}=4.50$ Å. This corresponds to the experimental situation of growing a pseudomorphic InN layer on top of a GaN substrate (or on a GaN epilayer thick enough to have relaxed to the GaN equilibrium lattice constant). As mentioned before, it may be difficult to actually grow such a structure, because the critical-layer thickness (beyond which strains cannot be accommodated elastically and dislocation formation sets in) is probably very small when the lattice mismatch is as large as 11%. However, our theoretical results for the binary compounds can be interpolated to derive results for GaN/InGaN heterojunctions, which are easier to grow. The strain in the pseudomorphic layer can be calculated using elastic theory, imposing an in-plane lattice constant equal to that of GaN, and allowing the material to relax in the perpendicular direction according to Poisson's ratio.[11] Our results are not sensitive to the values of the elastic constants, since the effects of strain are

TABLE I. Calculated deformation potentials, in eV, for zincblende AlN, GaN and InN. a_v is the absolute deformation potential for the VBM, a_g the deformation potential for the direct band gap, and b and d describe the splitting of the VBM under biaxial strain along [001], respectively [111]. Also listed are the experimental lattice constants (a, in Å) and room-temperature band gaps (E_g, in eV).

	AlN	GaN	InN
a	4.37	4.50	4.98
E_g	6.20	3.39	1.89
a_v	2.3	2.0	1.7
a_g	−9.1	−8.0	−5.0
b	−1.5	−1.7	−1.2
d	−4.5	−4.2	−3.0

[a)] Electronic mail: vandewalle@parc.xerox.com subtracted out of the offsets that we will present; we have used the elastic constants obtained from first principles by Kim *et al.*[12]

The actual calculations are carried out for superlattices consisting of alternating layers of GaN and strained InN. For sufficiently thick layers the charge densities and potentials in the center of each layer become bulk-like, and allow extraction of band lineups representative of an infinite interface. We have performed convergence tests to ensure that our superlattices (containing up to 12 atoms of each material) meet this requirement. Most of our calculations have focused on the (110) orientation of the zincblende phase. Wurtzite is the more stable phase for these semiconductors; however, the structures are similar enough (differing only beyond third nearest neighbors) to expect very similar band lineups. Indeed, we found that calculations for selected wurtzite structures produced the same natural band lineups for both phases.

The choice of the (110) orientation was motivated by the nonpolar nature of this interface (where each atomic plane parallel to the interface contains both a cation and an anion and is thus neutral). Nonpolar interfaces are usually easier to investigate because the charge-neutral character of these planes makes the generation of interface-specific dipoles less likely. We discovered that this expectation was not borne out in the strongly lattice-mismatched GaN/InN system: sizeable atomic relaxations did occur, which strongly affected the band offsets. We also carried out calculations for selected (001) interfaces and found that the natural band lineups agree with those for (110) to within 0.1 eV. Full results for other interface orientations will be published elsewhere.[5] Internal displacements,[13] which affect the positions of the atoms in the unit cell under (110) strain, were explicitly included using internal-displacement parameters calculated within the same computational framework.

Our first-principles calculations are based on density-functional theory and *ab initio* pseudopotentials, using the same highly optimized code which we have previously applied to the study of defects and impurities in GaN (see Ref. 14 and references therein). The effect of *d* electrons on GaN and InN was taken into account either through the so-called nonlinear core correction (nlcc) or by explicit inclusion of the *d* electrons as valence electrons; while there were some differences in the details of atomic relaxations around the interface, the resulting natural band lineups differed by less than 0.1 eV. In the following, the results obtained with the nlcc will be presented, for which an energy cutoff of 60 Ry was used. Spin-orbit splittings, which are very small in the nitrides, were not included. As in previous work,[2] we obtain the band offsets by extracting the lineup of average electrostatic potentials (labeled V_c) from the superlattice calculation, and by performing separate calculations for the bulk materials to find the position of the valence band with respect to the average potential (i.e., $E_v - V_c$). Deformation potentials are obtained by performing calculations on strained bulk materials. Our estimated error bars on band lineups are ± 0.1 eV.

In our example, the superlattice calculation yields a value for the offset in average electrostatic potentials, ΔV_c between GaN and strained InN. To obtain a valence-band offset, one needs to know $E_v - V_c$ in each of the bulk materials. In a strained material, this value depends on the hydrostatic (shifting the average position of the bands) and biaxial (splitting the valence bands) components of the strain. Rather than re-computing the band structure for every new strain situation, it is more convenient to express these shifts and splittings in terms of deformation potentials.[11] The shift in the valence-band maximum (VBM) due to hydrostatic strain is described by a so-called ''absolute'' deformation potential,[15] which can be calculated using a superlattice consisting of alternately strained layers of a single material.

TABLE II. Valence-band offsets $\Delta E_{v,av}$ for GaN/InN (110) heterojunctions for three different in-plane lattice constants, $a_{\parallel}$.[a]

$a_{\parallel}$ (Å)	$\Delta E_{v,av}$ (eV)	ΔE_v^{nat} (eV)
4.50	-0.08	0.34
4.74	0.12	0.34
4.98	0.21	0.31

[a] See Ref. 6.

Table I lists values for various relevant deformation potentials; the use of these parameters for calculating band positions was discussed in Ref. 11. Note that these deformation potentials were calculated for *small* deformations, well within the linear regime. For the large strains present in a hypothetical pseudomorphic GaN/InN heterostructure additional nonlinear terms are sizeable, and have been included in our analysis. However, for the strains that can practically be achieved in experimental pseudomorphic structures the linear terms will dominate.

In Table II we list the results for $\Delta E_{v,av}$, i.e., the discontinuity in the average valence-band positions;[6] splitting of the VBM due to biaxial strain is not included in these values. The low values of $\Delta E_{v,av}$ reflect the importance of atomic relaxations near the interface. Indeed, when no out-of-plane relaxations are allowed at the (110) interface, the resulting valence-band offsets are quite large. The difference in bond lengths between GaN and InN provides a driving force for significant out-of-plane relaxations, which lower the offset by as much as 1 eV. Accurate calculations of these relaxations require that the superlattice calculations be performed based on the *theoretical* lattice constant of the bulk materials. This theoretical lattice constant differs somewhat from the experimental value, and hence the $\Delta E_{v,av}$ values in Table II may differ from those that would be calculated based on the *experimental* lattice constants. Our main purpose, however, is to extract a natural, unstrained band offset, which will be expressed at the experimental lattice constants.

The $\Delta E_{v,av}$ values depend on the strain situation of the heterostructure, because $E_{v,av}$ is shifted due to hydrostatic strain. Using the a_v values listed in Table I (and including nonlinear contributions), we can subtract out this shift, and obtain a valence-band offset between *unstrained* materials; the second column of Table II lists the values for this natural valence-band offset, ΔE_v^{nat}. We conclude that $\Delta E_v^{nat} \approx 0.3 \pm 0.1$ eV for the GaN/InN system.

For AlN/GaN we have found a natural band lineup of $\Delta E_v^{nat} = 0.7 \pm 0.1$ eV; these lineups are illustrated in Fig. 1. One may wonder why the valence-band offset for AlN/GaN is larger than for GaN/InN. The difference is attributable to

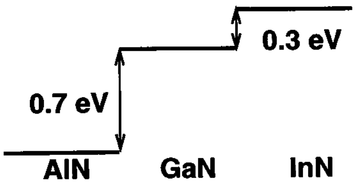

FIG. 1. Natural valence-band lineups between AlN, GaN, and InN, obtained from first-principles calculations for zincblende (110) interfaces.

the role of the *d* electrons in these materials. For common-anion systems such as the III-nitrides, one might expect the VBM to be nearly aligned—this is the old ''common-anion rule'' which was based on the notion that the character (and thus the energetic position) of the VBM is determined by the anion *p* states. This common-anion rule was found to fail in many systems, and Wei and Zunger[16] explained the failure in terms of the interactions between *d* states in the core and the VBM: *p*-*d* repulsion pushes the VBM upward, by a sizeable amount when the *d* states lie close enough to the VBM. This mechanism leads to a valence-band offset of ~0.6 eV between GaAs and AlAs: Al has no *d* states, and the Ga 3*d* states in GaAs push its VBM upward with respect to AlAs. The same effect leads to the ~0.7 eV valence-band offset between AlN and GaN. However, since both Ga and In contain *d* states, at roughly the same energetic position, the valence-band offset for GaN/InN is significantly smaller (closer to the common-anion rule). The role of the *d* core states in the nitrides was also discussed by Strite.[17]

The natural lineups illustrated in Fig. 1 would be modified, of course, by strain contributions. For example, at a heterostructure between unstrained GaN and strained $In_{0.2}Ga_{0.8}N$ the natural valence-band lineup would give an offset of 0.06 eV. (Parameters for the alloy can be obtained by linear interpolation, except for the conduction-band positions, for which bowing of the gap should be included.) Since the $In_{0.2}Ga_{0.8}N$ is under compression, the hydrostatic strain lowers the average valence band in this layer; simultaneously, the biaxial strain splits the VBM and raises the uppermost valence band. Using elastic constants from Ref. 12 and our calculated deformation potentials from Table I, we find that the final valence band offset at the GaN/$In_{0.2}Ga_{0.8}N$ heterojunction is still less than 0.1 eV.

After submission of the present work it came to our attention that Wei and Zunger[18] have recently calculated the unstrained band offsets based on core-level lineups. Their results are within 0.1 eV of the values reported here.

In summary, we have presented results of first-principles calculations which properly include strain and relaxation effects at the interface between III–V nitride semiconductors. For AlN/GaN, we find a natural valence-band lineup of 0.7 eV, consistent with previous determinations. For GaN/InN, we find an unexpectedly small valence-band offset ($\Delta E_v^{nat} = 0.3$ eV), which reflects the importance of atomic relaxations at this interface.

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[6] We denote ΔE_v at a heterojunction A/B as a positive value if the valence-band maximum (VBM) in B is higher in energy than the VBM in A.

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