OFFSETS AND POLARIZATION AT STRAINED AlN/GaN POLAR INTERFACES

Fabio Bernardini,* Vincenzo Fiorentini*, and David Vanderbilt**

* INFN – Dipartimento di Scienze Fisiche, Università di Cagliari, I-09124 Cagliari, Italy
** Department of Physics and Astronomy, Rutgers University, Piscataway, NJ, U.S.A.

ABSTRACT

The strain induced by lattice mismatch at the interface is responsible for the different value of the band discontinuities observed recently for the AlN/GaN (AlN on GaN) and the GaN/AlN (GaN on AlN) polar (0001) interface. We present a first-principles calculation of valence band offsets, interface dipoles, strain-induced piezoelectric fields, relaxed geometric structure, and formation energies. Our results confirm the existence of a large forward-backward asymmetry for this interface.

INTRODUCTION

A reliable determination of the valence-band offset (VBO) at the (0001) polar interface between wurtzite AlN and GaN is still missing. The few experimental investigations available [1, 2] are in mutual disagreement, and theoretical studies refer either to zincblende interfaces [3], or artificially lattice-matched wurtzite interfaces [4]. The latter approximation leads to a less accurate determination for the VBO, and cannot pick up the possible forward-backward asymmetry characteristic of lattice-mismatched interfaces. In the case of the AlN/GaN interface, lattice mismatch amounts to 2.5%, and may cause a very large asymmetry. This asymmetry has not yet been clearly determined experimentally (it was not even found in early experimental work [5]), being hidden by the large uncertainties in the measured data. Even the best experimental investigations available face two kinds of problem: (i) the determination of the core level alignment with the valence-band maximum (VBM) is obtained indirectly using theoretical estimates of the VBM position, which (as underlined by Vogel et al. [6]) is affected by large systematic errors; (ii) the existence of strong polarization fields in both the substrate and the overlayer tends to modify the apparent value of the VBO deduced from the core-level shift measurements.

The present ab-initio investigation includes all strain and relaxation-induced effects, and overcomes the difficulty in VBO determination due to polarization fields by the use of a novel charge-decomposition technique. An estimate of the formation energy of the interfaces studied is also given.

BULK PROPERTIES

Valence-band offset calculations at lattice-mismatched interfaces require the evaluation of the band structure energies for the bulk crystals in equilibrium, and subjected to biaxial strain. The calculations are done using density-functional theory in the local-density approximation (LDA) to describe the exchange-correlation energy, and ultrasoft pseudopotentials [7] for the electron-ion interaction. Plane-wave basis sets up to 25 Ry, and 24 special k-points are found to give fully converged values for the bulk properties. Since the properties of GaN are affected by Ga 3d states [8], our Ga pseudopotential includes 3d electrons in the valence. This yields very good structural bulk parameters (see below).
Table I: Predicted structural parameters and valence band maxima for equilibrium and strained AlN and GaN.

| Material | AlN | AlN | GaN | GaN |
|----------|-----|-----|-----|-----|
| Substrate | — | GaN | — | AlN |
| \(a\) | 5.814 | 6.04 | 6.04 | 5.814 |
| \(c/a\) | 1.619 | 1.51 | 1.6336 | 1.73 |
| \(u\) | 0.38 | 0.3927 | 0.3761 | 0.3653 |
| \(E_{\text{strain}}\) (eV) | +0.179 | | +0.155 |
| \(E_{\text{VBM}}\) (eV) | −0.16 | 0.09 | −4.90 | −4.69 |

In wurtzite crystals, the determination of the atomic structure at a given lattice constant \(a\) implies the calculation of the \(c/a\) and \(u\) parameters. The equilibrium \(c\) as been determined by fitting with a polynomial the total energy computed for six different values of \(c\), with \(u\) being determined for each value of \(c/a\) via minimization of the Hellmann-Feynman forces, with a threshold of \(10^{-4}\) Hartree/bohr. The calculated structural parameters are given in Table I. The structural parameters of AlN and GaN behave similarly under strain \([\Delta(c/a)/(c/a) \sim 7\%, \Delta u/u \sim 2\%] with similar total energy variations. Instead, the effect of strain on the valence-band edge is very different. A rationale for this difference is that the AlN (GaN) band edge is a singlet (doublet) formed by the hybridization along the \(c\)-axis (in the \(a\)-plane) of N 2s orbitals with Al \(p_z\) (Ga \(p_{xy}\)) states, so that biaxial compression pushes the edge upward in GaN and downward in AlN.

**BAND OFFSET**

As pointed out by Baldereschi *et al.* [9], the valence-band offset \(\Delta E_v\) may be split in two terms:

\[
\Delta E_v = \Delta E_{\text{VBM}} + \Delta V_{el}.
\]

The first contribution \(\Delta E_{\text{VBM}}\) is the difference between the valence-band edge energy in the two bulk materials, each edge being referred to the average bulk electrostatic potential. The second contribution, the potential lineup \(\Delta V_{el}\), is the drop of the macroscopic average of the electrostatic potential across the interface. The latter term requires a selfconsistent calculation of the electronic density distribution for the real interface system. Our interface has been modeled using a (GaN)_4/(AlN)_4(0001) superlattice (see below), both ideal and fully relaxed. The material being grown epitaxially on the chosen substrate, has been pre-strained to have the same \(a\) lattice constant as the substrate.

The lineup term is customarily obtained by solving the Poisson equation for the macroscopic average of the charge density, neutralized by a suitable distribution of gaussian charges centered on the ion sites. The potential drop across the interface is usually calculated as the difference of potential values in bulk-like regions inside the two interfaced materials. This turns out to be non-trivial for a system such as the present one, in which the existence of polarization fields in the equilibrium bulk makes it impossible to define asymptotic values for the electrostatic potentials. The existence of such fields, moreover, limits the maximum length of our slab. Indeed, beyond a certain critical thickness the drop of the potential inside each slab would make the system metallic, with a related transfer of charge, which would spoil the exact determination of the lineup term. Our choice of a
16-atom supercell is a compromise between the need to have an insulating system, and at the same time to avoid a spurious coupling of the interfaces at the sides of the slabs. Tests were performed in supercells of up to 40 atoms. In Fig. 1, we show the macroscopic average of the charge density and of the electrostatic potential. The potential drop is inextricably linked to the polarization fields within the AlN and GaN bulks. We have circumvented this problem by employing a new method. The basic idea is that at the polar AlN/GaN interfaces, the existence of polarization fields reveals itself by an accumulation of charge in the form of a monopole distribution whose density is proportional to the difference between the polarizations inside the two interfaced bulks. On top of this monopole term, we have the traditional dipole term representing the local charge transfer across the interface. This dipole term is the quantity we are interested in, as the band offset is by definition related to the dipolar part of the potential drop. Since the monopole contributions are related to the polarization fields, they must be equal and opposite for the two (geometrically inequivalent) interfaces in our AlN/GaN superlattice. To filter out the monopole term we superimpose the two interface distributions by folding them around a plane placed halfway between the two junctions. We define the dipole term $\bar{n}_{\text{dip}}$ as the average of the superimposed charges,

$$
\bar{n}_{\text{dip}}(z - z_0) = \frac{1}{2} \left[ \bar{n}(z - z_0) + \bar{n}(z_0 - z) \right],
$$

where $z$ is a coordinate along the $c$-axis, $z_0$ the plane position and $\bar{n}$ the macroscopic average for the charge density. The monopole term $\bar{n}_{\text{mono}}$ is just the difference between the dipole term and the total macroscopic charge:

$$
\bar{n}_{\text{mono}}(z) = \bar{n}(z) - \bar{n}_{\text{dip}}(z).
$$

Figure 1: Supercell electron density and electrostatic potential. Electron density has been compensated in the two bulks by a distribution of gaussians placed at the atomic sites.
Such a decomposition allows a determination of the polarization charges and dipole terms which is nearly independent of the position of the folding plane. Fig. 2 shows the decomposition for the AlN/GaN interface. The decomposition reveals the origin of the asymmetry in the total charge distribution, and at the same time it enables us to evaluate the lineup term. In Table II we report the values for the VBO obtained via this decomposition. There is a very large forward-backward asymmetry of 0.65 eV between AlN/GaN and GaN/AlN interface VBOs. This is only marginally due to the lineup term (contributing 0.18 eV), its main component being the band structure term (0.47 eV). The relaxation is responsible for

![Figure 2: Decomposition of the macroscopic average of the electronic density (dotted line) into monopole (solid) and dipole (dashed) terms. Such a decomposition allows the determination of the lineup term $\Delta V_{el}$ from the solution of the Poisson equation (dot-dashed) of the dipole term.](image-url)

| Interface  | AlN/GaN | GaN/AlN |
|------------|---------|---------|
| structure  | ideal   | relaxed | ideal   | relaxed |
| $\Delta E_v$ | 0.29    | 0.20    | 1.00    | 0.85    |
| $\Delta V_{el}$ | 5.28    | 5.18    | 5.52    | 5.36    |
| $\sigma_{int}$ | 0.029   | 0.014   | 0.022   | 0.011   |
| $\vec{E}$ | 32.7    | 15.6    | 24.4    | 12.9    |

| units | |
|-------|
| eV    |
| eV    |
| C/m²  |
| $10^8$ V/m |

comparatively small deviations of \( \sim 0.1 \) eV from the ideal-interface values. The relaxation pattern is characterized in both cases by a contraction of the Al-N axial interface bond (\( \sim -0.04 \) a.u.) and an expansion of the axial Ga-N bond (\( \sim +0.02 \) a.u.).

**POLARIZATION**

Supercell calculations are not the only way to obtain the interface charge density \( \sigma_{\text{int}} \). As shown in Ref. [10], given the polarization \( P_1 \) and \( P_2 \) and the dielectric constants \( \varepsilon_1 \) and \( \varepsilon_2 \) of the component materials, \( \sigma_{\text{int}} \) is given by

\[
\sigma_{\text{int}} = \pm 2 (P_2 - P_1)/(\varepsilon_1 + \varepsilon_2).
\]

in periodic boundary conditions. We have calculated the macroscopic polarization for equilibrium and strained GaN and AlN via the Berry phase technique of Ref. [11]. The (high-frequency) dielectric constants of AlN and GaN have been calculated using the relation

\[
\Delta P_T = \varepsilon_\infty \Delta P_L,
\]

where \( \Delta P_T \) is the (so-called transverse) polarization change induced by a small cation sublattice displacement in the bulk in zero field, and \( \Delta P_L \) is the (so-called longitudinal) polarization change due to a uniform displacement of few cation planes in a periodic bulk supercell. In the latter, a depolarizing field is present due to the periodic boundary conditions. As a by-product of our calculations, we obtained the Born effective charges for AlN and GaN which, as expected for highly polar semiconductors, are quite close to the nominal ionicity. The results are shown in Table III. Substituting \( P_{\text{tot}} \) and \( \varepsilon \) in Eq.1 we obtain for the AlN/GaN (GaN/AlN) interface a monopole density of 0.028 (0.023) C/m\(^2\) in embarrassing agreement with the outcomes of the supercell calculations. This proves directly that the sources of the internal fields in the interface system are the charges accumulated at the interface by the bulk polarization effects. Also, the latter finding provides an a posteriori justification of our somewhat ad-hoc charge decomposition procedure.

**FORMATION ENERGIES**

An important issue for the present selfconsistent calculation is the evaluation of the formation energy for the AlN/GaN interfaces. Contrary to the case of non-polar interfaces, for the wurtzite (0001) system it is impossible to build a superlattice with symmetric interfaces. This means that only the average value of the formation energy for the two

| System | \( a \) | \( P_{el} \) | \( P_{tot} \) | \( \partial P/\partial u \) | \( Z^* \) | \( \varepsilon_\infty \) |
|--------|--------|--------|--------|----------------|------|--------|
| AlN    | 5.814  | -0.178 | -0.0812| 10.51          | 2.69 | 4.59   |
| AlN    | 6.04   | -0.492 | -0.1712| 9.95           | 2.74 | 4.64   |
| GaN    | 5.814  | +0.223 | +0.0343| 10.69          | 2.74 | 5.27   |
| GaN    | 6.04   | -0.0511| -0.0308| 9.88           | 2.72 | 5.52   |
interfaces can be obtained from a total-energy calculation. We define the average formation energy for the AlN/GaN interface as

\[ E_f = \frac{1}{2A} \left[ E_{\text{tot}} - n^{\text{Ga}} \mu^{\text{GaN}} - n^{\text{Al}} \mu^{\text{AlN}} \right], \]

where \( \mu^X \) are the total energies per pair of GaN and AlN, \( n^X \) the number of Ga and Al atoms, \( E_{\text{tot}} \) the supercell total energy and \( A \) its cross-sectional area. A reliable determination of \( E_f \) requires equivalent k-point sampling for bulk and interface calculations. This is easily accomplished if the interface is lattice-matched. In the present case, the supercell length is not simply an integer multiple of the bulk unit cell of either constituent material. This means that an exact equivalence between k-point meshes cannot be achieved. A good approximation for \( E_f \) can however be obtained by defining, for each component material, an auxiliary bulk cell having the same lattice constant \( a \), and an axial length \( \bar{c} \) being a sub-multiple of the supercell length \( l \). This value in the present case is just the average of \( c_{\text{AlN}} \) and \( c_{\text{GaN}} \). It is then possible to downfold exactly the supercell mesh into the auxiliary bulk cell. The next step is to uniformly scale the k-points coordinates to adapt the mesh to the real value of \( c \). We should point out that the accuracy of this procedure (compared with an exact computation of the energy integral over the IBZ) increases with the number of points in the mesh. It is therefore possible to find a suitable mesh to accomplish any required accuracy. The results for the formation energies reported in Table IV have been obtained using a 6-point Chadi-Cohen mesh \[12\] in the supercell, which when downfolded in the auxiliary cell produces 24 special points. We estimate the k-point sampling error in the formation energies to be \( \sim 10 \) meV. It should be noted that such low formation energies are not surprising when compared with the results obtained by Chetty et al. \[13\] for GaAs/AlAs\,(111) interfaces.

Table IV: Average formation energy for the AlN/GaN \,(0001)\ interfaces.

| Interface   | AlN/GaN | GaN/AlN | units |
|-------------|---------|---------|-------|
|             | ideal   | relaxed | ideal | relaxed |
| \( E_f \)   | -3.4    | -16.4   | +11.7 | -6.2    | meV    |

REFERENCES

[1] J. W. Waldrop and R. W. Grant, Appl. Phys. Lett. 68, 2879 (1996).
[2] G. Martin, A. Botchkarev, A. Rockett, and H. Morkoc, Appl. Phys. Lett. 68, 2541 (1996).
[3] E. Albanesi, W. R. L. Lambrecht, and B. Segall, J. Vac. Sci. Tech. B 12, 2470 (1994).
[4] S. Wei and A. Zunger, to be published.
[5] G. Martin et al., Appl. Phys. Lett. 65, 610 (1994).
[6] D. Vogel, P. Krüger and J. Pollmann, to be published.
[7] D. Vanderbilt, Phys. Rev. 41, 7892 (1990).
[8] V. Fiorentini et al., Phys. Rev. B 47, 13353 (1993); V. Fiorentini et al., Proc. ICPS-22, D. J. Lockwood ed. (World Scientific, Singapore 1995), p.137; A. Satta et al., MRS Proc. 395, 515 (1996).
[9] A. Baldereschi, S. Baroni, and R. Resta, Phys. Rev. Lett. 61, 734 (1988).
[10] D. Vanderbilt and R. D. King-Smith, Phys. Rev. B 48, 4442 (1993).
[11] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1992).
[12] D. J. Chadi and Marvin L. Cohen, Phys. Rev. B 8, 5747 (1973).
[13] N. Chetty and R. M. Martin, Phys. Rev. B 45, 6089 (1992).