# Structural and electronic properties of ideal nitride/Al interfaces

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The structural and electronic properties of the relaxed GaN/Al interface are determined from first-principles local-density full-potential linearized augmented plane-wave calculations. The atomic-site projected electronic density of states and the charge density, calculated as a function of the distance from the interface, show that the gap states induced into the semiconductor by the presence of Al are strongly localized in the interface region with a decay length $\lambda \sim 3.5$ a.u. We also study two related systems, the Al/AlN and GaN/AlN interfaces, both grown on a GaN substrate. Our results indicate that Al does not provide good Ohmic contacts on the *atomically defect-free* nitrides considered, in contrast with experimental results on chemically treated GaN but in agreement with recent measurements on the *clean* surface. By comparing the three interfaces studied, we also find that the transitivity rule is approximately satisfied and that small deviations must be attributed to differences in the interface morphology. [S0163-1829(98)05008-5]

## I. INTRODUCTION

The great importance of gallium nitride in potential technological applications has stimulated strong interest in this material.[1,2] Since performances of all technological devices are strongly dependent on the realization of good Ohmic contacts,[3,4] many experimental works focus on the deposition of metals [e.g., $M$ = Au,[5,6] Pt,[7,8] Pd,[7,8] and Ti (Refs. 9, 3, and 10)] on GaN and on the study of the electronic properties of the GaN/metal interface. In particular, the deposition of Al films on a (0001) $1\times1$ GaN substrate was recently[11,12] characterized using Auger, electron-energy-loss, and photoelectron spectroscopies. From the theoretical side, while several calculations have been performed on the GaAs/metal interface,[13–17] to our knowledge the GaN/metal interface has not yet been explored theoretically.

In this work, we present results obtained from *ab initio* all-electron full-potential linearized augmented plane-wave (FLAPW) (Ref. 18) calculations for the (001)-ordered $N$-terminated GaN/Al junction. We show that the states induced in the GaN band gap by the presence of Al are highly localized in the interface region; moreover, the contact between GaN and Al was found to be strongly rectifying, in good agreement with experimental findings for Al films deposited on a *clean* GaN surface. In order to investigate the structural and electronic properties of the interface, we also considered two auxiliary systems: a semiconductor/metal AlN/Al interface and a semiconductor/semiconductor GaN/AlN heterojunction, both grown on a GaN substrate.[19] In Sec. II, we report some technicalities regarding the structures considered and the calculations performed; the results regarding the structural and electronic properties are shown in Sec. III. Finally, Sec. IV summarizes our main results and draws some conclusions.

## II. STRUCTURAL AND TECHNICAL DETAILS

It is well known[20] that nitrides (such as AlN, GaN, etc.) show an interesting polytypism, so that their crystallographic structure can be either zinc blende (cubic) or wurtzite (hexagonal). Since the total energies of the two phases differ only by as much as 9.88 meV/atom,[20] it is possible to stabilize either the cubic or the hexagonal GaN structure exerimentally if the growth conditions are properly changed. In our calculations we considered gallium nitride to be grown epitaxially in its zinc-blende crystallographic structure, since it best matches the Al fcc lattice. The substrate lattice constant was set equal to our calculated GaN bulk lattice parameter ($a_{\rm subs}=a_{\rm GaN}=8.47$ a.u.), which agrees perfectly with the available experimental data.[21]

All the interfaces considered were simulated using the conventional supercell approach. In order to check the convergence as a function of the GaN and Al thicknesses, we considered different cell dimensions, and found that bulk conditions in the semiconductor and metal regions were well recovered using a unit cell with 19 GaN layers (i.e., ten layers of N and nine layers of Ga) and nine layers of Al; the Schottky barrier height (SBH) changed less than 0.02 eV in going from the 15+7 to the larger 19+9 cell.

We started our calculations from the ''ideal'' GaN/Al interface, obtained assuming that the Al atoms occupy the Ga sites of the ideal GaN zinc-blende lattice. This structure is not expected to reproduce the real situation, since the lattice mismatch between bulk GaN ($a_{\rm GaN}^{\rm bulk}=8.47$ a.u.) and bulk fcc

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TABLE I. LDA calculated structural parameters for the systems examined (all values are in atomic units). Note that the calculated bulk bond lengths of AlN and Al are $d^{\rm bulk}_{\rm Al\text{-}N}$=3.56 a.u. and $d^{\rm bulk}_{\rm Al\text{-}Al}$=5.41 a.u., respectively.

| | $d^{\rm bulk}_{\rm Ga\text{-}N}$ | $d^{\rm interf}_{\rm Ga\text{-}N}$ | $d^{\rm interf}_{\rm Al\text{-}N}$ | $d^{\rm tetrag}_{\rm Al\text{-}N}$ | $d^{\rm tetrag}_{\rm Al\text{-}Al}$ |
|---|---|---|---|---|---|
| GaN/Al | 3.67 | 3.67 | 3.70 | | 5.60 |
| AlN/Al | | | 3.72 | 3.60 | 5.60 |
| GaN/AlN | 3.67 | 3.67 | 3.60 | 3.60 | |

Al [$a^{\rm bulk}_{\rm Al}$=7.65 a.u. (Ref. 22)] is as high as 9.6%; the Al atoms are therefore expected to move in order to compensate for the epitaxial strain. The relaxed geometry was determined using the calculated *ab initio* atomic forces (see Ref. 23 for details), letting the atoms move only along the ordering [001] direction.

We also examined two related [001]-ordered systems: a metal/semiconductor interface (i.e., Al/AlN) and a semiconductor heterojunction (i.e., GaN/AlN), both grown on a GaN substrate. In the first case, we use a supercell as large as the one used for the GaN/Al case (i.e., 19 layers of GaN and nine layers of Al), whereas in the second case, we simulated the GaN/AlN interface using a $({\rm GaN})_n/({\rm AlN})_n$ ($n$=3) superlattice. Previous calculations[24,25] showed that bulk conditions in semiconductor heterojunctions are already well recovered within one semiconductor layer away from the interface, so that the 3×3 supercell is expected to provide reliable results. On the other hand, much larger supercells are generally needed in the metal/semiconductor case, due to the presence of the metal induced gap states (MIGS's) (Refs. 26–28) whose charge tails into the semiconductor side.

Our *ab initio* calculations were performed within density-functional theory in the local-density approximation (LDA).[29] In the FLAPW self-consistent cycles, we used angular momenta up to $l_{\rm max}$=8 in the muffin-tin spheres ($R_{\rm Ga}$=$R_{\rm Al}$=2.1 a.u. and $R_{\rm N}$=1.4 a.u.) for both wave functions and charge-density and plane waves with wave vector up to $K_{\rm max}$=4.6 a.u., leading to about 5000 basis functions. The sampling of the tetragonal Brillouin zone was performed using three special $k$-points within the Monkhorst-Pack scheme.[30] As discussed in Ref. 31, the structural and electronic properties are crucially dependent on the treatment of the Ga 3$d$ states; therefore, all the calculations were performed considering these semicore electrons as part of the valence band.

## III. RESULTS AND DISCUSSION

### A. Structural properties

The LDA calculated structural parameters for the different relaxed systems are reported in Table I. Let us first discuss how AlN and Al relax in order to match the GaN substrate. In the case of the two nitrides, the mismatch between our LDA calculated bulk lattice parameters $a^{\rm bulk}_{\rm GaN}$=8.47 a.u. and $a^{\rm bulk}_{\rm AlN}$=8.23 a.u. (or, equivalently, between the bulk bond lengths $d^{\rm bulk}_{\rm Ga\text{-}N}$=3.67 a.u. and $d^{\rm bulk}_{\rm Al\text{-}N}$=3.56 a.u.) is ~ 3 %. The magnitude of the strains involved in this case is such that the macroscopic theory of elasticity (MTE) (Ref. 32) is expected to be valid; in fact, total-energy minimization for tetragonal AlN (i.e., strained to match the GaN substrate), gives $d^{\rm tetrag}_{\rm Al\text{-}N}$ (LDA)=3.60 a.u., in perfect agreement with the MTE (Ref. 32) predictions $d^{\rm tetrag}_{\rm Al\text{-}N}$ (MTE)=3.60 a.u.[33] (see the second and third rows of Table I). On the other hand, total-energy minimization of Al strained to GaN gives $d^{\rm tetrag}_{\rm Al\text{-}Al}$ (LDA)=5.60 a.u.; this result is at variance (by about ~ 10 %) with the MTE (Ref. 32) value $d^{\rm tetrag}_{\rm Al\text{-}Al}$ (MTE)=5.09 a.u. This is quite surprising, since MTE is known to predict the equilibrium distances correctly in the case of slightly strained semiconductor interfaces[13,34] (as shown above in the case of AlN strained on GaN). In this case, however, we are dealing with quite large mismatches (up to 9.6 % between $a^{\rm bulk}_{\rm GaN}$ and $a^{\rm bulk}_{\rm Al}$), which is probably too large for MTE to be still valid. In the following, we will refer to the calculated tetragonal bond lengths to those obtained from LDA total-energy minimization.

Let us now consider the interfacial bond lengths at the GaN/Al junction. Note that, within our numerical accuracy, the Al deposition is not seen to affect the atomic distance between the Ga and N atoms near the interface, with respect to the bulk distance (i.e., $d^{\rm interf}_{\rm Ga\text{-}N}$=$d^{\rm bulk}_{\rm Ga\text{-}N}$). However, we find the Al-N interfacial distance, $d^{\rm interf}_{\rm Al\text{-}N}$=3.70 a.u. to be considerably larger than the bond length in tetragonal AlN, $d^{\rm tetrag}_{\rm Al\text{-}N}$=3.60 a.u. It should be noted that this situation is similar to the results obtained by Dandrea and Duke[15] for the GaAs/Al interface: the interface Al-As bond length was found to be 10% larger than that of zinc-blende AlAs. Our results can be explained[15] by considering that the metallic bond between the interface Al atom and its bulk Al neighbors reduces the degree of $sp^3$ hybridization, therefore weakening the interface Al-N bond strength compared to the pure covalently bonded tetragonal AlN. A similar behavior is observed for the AlN/Al junction: the Al overlayer does not alter the distance between the two semiconductor atoms closer to the interface. On the other hand, the bond length ($d^{\rm interf}_{\rm Al\text{-}N}$) between the interfacial N atom and the Al metallic atom closer to the junction is longer (by as much as 3%) than $d^{\rm tetrag}_{\rm Al\text{-}N}$.

### B. Gap states

In Fig. 1, we report the partial density of states (PDOS) for the 19+9 GaN/Al relaxed structure projected for each Ga, N, and Al atomic site as a function of the distance from the interface; in particular, panel (i) shows the ''inner'' atom in the bulk regions, whereas panel (v) shows the atomic sites closest to the interface. The dashed lines in panels (i) and (v) show the PDOS in the bulk binary constituents GaN and Al (with Al strained as in the superlattice). Let us examine the energy-gap interval, which is the energy region of major interest (note that the experimental value for the bulk GaN band gap is $E^{\rm expt}_{\rm gap}$=3.39 eV,[5,11] whereas, due to well-known failures of the LDA, our calculated band gap is $E^{\rm th}_{\rm gap}$=1.80 eV). From Figs. 1(a) and 1(b), we observe that the atoms near the interface [see, for example panel ($v$) of Fig. 1(b)] show a relevant density of gap states. As expected, a detailed analysis of these states reveals that they originate mainly from Al $s$ and $p$ states hybridized with the $p$ states of the atoms closer to the interface (i.e., $N$ 8 and 10 [Fig. 1(b), panels (iv) and (v)] and Ga 9 [Fig. 1(a), panel (v)]). On the

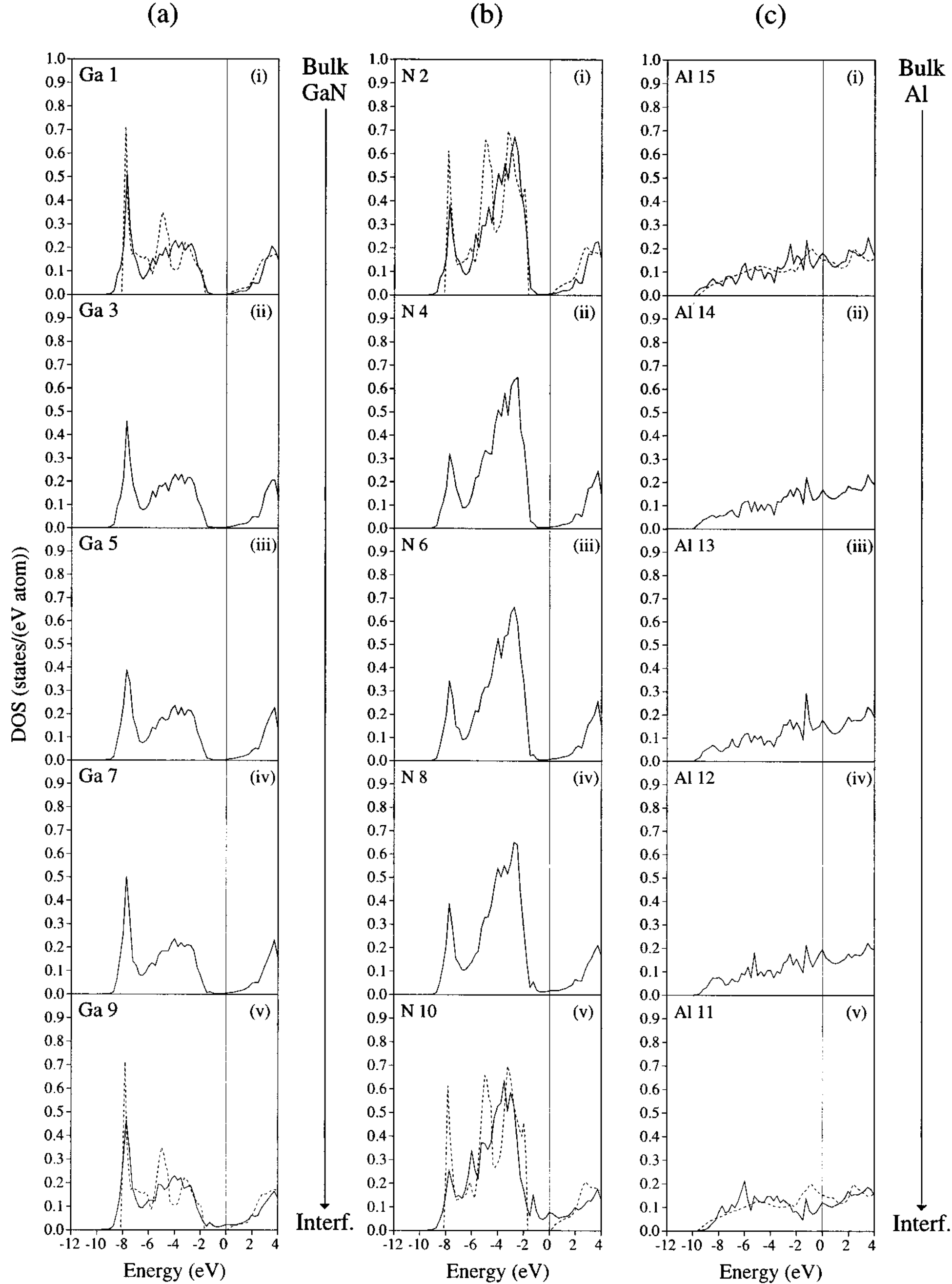


FIG. 1. Partial density of states (PDOS) of (a) the Ga atoms in the 19 + 9 GaN/Al supercell (solid line) compared to the PDOS of pure GaN (dashed line). [Panel (i) shows the ''inner'' Ga atom reproducing Ga in bulk GaN, whereas panel (v) shows the Ga atom near the interface.] (b) PDOS for the N atoms [with labels as in (a)] and (c) PDOS for the Al atoms [with labels as in (a)].

other hand, very few gap states are present in the Ga and N atoms far from the interface [see panel (i) of Figs. 1(a) and 2 (b)], indicating that GaN bulk conditions are almost perfectly recovered. This is also shown by the similarity between the bulk GaN DOS (dashed line) and the superlattice DOS (solid line).

In order to gain better insights, we constructed the charge density for the gap states (GS's);

$$\rho_{\mathrm{GS}}(\mathbf{r})=\sum_{i=1}^{n_{\mathrm{GS}}}\int_{\mathrm{BZ}}d\mathbf{k}|\Psi_i^{GS}(\mathbf{k},\mathbf{r})|^2 \qquad (1)$$

where $\Psi_i^{\mathrm{GS}}(\mathbf{k},\mathbf{r})$ are those solutions of the Kohn-Sham equations whose eigenvalues $\varepsilon_i$ are within the GaN energy gap and the integral is performed over the Brillouin zone (BZ). The gap state charge density $\rho_{\mathrm{GS}}$ is plotted in Figs. 2(b) and 2(c) in two planes [parallel to the (110) plane] containing all the atomic species in the cell. Following Ref. 35, we also performed the macroscopic average of this charge density, shown in Fig. 2(a). We first point out that the MIGS's in the semiconductor side of the junction are strongly localized in the interface region, as also indicated by the projected DOS plots. In particular, Fig. 2(a) shows that the charge density $\rho_{\mathrm{GS}}$ piles up on the atoms near the interface and rapidly vanishes from the interface. The charge density $\rho_{\mathrm{GS}}$ is ex-

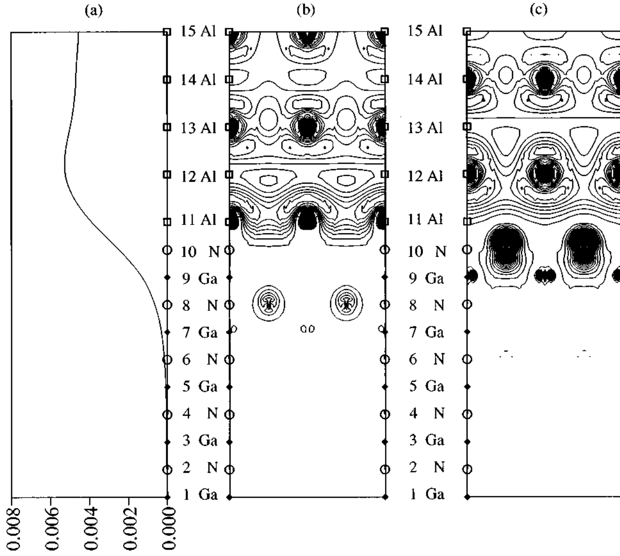


FIG. 2. Charge density of the gap states in the GaN/Al interface: (a) macroscopic average; (b) and (c) contour plots in the (110) plane through the center of the cell and a parallel plane displaced by $(\frac{1}{4},\frac{1}{4},0)$. Levels in units of 0.002 electrons/unit cell.

pected to decay exponentially in the semiconductor region as a function of the distance from the interface [i.e., $\rho_{\mathrm{GS}}(z) \propto e^{-|z-z_{\mathrm{interf}}|/\lambda}$, where $\lambda$ is the decay length and $z_{\mathrm{interf}}$ is the interface plane, defined for convenience as midway between the interface metal and semiconductor layers]. We may therefore estimate the extension of the gap states from Fig. 2(a), as the coordinate $\bar{z}$ at which $\rho_{\mathrm{GS}}(\bar{z}) = (1/e)\rho_{\mathrm{GS}}(z_{\mathrm{interf}})$. In this way, the MIGS decay length can be estimated to be $\lambda = z_{\mathrm{interf}} - \bar{z} \sim 3.5$ a.u. Therefore, the penetration depth $\lambda$ is so short that the MIGS's extend appreciably only up to the GaN layer (i.e., atoms 9 and 10) closer to the interface; their charge density is already highly reduced in the second GaN layer and completely disappears in the third GaN layer [see Figs. 2(b) and 2(c)]. We note that the calculated $\lambda$ value is smaller than the penetration depth for GaAs [$\lambda \sim$ 5.7 a.u., (Refs. 13 and 36)] in agreement with the qualitative idea[36] that $\lambda$ is smaller in materials with larger $E_{\mathrm{gap}}$ and smaller $\epsilon$ such as GaN and ZnSe [$\lambda \sim 3.5$ a.u. (Ref. 36)] than in more covalent semiconductors [i.e., GaAs, Si, with $\lambda \sim$ 5.7 a.u. (Ref. 36)].

### C. Band alignment: Schottky barrier heights and valence-band offset

We now discuss how the bands line up at the interface. The Schottky barrier height $\Phi_B$ is defined as the energy difference between the Fermi level of the metal ($E_F^{\mathrm{Al}}$) and the respective majority-carrier band edge of the semiconductor at the interface (i.e., the valence band maximum (VBM) $E_{\mathrm{VBM}}^{XN}$ ($X$=Ga, Al) and the conduction band minimum (CBM) $E_{\mathrm{CBM}}^{XN}$ ($X$=Ga, Al) for a $p$-doped and an $n$-doped semiconductor, respectively):

$$\Phi_{B_p} = E_F^{\mathrm{Al}} - E_{\mathrm{VBM}}^{XN},$$

$$\Phi_{B_n} = E_{\mathrm{CBM}}^{XN} - E_F^{\mathrm{Al}}.$$

TABLE II. $p$-type Schottky barrier heights ($\Phi_{B_p} = E_F^{\mathrm{Al}} - E_{\mathrm{VBM}}^{XN}$, $X$=Ga, Al) and VBO for the GaN/Al, AlN/Al, and GaN/AlN interfaces (values in eV), not including the quasiparticle correction. See text for details on the sign of the values.

| | GaN/Al | Al/AlN | GaN/AlN |
|---|---|---|---|
| $\Phi_{B_p}$ | 1.12 | 1.80 | |
| $\Delta E_v$ | | | 0.76 |

In analogy with the case of semiconductor heterojunctions, we can express the band discontinuity at the interface as the sum of two terms: $\Phi_{B_p} = \Delta b + \Delta E_b$, where $\Delta b$ and $\Delta E_b$ denote an ''interface'' and ''bulk'' contribution to the SBH, respectively. The two separate contributions can be evaluated using the core level binding energies as reference levels (see Ref. 37), following the procedure commonly used in both x-ray photoelectron spectroscopy (XPS) experiments and all-electron calculations.[24,25,37] In order to evaluate the interface contribution, we chose the ''bulk'' Ga 1$s$ and Al 1$s$ core levels as reference energies, and have calculated the difference of these two energy levels in the superlattice $\Delta b = E_{1s}^{\mathrm{Ga}} - E_{1s}^{\mathrm{Al}}$. The ''bulk'' contribution, on the other hand, was evaluated from separate calculations for bulk GaN and Al, measuring the difference between the binding energies of the same levels: $\Delta E_b = (E_{VBM}^{\mathrm{GaN}} - E_{1s}^{\mathrm{Ga}}) - (E_F^{\mathrm{Al}} - E_{1s}^{\mathrm{Al}})$. A similar procedure was used in the AlN/Al (GaN/AlN) case, for which we used the Al 1$s$ (N 1$s$) core levels on both sides of the junction and the semiconductor VBM.

In Table II we report the calculated $p$-type SBH and valence band offset (VBO) for the structures considered. The sign of the different band line-ups at the metal/semiconductor interface was considered to be positive if the Al Fermi energy was higher in energy than the semiconductor VBM; in the semiconductor/semiconductor case, the sign was considered to be positive if the GaN VBM was higher in energy than the AlN VBM. Due to the well-known failure of the LDA in describing properly the excitation energies in semiconductors, we cannot evaluate the $n$-type SBH $\Phi_{B_n}$ directly from our calculations. However, $\Phi_{B_n}$ can be approximately estimated from the data in Table II by considering the GaN experimental gap[5,11] ($E_{\mathrm{gap}}^{\mathrm{expt}}$=3.39 eV). For example, for the GaN/Al structure, we obtain $\Phi_{B_n} = E_{\mathrm{gap}}^{\mathrm{expt}} - \Phi_{B_p}$=2.27 eV. In this respect, we also note that our calculations do not include quasiparticle effects, which may be important due to differences in screening in the metal and in the semiconductor. On the basis of previous calculations within the GW approximation[38,39] for the quasiparticle correction in Al (Ref. 40) and GaN,[41,42] we find that we should add to our $\Phi_{B_p}$ values shown in Table II a quasiparticle correction of $\sim$ 0.1 eV.

After inclusion of quasiparticle (QP) effects, for the relaxed GaN/Al interface we obtain $\Phi_{B_p}^{\mathrm{QP}}$=1.22 eV (or $\Phi_{B_n}^{\mathrm{QP}}$=2.17 eV). This result is in sharp contrast with the original Schottky-Mott rule,[43,44] which gives $\Phi_{B_n}$ as the difference of the metal work function and the semiconductor electron affinity, and predicts[45,46] $\Phi_{B_n} = -0.02$ eV for GaN/Al. A more recent model, the MIGS-and-electronegativity

model,[47] which focuses on the electronegativity of the metal, predicts that all the ideal (i.e., abrupt, defect free, and laterally homogeneous) metal/$n$-doped GaN contacts should be rectifying.[48] In particular, according to this model[47] and using empirical tight binding calculations,[49] we should have a potential barrier $\Phi_{B_n} \sim 0.8$ eV (or equivalently $\Phi_{B_p} \sim 2.6$ eV) in the GaN/Al case. The predictions of the latter model[47,48] are in better qualitative agreement with our findings than the Schottky-Mott rule, but there still is an appreciable discrepancy with our *ab initio* calculated value ($\Phi_{B_p}^{\rm LDA}=1.22$ eV).

Let us now compare our results with the available experimental data. According to previous experimental results,[5] Al was supposed to give rise to good Ohmic contacts on GaN, in contrast with our findings. A more recent experiment,[6] however, shows that the $I$-$V$ characteristic for the GaN/Al junction (for clean GaN) deviates appreciably from linear behavior. Furthermore, in a very recent and detailed experimental study of the Al/GaN interface, Bermudez reported a measurement of the SBH (Ref. 12) for the unannealed (0001) 1×1 GaN/Al interface ($\Phi_{B_n}=1.4$ eV or equivalently $\Phi_{B_p} = E_{\rm gap}-\Phi_{B_n}=2.0$ eV). This experimental value corrects a result previously reported by the same authors[11] ($\Phi_{B_n}=1.9$ eV), taking into account a different extrapolation of the VBM position from XPS spectra. We might therefore say that our *ab initio* value and the experimental result are in qualitative agreement. In comparing our theoretical results [obtained for (001)-ordered zinc-blende GaN/Al] with available experimental values [obtained for (0001)-ordered wurtzite–GaN/Al (Refs. 11 and 12)]. we should also take into account that, even in the absence of strain, wurtzite GaN shows a spontaneous polarization[50] (on the other hand, due to symmetry properties, this effect vanishes in the zinc-blende structure), so that the final $p$-type SBH values may be affected by the ordering direction and polarization charges. The study of the possible dependence of the SBH on polarization effects is, in fact, a very interesting topic, but is beyond the aim of the present work. Further calculations are presently in progress, in order to also address this question.

A comparison with the more thoroughly studied Al/GaAs system might be natural at this point. In this regard we should recall that recent measurements[51] on Al/GaAs (001) as a function of pressure and composition (i.e., for various values of $x$ in the Al/Al$_x$Ga$_{1-x}$As system) agree with the predictions of *ab initio* calculations for ideal interfaces,[13] without invoking the presence of deep-level point defects.[52] We therefore infer that our predictions should also agree with experiments performed for the same interface orientation since the formation of point defects is quite unlikely for GaN (which is more stable than GaAs) so that the barrier height is expected to be mainly determined by *ideal* interface properties such as metal-induced states, which are naturally included in our calculations.

The existence of very different experimental findings deserves a more detailed discussion. It has been recently shown[12] that there is a substantial difference between the so-called *practical* surface and the *atomically clean* surface, as far as the conduction properties are concerned. In fact, while Al contacts on the chemically treated GaN surface lead to perfect Ohmic behavior, the deposition of Al on the clean

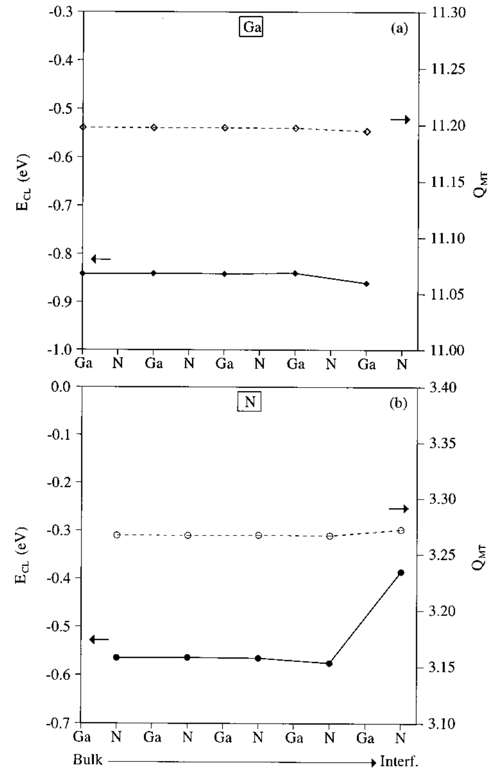


FIG. 3. 1$s$ core-level binding energies (filled symbols) and total muffin-tin charges (empty symbols) for (a) Ga and (b) N atoms, as a function of the distance from the interface.

surface results in quite a high SBH. In addition, it has been shown[11] that the major contribution to the SBH comes from the band bending on the bare surface (~0.9 eV) which is modified by the growth of the Al layers by ~0.5 eV. These observations can be explained in terms of surface states that in the clean surface case are able to pin the Fermi level. Following Bermudez *et al.*,[11,12] as the interface forms (before annealing), $E_F$ remains pinned, and in the absence of relevant charge transfer across the interface, there is only a small effect of Al on the SBH (see Fig. 11 of Ref. 12). Note that the situation is quite different in the case of Ni,[12] where the band bending is seen to be more sensibly modified by the metal coverage.

This picture can be analyzed on the basis of the results of our calculations. The band bending of the clean surface originates from Fermi-level pinning by surface states, and its position near the majority band edge well inside the bulk. This bending acts on a distance scale of many hundreds of angstroms and, of course, is not accessible to our calculations which focus on distances of a few monolayers from the interface. A further effect is related to the charge rearrangement that might be caused by the presence of the interface states. The characteristic length of such effects is of the order of the MIGS decay length, and therefore can be revealed in our calculations. In Fig. 3, we show the core-level binding energies and the total muffin-tin charge for Ga [panel (a)] and N [panel (b)] atoms, as a function of the distance from the interface. It is clear that the binding energies and the charge in the muffin-tin spheres are very flat and stable just after the interface N atom, which shares bonds with both Ga and Al. These results unambiguously show the absence of an

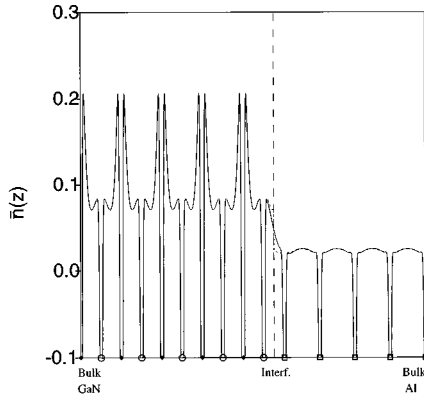


FIG. 4. Planar average of the charge density of the GaN/Al superlattice (solid line) and of bulk GaN and Al, in the respective regions (short dashed line). The two lines can hardly be distinguished (see the discussion in the text). By convention, the interface plane is placed halfway in the N-Al bond, i.e., in between atoms 10 and 11 of Fig. 2.

important bending in the effective potential.[53]

The most direct way of visualizing interface effects on the electron density is to compare the superlattice planar charge density and the planar charge densities of the two bulk materials, in their respective regions. This plot, shown in Fig. 4, has of course *no* physical meaning in terms of interface dipole, and no quantitative information can be obtained from it. Still, it contains a clear message: right away from the interface, already at the first atomic N and Al interface sites, the charge density resumes its bulk value. In fact, what we see in Fig. 4 is the fulfillment of the wave-function continuity requirement (of course, dependent on the particular metal and the interface orientation). The profile of core levels in Fig. 3 is perfectly consistent with Fig. 4. However, Fig. 4 may seem in contrast with Fig. 2(a), showing that MIGS's extend over a larger distance scale. As a matter of fact, according to Ref. 28, these results only imply that, away from the interface, the occupied gap states get most of their spectral weight from the semiconductor valence band. These observations might be consistent with a Fermi-level pinning in proximity of the charge neutrality level, as observed in the experiments.[11] However, at present, we do not have direct computational evidence to support this statement quantitatively.

Table II also reports the calculated SBH for the AlN/Al junction, and the valence-band offset at the GaN/AlN heterojunction, both grown on a GaN substrate. Unfortunately, at least to our knowledge, no experimental results are available for these systems. However, we can compare our calculated VBO ($\Delta E_v = 0.76$ eV) with other *ab initio* theoretical[54,55] results obtained for [001] ordered interfaces between zincblende GaN and AlN grown on an average substrate. In particular, Wei and Zunger[54] obtained $\Delta E_v = 0.84$ eV, whereas Albanesi, Lambrecht, and Segall[55] obtained $\Delta E_v = 0.85$ eV. Our value is expected to be perfectly consistent with these results. In fact, strain effects due to the 3% lattice mismatch between GaN and AlN, are expected to change the VBO by less than 0.2 eV.[55] Moreover (see, for example Refs. 25 and 56), it was shown that the VBO decreases as the substrate lattice constant is increased, since the *bulk* contribution (rather than the *interface* one) is strongly affected by strain conditions. Therefore, the GaN/AlN VBO value obtained[56,57] for the substrate with average lattice constant ($a_{\mathrm{subs}} = 8.35$ a.u.) is expected to decrease when the substrate lattice constant is increased up to the GaN value ($a_{\mathrm{subs}} = 8.47$ a.u.). This is in excellent agreement with the small difference [$\Delta(\Delta E_v) \sim 0.1$ eV] observed between the VBOs obtained in Refs. 54 and 55 and the present work.

We note that the transitivity rule[57] (whose validity is well established for [001] homopolar semiconductor heterojunctions[25,58] under the same strain conditions) also seems to be reasonably satisfied for this metal/semiconductor interface. In fact, as shown in Table II, the $p$-type SBH in the N-terminated GaN/Al and AlN/Al junctions are $\Phi_{B_p} = 1.12$ eV and 1.80 eV, respectively (neglecting quasiparticle corrections), so that application of the transitivity rule leads to $\Delta E_v^{\mathrm{trans}}(\mathrm{GaN/AlN})_{\mathrm{GaN\ subs.}} = 0.68$ eV (with the GaN VBM higher in energy than the AlN VBM), to be compared with our *ab initio* calculated result obtained for the VBO in the GaN/AlN interface, $\Delta E_v^{\mathrm{ab\ initio}}(\mathrm{GaN/AlN})_{\mathrm{GaN\ subs.}} = 0.76$ eV (see Table II).

In order to investigate the dependence of the transitivity rule upon the interface bond lengths, we performed FLAPW calculations for three additional N-terminated structures: (i) a GaN/Al interface in which $d^{\mathrm{bulk}}_{\mathrm{Ga\text{-}N}} = d^{\mathrm{int}}_{\mathrm{Ga\text{-}N}} = d^{\mathrm{int}}_{\mathrm{Al\text{-}N}} = 3.67$ a.u. and $d^{\mathrm{tetrag}}_{\mathrm{Al\text{-}Al}} = 5.60$ a.u.; (ii) an AlN/Al interface obtained from (i) by a complete Ga $\rightarrow$ Al substitution on the semiconductor side; and (iii) a GaN/AlN heterojunction, in which $d^{\mathrm{bulk}}_{\mathrm{Ga\text{-}N}} = d^{\mathrm{interf}}_{\mathrm{Ga\text{-}N}} = d^{\mathrm{interf}}_{\mathrm{AR\text{-}N}} = d^{\mathrm{tetrag}}_{\mathrm{AlN}} = 3.67$ a.u. Note that in all these additional structures, we did not consider any tetragonal or interfacial relaxation in order to simulate an hypothetically "lattice-matched" GaN/AlN/Al system. In this case, we found that the transitivity rule was completely fulfilled (within 0.02 eV). This is perfectly consistent with the results obtained for the lattice-matched GaAs/AlAs/Al case,[13] where the transitivity rule for the anion-terminated case was found to be satisfied within 0.03 eV. Therefore, the 0.08 eV discrepancy between our *ab initio* results for the relaxed structures [$\Delta E_v^{\mathrm{ab\ initio}}(\mathrm{GaN/AlN})_{\mathrm{GaN\ subs.}} = 0.76$ eV] and the value predicted by the transitivity rule [$\Delta E_v^{\mathrm{trans}}(\mathrm{GaN/AlN})_{\mathrm{GaN\ subs.}} = 0.68$ eV] must be ascribed to different atomic relaxations at the interfaces.

Finally, we would like to point out that the behavior of the SBH between Al and $X$N ($X$=Ga, Al) is similar to the results obtained in Ref. 13 for the SBH of Al and $X$As ($X$=Ga, Al). In particular, the $p$-type SBH was found[13] to increase by as much as 0.6 eV when going from GaAs to AlAs, in generally good agreement with experimental measurements.[59] In a similar way, as shown in Table II, our calculated $p$-type SBH increases by 0.68 eV in going from GaN to AlN.

## IV. CONCLUSIONS

We performed FLAPW calculations for the defect-free atomically abrupt relaxed GaN/Al junction. We discussed the electronic properties of the interface through the atomic site-projected DOS as a function of the distance from the

interface. We found that there are gap states (mainly arising from the metallic wave function tailing into the semiconductor energy gap) which are strongly localized at the interface; our estimated MIGS decay length ($\lambda \sim$ 3.59 a.u.) is significantly smaller than the values obtained[36] for Si and GaAs ($\lambda \sim$ 5.67 a.u.). This shows that the more covalent the bonding character of the material, the smaller the MIGS penetration depth. Our theoretical results have shown that Al does not provide good Ohmic contacts on clean GaN; in particular, we obtained a $p$-type SBH $\Phi_{B_p} \sim 1.2$ eV for the GaN/Al interface. This is in qualitative agreement with the experimental value $\Phi_{B_p} \sim 2$ eV,[11] obtained for Al films deposited on a (0001) $1\times1$ GaN substrate. For the Al/AlN interface, we showed that the contact is strongly rectifying with a calculated $p$-type barrier height $\Phi_{B_p} \sim 1.8$ eV. Finally, we found that the transitivity rule for the interfaces considered is satisfied within less than 0.1 eV.

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[1] B. Goss Levi Phys. Today **49** (4), 18 (1996).
[2] R. P. Vaudo *et al.*, J. Appl. Phys. **79**, 2779 (1996).
[3] J. D. Guo, C. I. Lin, M. S. Feng, F. M. Pan, G. C. Chi, and C. T. Lee, Appl. Phys. Lett. **68**, 235 (1996).
[4] Zhifang Fan *et al.*, Appl. Phys. Lett. **68**, 1672 (1996).
[5] J. S. Foresi and T. D. Moustakas, Appl. Phys. Lett. **62**, 2859 (1993).
[6] M. E. Lin, Z. Ma, F. Y. Huang, Z. F. Fan, L. H. Allen, and H. Morkoc, Appl. Phys. Lett. **64**, 1003 (1994).
[7] J. D. Guo, M. S. Feng, R. J. Guo, F. M. Pan, and C. Y. Chang, Appl. Phys. Lett. **67**, 2657 (1995).
[8] Lei Wang, M. I. Nathan, T-H. Lim, M. A. Khan, and Q. Chen, Appl. Phys. Lett. **68**, 1267 (1996).
[9] S. C. Binari, H. B. Dietrich, G. Kelner, L. B. Rowland, K. Doverspike, and D. K. Gaskill, Electron. Lett. **30**, 909 (1994).
[10] H. Cordes and Y. A. Chang, MRS Internet J. Nitride Semicond. Res. **2**, 2 (1997).
[11] V. M. Bermudez *et al.*, J. Appl. Phys. **79**, 110 (1996).
[12] V. M. Bermudez, J. Appl. Phys. **80**, 1190 (1996).
[13] J. Bardi, N. Binggeli, and A. Baldereschi, Phys. Rev. B **54**, 11102 (1996); C. Berthod, N. Binggeli and A. Baldereschi, Europhys. Lett. **36**, 67 (1996); C. Berthod, N. Binggeli, and A. Baldereschi, J. Vac. Sci. Technol. B **14**, 3000 (1996).
[14] A. Ruini, R. Resta, and S. Baroni, http://xxx.sissa.it/abs/cond-mat/9704157.
[15] R. G. Dandrea and C. B. Duke, J. Vac. Sci. Technol. A **11**, 848 (1993).
[16] M. V. Schilfgaarde and N. Newman, Phys. Rev. Lett. **65**, 2728 (1990).
[17] J. P. A. Charlesworth, R. W. Godby, and R. J. Needs, Phys. Rev. Lett. **70**, 1685 (1993).
[18] H. J. F. Jansen and A. J. Freeman, Phys. Rev. B **30**, 561 (1984); E. Wimmer, H. Krakauer, M. Weinert and A. J. Freeman, *ibid.* **24**, 864 (1981), and references therein.
[19] We refer to AlN as a semiconductor. Note, however, that AlN is often referred to as an insulator, due to its large indirect and direct energy gaps ($E_{gap}^{\Gamma\text{-}X}$=4.9 eV and $E_{gap}^{\Gamma\text{-}\Gamma}$=6.0 eV, respectively, as shown in Ref. 41).
[20] C. Y. Yeh, W. Lu, S. Froyen, and A. Zunger, Phys. Rev. B **46**, 10 086 (1992).
[21] *Semiconductors, Physics of Group IV Elements and III-V Compounds,* edited by K. H. Hellwege, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. a (Springer-Verlag, Berlin, 1982).
[22] N. W. Ashcroft and N. D. Mermin, in *Solid State Physics* (Saunders College, Philadelphia, 1976).
[23] A. Di Pomponio, A. Continenza, R. Podloucky, and J. Vackár, Phys. Rev. B **53**, 9505 (1996).
[24] A. Continenza, S. Massidda, and A. J. Freeman, Phys. Rev. B **42**, 3469 (1990).
[25] S. Picozzi, A. Continenza, and A. J. Freeman, Phys. Rev. B **53**, 10 852 (1996).
[26] V. Heine, Phys. Rev. **138**, A1689 (1965).
[27] C. Tejedor, F. Flores, and E. Louis, J. Phys. C **10**, 2163 (1977).
[28] J. Tersoff, Phys. Rev. Lett. **52**, 465 (1984).
[29] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1984); W. Kohn and L. J. Sham, *ibid.* **145**, 561 (1966).
[30] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[31] V. Fiorentini, M. Methfessel, and M. Scheffler, Phys. Rev. B **47**, 13 353 (1993).
[32] C. G. Van de Walle, Phys. Rev. B **39**, 1871 (1988).
[33] Note that, in order to predict the deformation of AlN on GaN according to MTE, we used the theoretical AlN elastic constants as given in K. Kim, W. R. Lambrecht, and B. Segall, Phys. Rev. B **53**, 16 310 (1996).
[34] S. Picozzi, A. Continenza, and A. J. Freeman, Phys. Rev. B **52**, 5247 (1995).
[35] A. Baldereschi, S. Baroni, and R. Resta, Phys. Rev. Lett. **61**, 734 (1988).
[36] S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B **15**, 2154 (1977).
[37] S. Massidda, B. I. Min, and A. J. Freeman, Phys. Rev. B **35**, 9871 (1987); S. H. Wei and A. Zunger, Phys. Rev. Lett. **59**, 144 (1987).
[38] L. Hedin, Phys. Rev. **139**, A796 (1965).
[39] R. W. Godby, M. Schluter and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986).
[40] R. J. Needs, J. P. A. Charlesworth, and R. W. Godby, Europhys. Lett. **25**, 31 (1994).
[41] A. Rubio, J. L. Corkill, M. L. Cohen, E. L. Shirley, and S. G. Louie, Phys. Rev. B **48**, 11 810 (1993).
[42] M. Palummo *et al.*, Europhys. Lett. **26**, 607 (1994).
[43] W. Schottky, Z. Phys. **41**, 570 (1940).
[44] N. F. Mott, Proc. Cambridge Philos. Soc. **34**, 568 (1938).

[45] K. W. Boer, *Survey of Semiconductor Physics* (Van Nostrand, New York, 1990).
[46] J. I. Pankove and H. E. Schade, Appl. Phys. Lett. **25**, 53 (1974).
[47] W. Mönch, Phys. Rev. Lett. **58**, 1260 (1987).
[48] T. U. Kampen and W. Mönch, MRS Internet J. Nitride Semicond. Res. **1**, 41 (1996).
[49] W. Mönch, J. Appl. Phys. **80**, 5076 (1996).
[50] F. Bernardini, V. Fiorentini and D. Vanderbilt, Phys. Rev. B **56**, R10 924 (1997).
[51] M. Cantile, L. Sorba, S. Yildirim, P. Faraci, G. Biasiol, and A. Franciosi, Appl. Phys. Lett. **64**, 988 (1994).
[52] M. Van Schilfgaarde, E. R. Weber, and N. Newman, Phys. Rev. Lett. **73**, 581 (1994); P. Phatak, N. Newman, P. Dreszer, and E. R. Weber, Phys. Rev. B **51**, 18 003 (1995).
[53] The concept of band bending assumes the definition of local band structure, which is impossible over a scale of a few angstroms.
[54] Su-Huai Wei and Alex Zunger, Appl. Phys. Lett. **69**, 2719 (1996).
[55] E. A. Albanesi, W. R. Lambrecht, and B. W. Segall, J. Vac. Sci. Technol. B **12**, 2470 (1994).
[56] N. Tit, M. Peressi, and S. Baroni, Phys. Rev. B **48**, 17 607 (1993).
[57] G. Margaritondo and P. Perfetti, in *Heterojunction Band Discontinuities*, edited by F. Capasso and G. Margaritondo (North-Holland, Amsterdam, 1987), p. 59.
[58] Y. Foulon and C. Priester, Phys. Rev. B **45**, 6259 (1992).
[59] M. Missous, W. S. Truscott, and K. E. Singer, J. Appl. Phys. **68**, 2239 (1990); P. Revva, J. M. Langer, M. Missous, and A. R. Peaker, *ibid.* **74**, 416 (1993).