

Macroscopic polarization and band offsets at nitride heterojunctions

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Ab initio electronic structure studies of prototypical polar interfaces of wurtzite III-V nitrides show that large uniform electric fields exist in epitaxial nitride overlayers, due to the discontinuity across the interface of the macroscopic polarization of the constituent materials. Polarization fields require a nonstandard evaluation of band offsets and formation energies: we find a large strain-induced asymmetry of the offset [0.2 eV for AlN/GaN (0001), 0.85 eV for GaN/AlN (0001)], and tiny interface formation energies. [S0163-1829(98)52116-9]

Due to their low-symmetry crystal structure, wurtzite III-V nitrides exhibit a nonzero macroscopic polarization even in equilibrium (spontaneous polarization).¹ Because of the appreciable lattice mismatch between nitrides, and of the fact that nitride heterostructures are usually grown along the polar (0001) axis, the macroscopic polarization in an epitaxially grown nitride layer will include a piezoelectric term. Piezoelectric constants¹ much larger than in most other semiconductors imply that small strains can produce unusually large polarizations in III nitrides. Also, spontaneous and piezoelectric polarizations are comparable in magnitude.¹ Therefore, a major influence of polarization on interface and device properties should be anticipated.

In this paper we present a detailed first-principle density-functional theory study (with full account of strain and polarization effects) of a prototypical strained, polar, wurtzite nitride interface: GaN/AlN (0001). The central results discussed below are (i) the change in macroscopic polarization across the heterointerfaces generates large uniform electric fields in the layers composing the nanostructure, and (ii) a large forward-backward band offset asymmetry exists, due to the effects of epitaxial strain on the bulk band structure. While analogous (though much smaller) fields have been previously predicted in strained superlattices of zinc-blende compounds and in ordered III-V alloys,² III-V nitrides stand alone because of their unusually strong polarization,¹ both spontaneous and piezoelectric. The presence of large polarization fields has a host of interesting consequences on device design which will be discussed in detail elsewhere.³

Most investigations so far have focused on the interface band offset and its possible asymmetry (the offset for AlN on GaN may differ from that of GaN on AlN). It is clear that measurements and theoretical predictions of this basic ingredient of heterostructure design may be significantly influenced by macroscopic polarization and by strain effects (both direct on the band bulk structures, and indirectly through piezoelectric effects). Surprisingly, apart from notable exceptions,^{4,5} the recent experimental^{6,7} and theoretical⁸⁻¹⁰ literature in this field did not address the issue of the effects of macroscopic bulk polarization on interface electronic structure. In particular, theoretical work so far mostly dealt with zinc-blende^{8,10} or artificially lattice-matched wurtzite⁹ interfaces.

Technical details of the local-density-functional ultrasoft-pseudopotential¹¹ plane-wave technique and of the theory of polarization¹² employed here are reported in recent papers.^{1,3,4,13} Results on bulk lattice parameters,¹ dielectric¹³ and piezoelectric¹ constants, and spontaneous polarization have also been reported previously. Technicalities specific to interface calculations will be reported elsewhere.³ Here we only mention that we accurately reproduced previously reported studies^{9,10} for GaN/AlN (111) interfaces, and that our results for GaN/AlN (0001) are in good agreement (where they can be compared) with similar calculations by a different group.⁵

Here we study (GaN)_n/(AlN)_m(0001) superlattices such that internal fields do not cause metallization and at the same time the repeated interfaces are fully decoupled ($n=m=4$). Polarization effects on arbitrary nitride quantum structures will be discussed in Ref. 3. We impose to the superlattice the in-plane lattice constant of either GaN or AlN in order to simulate the epitaxial relation of a heterooverlayer on either a GaN or an AlN substrate. The axial lattice parameter and internal parameters of the epitaxial material are optimized at the imposed substrate in-plane lattice parameter.

We evaluate the valence-band offset by splitting it conventionally¹⁴ into the difference ΔE_v of the bulk valence-band energies for the two bulks, and the interface potential lineup ΔV . The latter is generally just a jump in potential across the interface from one constant value to another. Our first result is that the potential does not exhibit a simple steplike shape at polar nitride interfaces, so that the lineup cannot be obtained in a conventional fashion. Indeed, consider Fig. 1, which shows the macroscopic average¹⁴ of the total charge density, and the ensuing electrostatic potential, of a GaN-matched GaN/AlN (0001) superlattice. The foremost unusual feature is, of course, the presence, in the bulk-like regions between the interfaces, of very large ($\sim 10^9$ V/m) uniform electric fields generated by the different charge distributions at the two interfaces (the density vanishes far from the interfaces, which indicates that the bulk-like regime is reached in our simulation).

The main consequences are (a) the difference between the bulk values of the electrostatic potential at the two sides of the interface is not defined unambiguously,¹⁵ as it will depend on the choice of the interface position or of the center of the bulklike region, which are of course ill defined; (b)

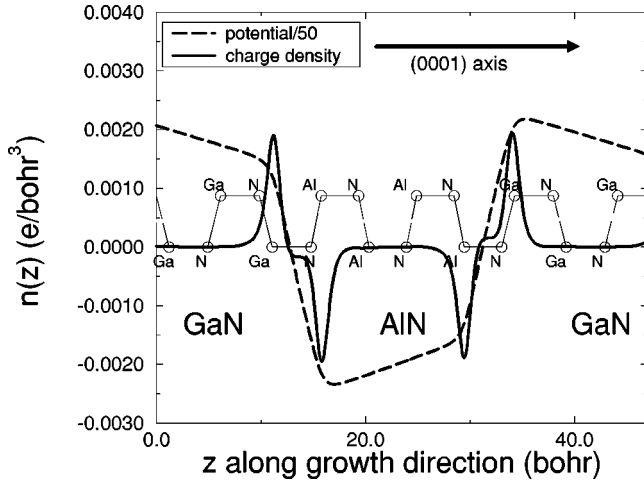


FIG. 1. Total (electronic plus ionic) density and ensuing electrostatic potential (in Hartree) for an AlN/GaN superlattice matched lattice to GaN. The magnitude of the fields in the bulk regions is $\sim 10^9$ V/m.

because of energy contributions due to strain and the electrostatic field, the formation energy cannot be extracted as a straightforward difference between total energies and chemical potentials. In addition (c) the origin of the interface charge asymmetry must be identified; we will show that an interface charge accumulation takes place because of the discontinuity of the macroscopic (spontaneous and piezoelectric) polarization across the interface.

We now show that the determination of the potential lineup [point (a)] and the identification of the sources of the uniform fields [i.e., charge asymmetry, point (c)] can be obtained via a *multipole decomposition* of the macroscopically averaged interface charge density. The latter contains multipoles of all order, which in one-dimensional space are its moments. We are interested in the constant potential drop across the interface: this is uniquely determined by the interface *dipole*.¹⁶ We are also interested in understanding the ∇ -shaped superlattice potential: these are, of course, generated by the interface *monopole*.¹⁷ All higher multipoles do not generate any potential jumps or uniform fields, but only minor potential bumps at the interface, symmetric and anti-symmetric for even and odd multipoles, respectively. Therefore, in practice, to extract the effects of monopoles and dipoles, we simply need to decompose the total macroscopically averaged charge density \bar{n} into two components comprising, respectively, all its even and odd multipoles.

For the sake of clarity, we name the odd and even components, respectively, the dipole density \bar{n}_{dip} , and the monopole density \bar{n}_{mono} . This is admissible since these densities produce all the effects of dipolar and monopolar charges relevant to our problem, plus other minor effects related to higher multipoles (irrelevant for our purposes).

Unfortunately, such a decomposition can be done in an infinite number of ways. Our procedure to obtain \bar{n}_{mono} is to fold the density with respect to a mirror plane placed at a point z_0 roughly halfway between two adjacent interfaces, and then perform an antisymmetric combination of the two charge distributions thus superimposed, i.e.,

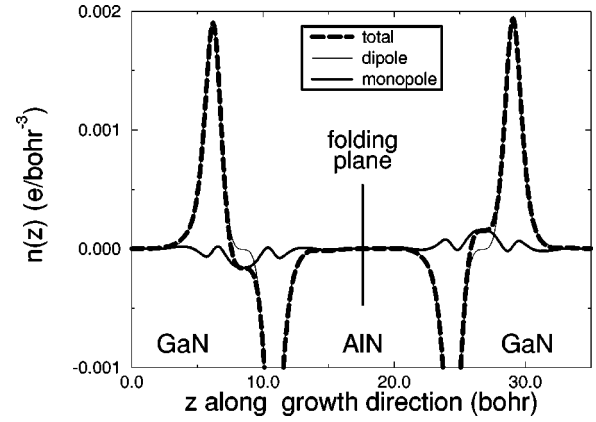


FIG. 2. Full density (dash-dotted), and monopole (solid) and dipole (dashed) components for the superlattice of Fig. 1.

$$\bar{n}_{\text{mono}}(z-z_0) = \frac{1}{2}[\bar{n}(z-z_0) - \bar{n}(z_0-z)], \quad (1)$$

where z_0 is the position of the folding plane. The dipole density \bar{n}_{dip} is defined as the difference between the full density and the monopole term, or (which amounts to the same) the symmetric combination of the two superimposed densities

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

The key point of this procedure is, of course, the choice of the position z_0 for the folding plane, which implicitly selects one specific realization of the decomposition. Our criterion for choosing z_0 is that the *norm* of the monopole component,

$$S(z_0) = \int |\bar{n}_{\text{mono}}(z-z_0)|^2 dz, \quad (3)$$

should be minimized. This choice produces (a) a dipole distribution that deviates *minimally* in a least-squares sense from the total density; (b) a \bar{n}_{mono} optimally localized at the interface; (c) a position for the folding plane that coincides with the intuitively appealing idea of midpoint between adjacent interfaces.

The monopole and dipole distributions obtained by the above decomposition are shown in Fig. 2 for a typical case. The dipole is related to a jump in potential across the interface, and it allows the direct determination of the lineup potential, and therefore of the band offset. In turn, the interface monopole can be further analyzed to ascertain its physical origin.

Let us first present the valence-band offset of the GaN/AlN (0001) interface. The offset is of type I. As reported in

TABLE I. Valence-band offset ΔE_v (eV) and monopole charge σ_{int} (C/m²) at AlN/GaN (0001) for different epitaxial matching conditions, and fully relaxed superlattices (in parentheses: unrelaxed case).

Substrate \rightarrow	GaN		AlN	
ΔE_v	0.20	(0.29)	0.85	(1.00)
$\sigma_{\text{int}}^{(\text{SL})}$	0.014	(0.029)	0.011	(0.022)
$\sigma_{\text{int}}^{(\Delta P)}$	0.014	(0.028)	0.011	(0.022)

Table I, we obtain $\Delta E_v = 0.20$ eV for AlN lattice matched to GaN, and $\Delta E_v = 0.85$ eV for GaN matched to AlN. We thus confirm the existence of a large forward-backward asymmetry (0.65 eV) of the offset. This asymmetry is strain-induced, and is due mostly to band-edge shifts in the bulk band structures (contributing 0.47 eV), with moderate contributions from the lineup term (0.18 eV). The large band offset asymmetry is thus mostly to be ascribed to the different nature of the valence-band edge in GaN and AlN. Indeed, 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 edges upward in GaN and downward in AlN. We note that our findings are semiquantitatively in agreement with those reported by Nardelli *et al.*⁵ for zinc-blende (001) interfaces, namely 0.44 eV for AlN on GaN, and 0.73 eV for GaN on AlN.

Let us now turn to the interface monopole. The dipole is understood to be¹⁸ a response to the electrostatic perturbation induced by interface formation (for the present system, in which this effect is adulterated by monopole contributions, our decomposition gives the best approximation to this response). On the other hand, the monopole may be expected to be the difference in macroscopic polarization between the constituents of the junction: indeed, according to Poisson's equation, a polarization discontinuity at the interface between two different media produces an interface charge accumulation. In particular, in a superlattice made of alternating layers of materials A and B of respective thicknesses l_A and l_B and dielectric constants ϵ_A and ϵ_B , the areal charge density at the interface is directly connected^{4,13,19} with the *transverse* bulk polarizations P_A^T and P_B^T of the interfaced materials by

$$\sigma_{\text{int}} = (P_A^T - P_B^T) / (l_A \epsilon_B + l_B \epsilon_A), \quad (4)$$

where we have assumed conventionally that P_B^T (P_A^T) is the transverse polarization on the right (left) side of the interface.²⁰ This relation allows an *independent prediction* of what the polarization-induced interface monopole should be, which can be compared with the minimal monopole *calculated for the actual interface*. Fortunately, the transverse polarization P^T of the nitrides can be computed accurately¹ by means of the geometric quantum phase approach¹² in an arbitrary strain state, for instance, for the epitaxially strained overlayer material. The dielectric constants (static or electronic) can also be evaluated independently using a recently developed technique.¹³

For the unrelaxed structure (clamped ions), the electronic dielectric constant should be used in Eq. (4), as appropriate to purely electronic screening. In the real system, however, the electric field induces a lattice distortion that extends over the whole slab, i.e., a long-wavelength optical phonon gets frozen-in: it is then appropriate to use in Eq. (4) the static dielectric constant as calculated in our previous work.¹³ In Table I we report the actual interface charge density $\sigma_{\text{int}}^{(\text{SL})}$ obtained via the multipole decomposition, and the value $\sigma_{\text{int}}^{(\Delta P)}$ obtained from Eq. (4), for both the ideal and the relaxed superlattice. The excellent agreement of the pairs of independently determined values confirms indeed the identification of the interface charge with a polarization charge.

TABLE II. Formation, electrostatic, and elastic energy for an AlN/GaN superlattice for different substrate choices (meV/cell or unit area).

Substrate ↓	E_f^{int}	η^{AlN}	η^{GaN}	ξ^{AlN}	ξ^{GaN}
GaN	3.9	5.6	9.7	179	
AlN	0.4	10.9	6.3		155

A final important issue is the evaluation of the interface formation energy. For the present system it is impossible to build a superlattice with equivalent interfaces, so that a total-energy calculation can only provide an average interface formation energy; this is hardly a severe problem, as the two interfaces are very similar.¹⁶ An additional problem is that the superlattice total energy contains elastic and electrostatic energy contributions due to, respectively, lattice mismatch and polarization fields. Clearly, these contributions are extensive, i.e., they depend on the overlayer thickness when referring formation energies to the unit area. In analogy to surface energies, we write the total energy per superlattice unit cell as

$$E_{\text{tot}}^{\text{SL}}(n^X) = 2E_f^{\text{int}} + \sum_X n^X (\mu^X + \xi^X + \eta^X) \quad (5)$$

where μ^X are the total bulk energies per Ga-N or Al-N pair (in the appropriately strained geometries), ξ^X are the elastic energies and η^X the electrostatic energies stored in the (possibly) strained bulks under the polarization field, and n^X is the number of atom pairs of type X (GaN or AlN).

In the present case of a strained low-symmetry system, an exact numerical equivalence of bulk and interface (in particular, between k -point meshes) cannot be achieved, and the use of μ , ξ , and η evaluated from separate bulk calculations might lead to inaccuracies. A solution to this issue, as in the case of surfaces,²¹ is to recognize that $E_{\text{tot}}^{\text{SL}}$ depends linearly on n^X , so that E_f^{int} can be extracted as the intercept of the linear E_{tot} vs n_X relation, i.e., from a series of total-energy calculations for superlattices of different lengths (whereby equivalent k -point sets are easily obtained).

In Table II we list the formation energies for the ideal and relaxed interfaces obtained by linear extrapolation. The same table reports bulk values of the elastic and electrostatic energy, the former obtained as total energy difference with the unstrained lattice, and the latter as

$$\eta^X = \frac{1}{2} \epsilon_X \Omega^X E^2 \quad (6)$$

with Ω^X is the bulk cell volume, E the modulus of the electrostatic field, and ϵ_X the static dielectric constant of material X (the static dielectric constant implicitly accounts for the field-lattice coupling¹³). The strain energy is much larger than the interface energy and the electrostatic energy, even for modest thicknesses. Assuming an order of magnitude for the dislocation core formation energy of ~ 0.5 eV,²² we see that the formation of such strain-related defects should start at typical thicknesses of ~ 20 Å. A comparable electrostatic energy would be stored in (perfect) layers of thickness in the order of 500 Å, and is therefore irrelevant to the layer's stability, since metallization or screening effects set in at much smaller thicknesses.³ Thus, it can be safely stated that

(0001) nitride interfaces are abrupt, and that the electrostatic energy should not prevent their stability, as it may in heterovalent systems such as ZnSe/GaAs.

In summary, our study of AlN/GaN(0001) interfaces has revealed the presence of large uniform electrostatic fields which we demonstrated to originate from the macroscopic polarization of the junction constituents. We have also indicated ways of extracting band offsets and formation energies,

for which conventional definitions are useless in the present situation. We found a sizable forward-backward band offset asymmetry, tiny interface formation energies, and large epitaxial strain energies.

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- ¹⁵The internal fields will, of course, affect in the very same way the position of core levels, which are generally used as reference levels in all-electron calculations (see, e.g., Ref. 9).
- ¹⁶Different dipoles at inequivalent interfaces in the same simulation cell (as in the present case) may generate an asymmetric-sawtooth-shaped potential. This appears not to be present in Fig. 1, and we explicitly tested [using a procedure to be discussed elsewhere (Ref. 3)] that the fields due to interface asymmetry are zero to numerical accuracy. This implies a negligible difference between dipoles at inequivalent interfaces and therefore essentially identical offsets.
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