Influence of the exchange reaction on the electronic structure of GaN/Al junctions

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Ab initio full-potential linearized augmented plane-wave (FLAPW) calculations have been used to study the influence of the interface morphology and, notably, of the exchange reaction on the electronic properties of Al/GaN (100) interfaces. Although the detailed mechanism is not understood, the exchange reaction has been purported to influence the Schottky barrier height (SBH) as a result of the formation of an interfacial $Ga_xAl_{1-x}N$ layer. In particular, the effects of interface structure (i.e., interfacial bond lengths, semiconductor surface polarity, and reacted intralayers) on the SBH at the Al/GaN (001) junction are specifically addressed. Thus, the electronic structure of the following atomic configurations have been investigated theoretically: (i) an abrupt, relaxed GaN/Al interface; (ii) an interface that has undergone one monolayer of exchange reaction; and interfaces with a monolayer-thick interlayer of (iii) AlN and (iv) $Ga_{0.5}Al_{0.5}N$. The exchange reaction is found to be exothermic with an enthalpy of 0.1 eV/atom. We find that the first few layers of semiconductor are metallic due to the tailing of metal-induced gap states; therefore, the presence of a monolayer-thick interfacial alloy layer does not result in an enhanced band gap near the interface. Intermixed interfaces are found to pin the interface Fermi level at a position not significantly different from that of an abrupt interface. Our calculations also show that the interface band lineup is not strongly dependent on the interface morphology changes studied. The *p* type SBH is reduced by less than 0.1 eV if the GaN surface is Ga terminated compared to the N terminated one. Moreover, we show that both an ultrathin $Ga_xAl_{1-x}N$ ($x=0$, 0.5) intralayer and a Ga↔Al atomic swap at the interface do not significantly affect the Schottky barrier height. [S0163-1829(98)07335-4]

I. INTRODUCTION

In the last few decades, a significant number of studies have investigated metal/semiconductor interfaces, due to the key role played by ohmic and Schottky contacts in technological III-V semiconductor devices. However, from both the experimental and the theoretical points of view, the fundamental mechanism involved in the Schottky barrier formation has not been fully elucidated.[1–4]

Al/III-V semiconductor junctions have been the most extensively studied interfaces to date. This has occurred due to both practical and fundamental reasons. Al contacts are inexpensive to manufacture and have stable electrical, chemical, and structural characteristics at moderate temperatures.[5] Al contacts also are of practical interest since they are commonly used in III-V commercial device technology, particularly as the gate of field effect devices.

In the field of *ab initio* computational physics, many works have addressed band alignment at semiconductor heterojunctions,[6] whereas few calculations have studied the barrier height of metal/semiconductor interfaces. Al has been used almost exclusively as the metal layer in theoretical investigations of metal/semiconductor contacts.[7–12] This arose because Al is found to be advantageous since it lacks *d* electrons, forms a free-electron metal, and lattice matches a number of III-V semiconductors. Recently, the GW method has been used to study the Al/GaAs interface.[12]

More recently, theoretical work on III-V interfaces demonstrated that the pressure-induced barrier height changes can be used to critically determine the nature of the states that pin metal/III-V interfaces.[13,14] Experimental measurements of the pressure-induced change in Al/GaAs and Al/AlGaAs barrier heights are consistent with defect-free interfaces,[13,15] validating Al/III-V interfaces as a model system. In contrast, Au, a metal that reacts with GaAs to release near-interfacial As at GaAs interfaces, exhibits pressure-induced barrier height changes consistent with an interface decorated with a deep-level point-defect, such as the As antisite (As_{Ga}).[15] Because GaN solid is significantly more stable than GaAs, the Fermi-level pinning position of Al/GaN interfaces would also be expected to be determined by the properties of interfaces without deep-level defects.

In the study reported here, we start an investigation of an important aspect of Schottky barriers that only recently has begun to be explored using modern electronic structure calculations: the role that interface chemical exchange plays in the electrical and electronic properties of interfaces. Al/GaN interfaces were used in this study due to the well-known chemistry and atomic structure of the interface. GaN,[16] GaAs,[17] and InP,[18] among others, are found to exhibit an exchange reaction in which Al replaces the Group III element at the surface. The extent of the reaction is found to be of the order of a monolayer for unannealed contacts and increases at elevated annealing temperatures.[19] Changes in the electrical properties, as reported in a large number of III-V studies, have attributed the increase in the barrier for *n*-type semiconductors to the increased band gap.[20] However, a more recent study on both *n*-type and *p*-type contacts indicates that the observed behavior can be attributed to a shift in interfacial Fermi-level pinning position, rather than due to the formation of an increase in interfacial band gap.[21] A strong fundamental understanding of the influence of the chemical reaction on the interface electronic structure has not yet been established.

Density functional calculations are able to quantitatively address many of the questions including the energetics of the exchange reaction, the nature and extent of the metal-induced gap states (MIGS) and the role of the larger band gap AlGaN interface layer on the interface electronic structure. In a previous work,[22] we performed *ab initio* calculations to determine the electronic properties of the [001] ordered atomically abrupt N-terminated XN/Al (X=Ga,Al) interface, focusing mainly on the Schottky barrier height and the resulting interface states. In the work reported here, the structural and electronic properties of several Al/GaN interface configurations are investigated. In particular, the effects of interface structure (i.e., interfacial bond lengths, semiconductor surface polarity, and reacted intralayers) on the Schottky barrier height (SBH) at the Al/GaN (001) junction are specifically addressed. It should be noted that some experimental results[16] are available for the (0001) wurtzite GaN/Al interface and that some caution has to be taken in comparing our results with the experiments, since the polarization effects and the different coordinations of the surface bonds may both play a role in determining the structural and electronic properties.

Starting from the atomically abrupt N-terminated GaN/Al junction (in the following denoted as the *A* structure), we consider four other different interface morphologies: (i) the ideal, abrupt, relaxed Ga-terminated GaN/Al interface (*B*); (ii) the configuration with an AlN intralayer (*C*); (iii) the configuration in which an Al atom has undergone an exchange reaction with a surface Ga atom (*D*), and finally (iv) the configuration with a $Ga_{0.5}Al_{0.5}N$ alloy layer at the interface (*E*). Our calculations show that the interface band line up is not strongly dependent on the interface morphology. In particular, we find that the exchange reaction is found to be exothermic with an enthalpy of 0.1 eV/atom. We show that both an ultrathin $Ga_xAl_{1-x}N$ ($x=0$, 0.5) intralayer and a Ga↔Al atomic swap at the interface does not significantly affect the *p*-type SBH. The *p*-type SBH is smaller by 0.1 eV for a Ga-terminated surface than a N-terminated one.

In Sec. II, we describe the theoretical method and the atomic configurations used in this study. In Sec. III, we discuss our results, focusing in Sec. III A on the structural properties (i.e., equilibrium atomic distances, nature of the interface bonds—metallic versus covalent) whereas in Sec. III B we discuss effects of the interface morphology on the interface states and the resulting SBH. Finally, our results are summarized in Sec. IV.

II. COMPUTATIONAL METHOD AND ATOMIC CONFIGURATIONS USED IN CALCULATIONS

First principles full-potential linearized augmented plane-wave (FLAPW)[23] calculations within the local-density approximation to density-functional theory[24] were used in this work. Plane waves with wave vector up to $K_{max}=4.6$ a.u., leading to about 5000 basis functions, were used. Angular momenta up to $l_{max}=8$ in the muffin tin spheres ($R_{Ga}=R_{Al}=2.1$ a.u. $R_N=1.4$ a.u.) for both wave functions and charge density were used in the self-consistency cycles. Three special *k* points, obtained following the Monkhorst-Pack scheme,[25] were used to sample the tetragonal Brillouin zone.

The widely adopted supercell approach was used to simulate the different types of interfaces. In particular, we performed *ab initio* calculations for supercells containing 15 GaN+7 Al (13 GaN+7 Al) layers in the N-terminated (Ga-terminated) case. The thickness of these layers is sufficiently large enough that the metal and semiconductor layers farthest from the interfaces have properties similar to the bulk (see below).

The method employed to evaluate the SBH uses the metal and semiconductor atomic core levels as reference energies located sufficiently far from the interface to have bulk-like bandstructure. In particular, the SBH can be expressed as $\Phi_{B_p}=\Delta b+\Delta E_b$, where Δb and ΔE_b indicate an ''interface'' and ''bulk'' contribution, respectively (see Ref. 22 for details in the GaN/Al case). This simple procedure is commonly used in *ab initio* all-electron calculations to evaluate the interface band line up at semiconductor heterojunctions or metal/semiconductor junctions. We considered all the structures for a cubic (i.e., zincblende) [001] ordered GaN substrate, with a calculated lattice constant $a_{subs}=a_{GaN}=8.47$ a.u..[26] Further structural details can be found in Ref. 22. All the structures considered are shown in Fig. 1 and summarized in Table I.

The choice of these structures (in particular the *C*, *D*, and *E* systems) has been suggested by a recent surface investigation of Al films deposited on wurtzite GaN(0001)-(1×1) surfaces,[16] reporting that the interface is very reactive. It was experimentally observed, in fact, that metallic Ga was released from the interface after monolayer depositions of Al. This suggests that an exchange reaction occurs in which the Al atom replaces the group-III element within the semiconductor, in analogy to that found for GaAs (Ref. 17) and InP (Ref. 18). After repeated cycles of Al deposition and annealing, evidence was found[16] for the presence of a $Ga_xAl_{1-x}N$ alloy interfacial layer.

In Table I (structure *E*) the interface plane X_i indicates the fcc cationic sites occupied either by Ga or Al (50% of Ga and 50% of Al), with an ordered superstructure that aims to simulate the $Ga_{0.5}Al_{0.5}N$ alloy. In this case, we consider a

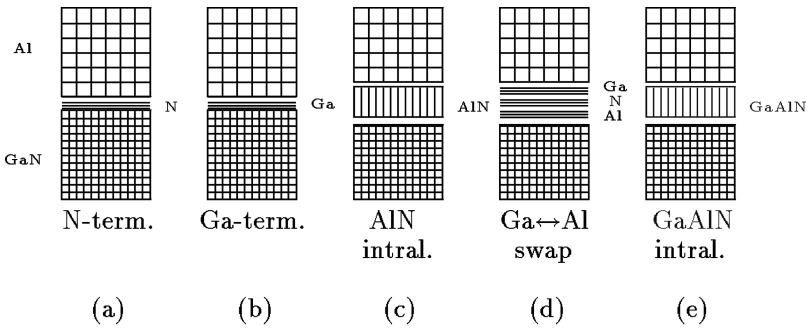

FIG. 1. Different interface geometries considered. Small squares regions indicate the GaN substrate; large square regions represent the Al overlayer. Abrupt GaN/Al N-terminated interface—system *A* [panel (a)]; abrupt GaN/Al Ga-terminated interface—system *B* [panel (b)]; AlN intralayer—system *C* [panel (c)]; system *D* showing the Ga↔Al atomic swap [panel (d)]; GaAlN alloy intralayer—system *E* [panel (e)].

supercell with doubled dimensions in the $x-y$ plane. The resulting increase in the computational cost was compensated for by reducing the thickness of the supercell (i.e., 11 GaN+5 Al layers). This is expected to affect the final value of the SBH, since bulk conditions in the thinner GaN and Al regions may not be completely recovered (see below). However, the effects of the alloy $Ga_{0.5}Al_{0.5}N$ intralayer on the structural and electronic properties can be determined by comparing the results to the ideal atomically abrupt N terminated GaN/Al interface having the same size and in-plane dimensions; the only difference between them being the last cationic plane of the semiconductor side, which is made of 50% Ga and 50% Al atoms and all Ga atoms, in the first and second case, respectively.

For configurations *A*-*D*, structural relaxations along the [001] direction were performed according to *ab initio* atomic forces.[27] Other degrees of freedom including in-plane atomic relaxations and formation of extended defects, such as dislocations, were neglected. In the case of configuration *E*, due to onerous computational costs for the in-plane doubled supercells, structural minimization was not performed. Instead, the calculated interplanar distance from structure *A* was used. Despite this limitation, the comparison of the results for configurations *A*-*E* can be used to determine the dependence of the interfacial electronic properties on the chemistry and structure of the interface.

III. RESULTS AND DISCUSSION

A. Stability and structural properties

Since the supercells do not have the same number of each atomic species, a fully consistent determination of the relative stability of the configurations is in general not possible from the superlattice calculations alone.[28] The problem can be avoided by obtaining the chemical potentials μ of the atomic species of pure solids from independent total energy calculations. However, the problem of biggest interest in the present contest is the one of the exchange reaction, and we can get the relevant figure by comparing the ideal N-terminated interface (A) with the structure showing the Ga↔Al swap (D), since the two supercells contain the same number of atoms of the same species. As for the Ga vs N termination, this problem is of more concern in the study of the GaN surface, and has already been addressed in the literature.[29] As shown in Ref. 22 and mentioned earlier in this work, the atomic forces acting on the interface Al_i in configuration A do not decrease the $z_{Al_i-N_i}$ pushing the Al towards the GaN region. Instead, we find an equilibrium structure having a bond length $d_{Al_i-N_i}$ larger than both d^{bulk}_{Al-N} and d^{bulk}_{Ga-N} (where d^{bulk}_{X-N} (X=Ga, Al) denotes the bulk bond length of XN). However, our calculations show that the total energy of configuration D is lower (by about 0.1 eV/atom) than the total energy of structure A, confirming that the Ga↔Al exchange reaction observed experimentally[16] is energetically favorable. Intuitively, this can be understood by noting that the AlN bond has a significantly higher bond energy than GaN. We note that a further displacement of Ga inside the Al overlayer will imply a more ionic N-Al interface bond (greater cohesive energy), and one more partially covalent Ga-Al bond on the metal side. We can therefore reasonably expect that such an exchange will lead to a further total energy reduction. The heat of formation for the Al/GaN exchange reaction is significantly less than the values predicted for the Al/GaAs system by Ihm (0.48 eV) (Ref. 9) and Swarts (0.62 eV) (Ref. 10).

The theoretically-determined interplanar distances along the [001] direction are summarized in Table I. Since the

TABLE I. Structural parameters for the configurations examined (all values in atomic units).

Sys.	Interface configuration and interplanar atomic distances
A	$Ga_i \leftarrow 2.12 \rightarrow N_i \leftarrow 2.17 \rightarrow Al_i \leftarrow 3.67 \rightarrow Al$
B	$N_i \leftarrow 2.23 \rightarrow Ga_i \leftarrow 3.04 \rightarrow Al_i \leftarrow 3.67 \rightarrow Al$
C	$Ga_i \leftarrow 2.12 \rightarrow N_i^1 \leftarrow 2.12 \rightarrow Al_i^1 \leftarrow 2.13 \rightarrow N_i^2 \leftarrow 2.17 \rightarrow Al_i^2 \leftarrow 3.67 \rightarrow Al$
D	$Ga_i \leftarrow 2.12 \rightarrow N_i^1 \leftarrow 2.12 \rightarrow Al_i^1 \leftarrow 2.12 \rightarrow N_i^2 \leftarrow 2.12 \rightarrow Ga_i^2 \leftarrow 3.00 \rightarrow Al_i^2 \leftarrow 3.67 \rightarrow Al$
E	$Ga_i \leftarrow 2.12 \rightarrow N_i^1 \leftarrow 2.12 \rightarrow X_i \leftarrow 2.12 \rightarrow N_i^2 \leftarrow 2.17 \rightarrow Al_i^2 \leftarrow 3.67 \rightarrow Al$

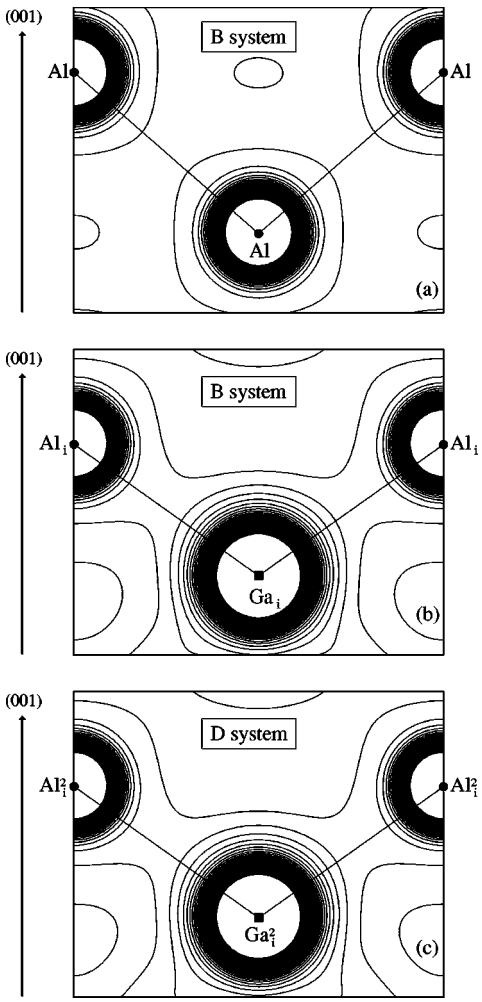

FIG. 2. Valence charge density projected on planes cutting different interface bonds: (a) bulk Al atoms in configuration *B*; (b) Ga_i-Al_i atoms in configuration *B*; (c) Ga_i^2-Al_i^2 atoms in configuration *D*. Contour lines are spaced by 0.01 electrons/cell.

electronic properties of configuration *A* have been discussed in a previous work,[22] we describe these results only in comparison with the other configurations. In the atomically abrupt interface *B*, the interplanar distance in the last GaN plane ($\Delta z_{\mathrm{Ga}_i-\mathrm{N}_i}=2.23$ a.u.) is larger than in bulk GaN (2.12 a.u.), which indicates that the interface Ga_iN_i covalent bond is weakened with respect to the GaN bond in the bulk. This can be explained in terms of the *half-metal/half-semiconductor* character of the interface Ga_i atom. In fact, as already pointed out in Ref. 22 for the *A* configuration, the interface cation (i.e., Al_i and Ga_i in the *A* and *B* case, respectively) forms with the other Al atoms a metallic bond, which reduces its possibility of full sp^3 hybridization, thus weakening the covalent character of the N-cation bond. A similar mechanism is also responsible for making the interplanar distance $\Delta z_{\mathrm{N}_i^2\mathrm{Al}_i^2}$ larger for the *C* configuration than $\Delta z_{\mathrm{Al}_i^1\mathrm{N}_i^2}$. In order to substantiate this, we report in Figs. 2(a) and 2(b) the charge density contour plots relative to the *B* configuration for the bulk Al atoms and the interface Ga_i-Al_i atoms, respectively. The interface Ga_i-Al_i bond is predominantly metallic, although it is slightly different from the pure Al-Al bond, due to different Ga and Al electronegativities [compare Figs. 2(a) and 2(b)].

In Fig. 2(c) we report the charge density contour plots for the interface Ga_i^2 and Al_i^2 atoms in configuration *D*; the similarity of panels (b) and (c) in Fig. 1 shows that the Ga atom released in the swap mechanism tends to form metallic bond with the deposited Al atoms. This is consistent with the results from *ab initio* atomic forces, which give an interplanar distance for interface *D* nearly equal (within 1%) to that in the *B* configuration (see Table I). We note that the results obtained in the present work for configuration *B* are similar to those obtained from *ab initio* pseudopotential calculations performed for the Ga-terminated Al/GaAs(001) interface:[30,31] the top Ga atomic layer was found to relax outwards, thus elongating the interface Ga-As bonds, as a result of metallization of the Ga-Al layer.

Table I shows that in the fully relaxed *C* configuration, the N_i^1-Al_i^1 and Al_i^1-N_i^2 interplanar distances ($\Delta z_{\mathrm{Al}_i^1-\mathrm{N}_i}$ ~ 2.12 a.u.) are equal to the interplanar distance ($\Delta z_{\mathrm{Ga}_i-\mathrm{N}_i}$ ~ 2.12 a.u.) in configuration *A*. On the other hand, the local-density approximation (LDA)-calculated equilibrium interplanar distance for tetragonal AlN with the in-plane lattice constant fixed to that of the GaN substrate is $\Delta z_{\mathrm{Al-N}}^{\mathrm{tetrag}}=2.00$ a.u., leading to a bond length $d_{\mathrm{Al-N}}^{\mathrm{tetrag}}=3.60$ a.u.[22]

Therefore, our structural results regarding configuration *C* suggest that the AlN intralayer, constrained on a GaN substrate, cannot attain the equilibrium tetragonal bond length within one layer. Instead, when Al replaces the surface Ga atom, the Al is found to occupy the same position without significant structural relaxation. Based on these results, we can reasonably expect a similar situation in the case of configuration *E*, with the Al atoms of the $Ga_{0.5}Al_{0.5}N$ layer substituting 50% of the Ga atomic sites without appreciably modifying the bond lengths, thus excluding the possibility of *buckling* effects. Hence, the unrelaxed *E* configuration, whose interplanar distances are set to those of configuration *A*, should not be radically different from the fully relaxed structure.

B. Schottky barrier heights

This subsection focuses on the influence of the interface morphology on the SBH. We recall that for the GaN/Al interface we found that the metal-induced gap states (MIGS) tail into the semiconductor side with a decay length of about $\lambda \sim 3.5$ a.u.;[22] in fact, in the present cases we find that the first few layers of the semiconductor have metallic character. For this reason, the presence of a monolayer-thick interfacial alloy layer does not result in an enhanced band gap near the interface. As a consequence, in this case changes in the electrical properties arise from shifts in the interface Fermi-level pinning position within the GaN band gap. Table II lists our theoretical results for the *p*-type SBH $\Phi_{B_p}=E_F-E_{VBM}$ calculated as the difference between the Fermi level (E_F) and the GaN valence-band maximum (E_{VBM}) sufficiently far from the interface. Note that the *n*-type SBH, Φ_{B_n}, can be obtained from the *p*-type SBH through the following relation

$$\Phi_{B_n}=E_{\mathrm{gap}}-\Phi_{B_p},$$

TABLE II. p-type Schottky barrier heights for the different n GaN+m Al interfaces (values in eV).

$n+m$	*A* GaN/Al N-term.	*B* GaN/Al Ga-term.	*C* AlN intral.	*D* Ga↔Al swap	*E* $Ga_{0.5}Al_{0.5}N$ intral.
15+7	1.12	1.06	1.07	1.11	
11+5	1.30				1.30

E_{gap} being the experimental semiconductor band-gap energy [$E_{gap}^{expt}(GaN)=3.39$ eV].[32,16]

We point out that all the results reported in the first row of Table II refer to supercells with 15 GaN+7 Al layers. In order to check the convergence of our SBH values as a function of the cell dimensions, we also performed calculations for a larger supercell, containing 19 GaN+9 Al layers. From this case,[22] we obtained variations of the SBH of less than 0.02 eV, showing that bulk conditions are well recovered also in the smaller 15 GaN+7 Al supercell. Note also that for configuration *A* we used an even smaller cell size (11 GaN+5 Al layers—see the second row in Table II) in order to compare with configuration *E*, which due to the in-plane doubling of the cell was calculated with a shorter periodicity along the growth direction. The different value (by about 0.2 eV) obtained for the 15 GaN+7 Al (configuration *A*, first row) with respect to the 11 GaN+5 Al (configuration *A*, second row) is related to the insufficient thicknesses considered. However, this is not going to affect our conclusions, since in this case we are interested in SBH trends rather than absolute values. The results shown in Table II do not include *quasi-particle* corrections ($\Delta_{QP} \approx 0.1$ eV[22]) related to the difference in screening on the two sides of the interface. This correction should be added to the p-type SBH value before a direct comparison to experiment is made.

Our calculations show that the interface band line up is not strongly dependent on the interface morphology and that all the SBH values found are in qualitative agreement with the experimental value reported for the atomically clean wurtzite–GaN/Al interface.[16] We first discuss the results obtained for the two atomically abrupt defect-free interfaces (configurations *A* and *B*). Table II shows that the p-type SBH is only slightly reduced (by 0.05 eV, of the same order of magnitude of our numerical precision) in going from the N- to the Ga-terminated interface. Similar results[13,30] were obtained for the GaAs/Al interface, where the p-type SBH was found to be reduced by as much as 0.1 eV in going from the As- to the Ga-terminated case, in agreement with experiment.[33,34] This trend was attributed[35] to the higher electron affinity of the anion-terminated compared to the cation-terminated interface, which tends to lower the n-type SBH.

If we compare the SBH values for the *A* and *C* configurations, we note that the p-type SBH is almost unaffected by the presence of the AlN intralayer (the 0.05 eV difference being of the order of our numerical precision). Let us explain our findings. Since the resulting structural relaxations are negligible, the *A* and *C* structures differ significantly only for the chemical influence of the Al atom's presence in the layer closest to the interface. We have calculated the difference between the double macroscopic average of the valence charge density for the *A* and *C* structures [denoted in the following as $\bar{\bar{n}}_{diff}^{A-C}(z)$]. A large difference in the interfacial dipole was not observed due to the similarity of the electronegativity of the Ga and Al species. We evaluated its even and odd contribution relative to the substituted cation position taken as zero. The even contribution of $\bar{\bar{n}}_{diff}^{A-C}(z)$ represents the chemical difference between Ga and Al (e.g., the different atomic wave functions) and, being a quadrupolar periodic charge (the monopole term of the electronic part being exactly compensated by the nuclear part), that is periodic along x and y but monolayer thick along z, it does not give rise to any potential discontinuity, which could affect the SBH. On the other hand, the odd contribution is expected to represent the charge rearrangement due to chemical substitution, which should give rise to charge depletion accumulation or, equivalently, to an extra dipole that may modify the GaN/Al SBH. Such a dipole can only arise from the asymmetry around the substituted cation (due to the presence of the interface), and therefore represents a next nearest-neighbors effect. In Fig. 3, we show the even (solid line) and odd (dashed line) terms of $\bar{\bar{n}}_{diff}^{A-C}(z)$; it is clear that the odd contribution is very small, relative to the even one. Therefore, as expected, $\bar{\bar{n}}_{diff}^{A-C}(z)$ does not modify the final SBH between GaN and Al. (Similar results were obtained from first principles calculations performed on the GaAs/Al system.)[30]

Let us now consider configuration *E*. Since we have just shown that the presence of an interface AlN layer (configuration *C*) in place of the usual GaN layer (configuration *A*) does not modify the SBH, in a similar way we expect that the presence of an interface $Ga_{0.5}Al_{0.5}N$ layer will not affect the final SBH as well. This is exactly what happens, as shown by an essentially identical SBH for configurations *A* and *E* (see Table II, second row).

We now discuss the transitivity rule[36] for configuration *C*. In Ref. 22 we showed that this simple rule in the *abrupt*

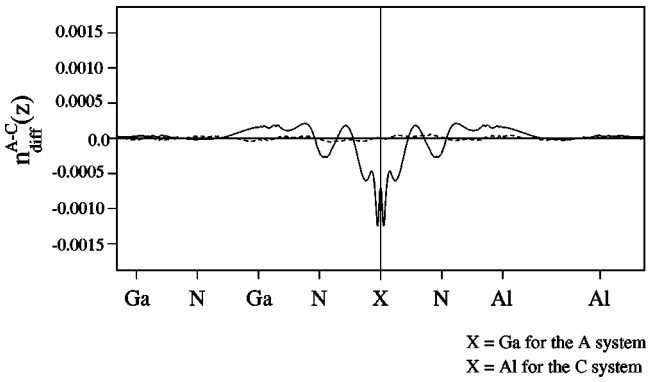

FIG. 3. Even (solid line) and odd (dashed line) contributions to $n_{diff}^{A-C}(z)$, defined as the difference between the double macroscopic average of the valence charge density for the *A* and *C* configurations. Units in electrons/basis-area.

system is fulfilled almost exactly for hypothethically ''lattice matched'' systems. In contrast, the difference in lattice constants inherent to the GaN/AlN/Al system was seen to produce deviations of about 0.1 eV, due to differences in structural interface relaxations.[22] Let us now observe that configuration C can be seen as a sequence of two interfaces (as far as a single monolayer may represent most of electrostatic potential line up): a GaN/AlN heterojunction and an AlN/Al semiconductor/metal interface. According to the transitivity rule and recalling the results obtained for the potential discontinuity in the AlN/Al and GaN/AlN cases,[22] we should therefore obtain: $\Phi_{B_p}(GaN/Al)=\Phi_{B_p}(AlN/Al)-\Delta E_v(GaN/AlN)=1.80-0.76=1.04$ eV, which is in excellent agreement with our FLAPW result, $\Phi^C_{B_p}(GaN/Al)=1.07$ eV.

Now consider the D structure; note that its p-type SBH is very similar to the value obtained for the other structures. This can be explained considering that the D and B structures differ essentially by the isovalent substitution Ga↔Al in the semiconductor layer closest to the interface. As shown for the A and C structures, the AlN intralayer does not alter appreciably the SBH; a similar situation can therefore be expected upon going from the B to the D structures, as actually found in Table II. In more detail, the SBH variation on going from B to D has opposite sign, relative to the one seen on going from A to C; this may be related to slightly different atomic relaxations in the two cases.

Let us now discuss how the SBH can be altered by displacing the atoms in the metallic side of the interface. In order to investigate this subject, we make use of the Born effective charges (Z^*) concept, Z^* being the dipole linearly induced by a unitary displacement of a single ion in an otherwise perfect crystal.[37] According to Ref. 38, if an atom with Z^* is displaced by an amount u from its equilibrium position, the resulting SBH change can be expressed as: $\Delta V=8\pi e^2 Z^* u/(\varepsilon_\infty a^2)$, where ε_∞ is the dielectric constant and a is the cubic lattice constant of the medium. Of course, it is expected that in a metal, Z^* vanishes due to perfect screening. In order to evaluate the Z^* of the metallic Ga and Al atoms, we performed FLAPW calculations for some D-type structures, obtained by varying the interface distance between the Ga_i^2 and Al_i^1 atoms with respect to the equilibrium distance. We found, taking u as large as $u=0.6$ a.u., that the variation of the SBH was less than 0.05 eV. This confirms, as expected, that the Z^* for the metallic atoms is nearly vanishing and that variations of the SBH as a function of the displacements of the metallic atoms in the metal side are therefore negligible.

IV. CONCLUSIONS

First principles calculations have been performed for the GaN/Al junction, considering various interface morphologies, namely different atomic terminations for GaN, interface atomic exchanges and $Ga_xAl_{1-x}N$ intralayers. Our results show that the Ga↔Al atomic exchange has an enthalpy change of 0.1 eV per atom.

We find that the first few layers of semiconductor are metallic due to the penetration of MIGS. For this reason, the presence of ultra-thin intralayers does not result in a band-gap enhancement near the interface. In addition, the effects of the interface configuration on the electrical properties of the junction are found to be negligible: the Schottky barrier height varies by less than 0.1 eV, changing the interface morphology. In particular, we found that the p-type Schottky barrier height is only slightly reduced by the presence of (i) a Ga-termination of the semiconductor side of the junction, (ii) a Ga↔Al atomic swap at the immediate interface, and (iii) a $Ga_xAl_{1-x}N$ ($x=0.5$, 1) intralayer. Changes in the SBH are explained in terms of the different character of the interface bonds in the two Ga- and N-terminated atomically abrupt cases and of the $Ga_xAl_{1-x}N$ ($x=0.5$, 1) intralayer electronic properties. Our results show good agreement with other theoretical values for the p-type SBH obtained for the similar GaAs/Al system.

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