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Band gap engineering of wurtzite and zinc-blende GaN/AlN superlattices from first principles

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Based on all-electron density functional theory calculations, we systematically investigate the electronic structure of (0001)-oriented wurtzite (wz) and (111)-, (100)-, and (110)-oriented zinc-blende (zb) GaN/AlN superlattices, where the band gap, strength of the electric field and their correlation with biaxial strain as a function of the superlattice thickness are calculated. For the polar wz-(0001) and zb-(111) systems, the band gap values are found to continuously decrease with increasing thickness of the superlattice period due to the built-in electric field. By mapping the core-level shift, we demonstrate the presence of spontaneous polarization in both wz-(0001) and zb-(111) superlattices. The built-in electric field is calculated to be about $5.1 \pm 0.3$ and $1.4 \pm 0.4$ MV/cm in the “free-standing” (fully relaxed) wz-(0001) and zb-(111) superlattices, respectively. Strain-induced piezoelectric polarizations are estimated to contribute only about 5% for the wz-(0001) superlattice, and about 30% for the zb-(111) systems. The zb-(100) and (110) superlattices are characterized by flat core-level bands in the well and barrier regions. The zb-(100) superlattices are predicted to have a stronger quantum confinement than the zb-(110) superlattices.

In both systems, confinement effects lead to a marked band gap increase with decreasing thickness of the superlattice period. © 2010 American Institute of Physics. [doi:10.1063/1.3505752]

I. INTRODUCTION

Wide band gap semiconductors GaN, AlN, and their solid solutions represent a family of semiconductors of crucial importance for modern optoelectronics, such as short-wavelength light emitting diodes, laser diodes, optical detectors, as well as for high-power, high-temperature, and high-frequency electronic devices, such as field-effect transistors.

Under ambient conditions AlN and GaN crystallize in the hexagonal wurtzite (wz) structure. A metastable cubic zinc-blende (zb) structure can be stabilized by epitaxial growth of thin films on (001) crystal planes of cubic substrates such as 3C-SiC and GaAs. Besides the fact that the zb phase has facets compatible with various cubic substrates, the zb-phase offers several technological advantages over the wz-counterpart, such as (i) better optical gain due to the lower effective mass, (ii) higher mobility due to the decrease in the phonon number for the higher symmetry structure, and (iii) better suited for n- and p-type doping due to the fact that the common acceptor and donor levels have smaller ionization energies with respect to the band edges.

In view of further extending the domain of application of this group-III nitride family, it is desirable to be able to tune the band gap values to enable device wavelength selectivity. In general, the electronic structure of materials is determined by their chemical composition and specific arrangements of atoms. Currently, two approaches are widely employed for fabricating nitride-based devices with the targeted band gaps. The first one is the well-known alloy approach, i.e., the band gap is tailored by varying the mole fraction $x$ of the $\text{Al}_{1-x}\text{Ga}_x\text{N}$ alloy, for which the targeted band gap values are limited between those of the parent semiconductors (AlN and GaN). The second approach relies on the quantum confinement effects in low-dimensional semiconductor systems, such as quantum wells, wires, and dots. Most of the optoelectronic and electronic nitride devices are fabricated as heterostructures. In particular, the creation of a multiple quantum well (MQW) structure is widely used. In such an approach, the band gap is easier to control than the alloy method because it depends on layer thickness rather than composition owing to the advances in material growth technologies, particularly molecular-beam epitaxy, and metalorganic chemical vapor deposition, that enables the fabrication of high quality prescribed nanoscale semiconductor structures, and electronic devices. Moreover, MQWs often offer a complimentary and wider range of band gap tunability than the alloy approach.

For the much studied wz-phase GaN/AlN(0001) heterostructures, a key property is the fact that they possess huge macroscopic polarization fields. On one hand, sizable lattice mismatch between AlN, GaN, [2.41% at 300 K (Ref. 12)] and the associated substrates results in huge piezoelectric effects along the epitaxial growth [0001] direction because of the very large piezoelectric constants of the nitrides. On the other hand, spontaneous polarization occurs along the [0001] polar axis even for the zero-strain state in wz-III-V nitride thin films and multilayers. Macroscopic polarization manifests itself as accumulated charge at heterointerfaces and built-in electrostatic fields in polarized layers interfacial to each other. Such fields originate from heterointerface discontinuities of the macroscopic bulk polar-
ization of the nitrides. The strong internal electric fields have a dramatic effect on the electronic and optical properties of these systems. It can be engineered, for example, to influence favorably transistor characteristics and spin injection.

Despite the intense studies of GaN/AlN or GaN/(Al,Ga)N(0001) superlattices, the reported values of the magnitude of the electric field—a key parameter governing the optical properties of GaN/AlN heterostructures, and often used as an input parameter for non-self-consistent simulations (e.g., tight binding methods), show a wide disparity. For example, while fitting the emission energy to the well width, the electric field in the wells was deduced to be $10 \pm 1$ (Ref. 25) and $9.2 \pm 1$ MV/cm (Ref. 26) in GaN/AlN(0001) MQWs, recent experiments reported that for GaN/AlN MQWs with well widths of 2.3 and 1.4 nm and barrier width 1.9 nm the intrinsic electric field strength in the wells were 5.04 MV/cm and 6.07 MV/cm, respectively. Moreover, it was reported that the spontaneous and piezoelectric components are competitive, i.e., 1.14 MV/cm and 1.12 MV/cm, respectively, for a GaN/Al$_x$Ga$_{1-x}$N superlattice. We will show that from first-principles calculations, the built-in electric field is calculated to be about $5.1 \pm 0.3$ MV/cm in the wz-(0001) superlattices. Furthermore, it is predicted that spontaneous polarization dominates the electric field and the strain-induced piezoelectric polarizations are estimated to contribute only about 5% for the wz-(0001) superlattices.

Much less is known for zb-GaN/AlN superlattices. Experimentally, to our knowledge, the growth of zb-GaN/AlN superlattices has not been reported. Theoretically, the piezoelectric effect in strained-layer zb superlattices has long been recognized. Smith and co-workers derived that for a [111] growth axis, the induced polarization is longitudinal, and for a [110] or [100] growth axis, the induced polarization is purely transverse (does not generate electric fields). The strain-induced electric field, largest for a [111] growth axis, induces a two-dimensional electron gas at the interface regions for field-effect transistors, resembling the case of wz-(0001) superlattices. So far, the possibility of spontaneous polarization in zb-GaN/AlN(111) superlattices has been overlooked. For example, it is reported that the electronic structure is affected significantly only by the strain-induced piezoelectric field in the zb-(111) systems. By contrast, for the wz-(0001) superlattices, both spontaneous and piezoelectric polarization play significant roles. It was further suggested that the polarization difference between the wz- and zb-phases could be calculated by considering an interface between the two phases and by defining spontaneous polarization to be zero in the zb-phase. We demonstrate, however, as will be shown below, that besides the strain-induced piezoelectric field, a rather strong spontaneous polarization induced electric field is also present in the atomically relaxed (strain-free) zb-GaN/AlN (111) superlattices due to the symmetry breaking in the [111] direction after forming heterostructures.

For the zb-GaN/AlN superlattices in the [100] and [110] growth directions, Park and Chuang derived analytical expressions for the band-edge effective masses and interband optical matrix elements with strain dependence. Based on the linear muffin-tin orbital method within the atomic-sphere approximation (LMTO-ASA), Ke et al. reported that the band gap is almost independent of the thickness—i.e., up to six layers of GaN and AlN, for (100)- and (110)-oriented zb-GaN/AlN superlattices. We will demonstrate that for both systems, quantum confinement plays a significant role in affecting the band gap values—the band gap increases with decreasing the thickness of superlattice.

In practice, both wz- and zb-GaN/AlN superlattices are commonly subjected to large built-in strains, which is expected to affect the polarization and consequently the related electronic structures. Accurate knowledge of the magnitude of the band gap and the built-in electric field and their correlation with sample structure and associated strain are important for the design and characterization of optoelectronic and electronic devices. Theoretically, it is also important to compare the electrical properties of both zb and wz superlattices systematically. In this paper, we, therefore, investigate the electronic properties, including the spontaneous polarization and piezoelectric field effects, of (100)-, (110)-, and (111)-oriented zb, and (0001)-oriented wz GaN/AlN superlattices. In particular, we study the band gap and electric field as a function of thickness of the superlattices, and as a function of the strain for these systems. Another merit of our results lies in that, unlike most of the experiments and previous first principles studies which are focused on short-period superlattices, we investigate a range of superlattices with various thickness, thus our systematic study is expected to provide a reliable database for the key properties mentioned above.

II. COMPUTATIONAL DETAILS

MQWs, which consist of a large number of alternating well (GaN) and barrier (AlN) layers, can be conveniently simulated using periodic superlattices. We perform all-electron density functional theory (DFT) calculations using the generalized gradient approximation (GGA) (Ref. 35) for the exchange correlation functional as implemented in the DMol (Ref. 3) code. The wave functions are expanded in terms of a double-numerical quality localized basis set with a real-space cutoff of 9 Bohr. We construct various sized (GaN)$_n/(AlN)_n$ structures for each type of superlattice, where $n$ is the number of double layers (DLs) of GaN and AlN in the well and barrier region, respectively. Each DL contains one N atom and one Al or Ga atom. For short, we label it a “$n+n$” superlattice. The superlattices with wz-[0001] and zb-[111] growth directions have planar unit cells that are hexagonal, with the in-plane lattice constants being $(a_{11}^{\text{wz}}, a_{12}^{\text{wz}})$ and $(a_{11}^{\text{zb}}, a_{12}^{\text{zb}})$, respectively. Those with zb-[100] and zb-[110] growth directions have square and rectangular planar unit cells, with the in-plane lattice constants being $(a_{11}^{\text{zb}}/\sqrt{2}, a_{12}^{\text{zb}}/\sqrt{2})$, and $(a_{11}^{\text{zb}}/\sqrt{2}, a_{12}^{\text{zb}})$, respectively, where $a_{12}^{\text{wz}}$ is the in-plane lattice constants for the wz- and $a_{12}^{\text{zb}}$ is the lattice constant of the zb conventional unit cell. As examples, Fig. 1 shows the various superlattices. It is important to note that the zb-(100) and (110) superlattices possess a mirror plane, while the wz-(0001) and zb-(111) systems do not. These latter systems involve two different interfaces,
which we label “type A” and “type B.” The Brillouin-zone integrations are performed using a $10 \times 10 \times 4$ k-point grid for the wz-6+6 structure. For other superlattices, the same/similar sampling of reciprocal space is used.

We impose the assumption of pseudomorphic growth, i.e., the in-plane lattice constants of the GaN region and AlN region are equal. Three approaches regarding the geometry relaxation are employed. (i) Full relaxation, including lattice constants ($a$ and $c$) and internal parameters, representing “free-standing” superlattices, then, in order to investigate the effect of strain, we fix the in-plane lattice constant of the superlattices at that of either (ii) GaN or (iii) AlN, relaxing the $c$ lattice constant and internal parameters. Fixing the lateral lattice constant of the superlattices at that of GaN (fix-GaN), and of AlN (fix-AlN), represents two “extremes” of the compressive and tensile strained superlattices.

### III. RESULTS

#### A. Bulk wz- and zb-AlN and GaN

It is instructive to first study the parent semiconductors—bulk AlN and GaN in both the wz and zb structures. In the wz structure, the hexagonal lattice points are occupied in the following stacking sequence $\cdots$ABABABAB$\cdots$ along the [0001] direction. In the zb structure, on the other hand, all three lattice points are occupied leading to the stacking sequence $\cdots$ABCABCABC$\cdots$ along the [111] direction. The lattice constants, internal parameter, cohesive energy and band gap values are compiled in Table I. For the crystalline structural data, our results compare well with other DFT-GGA results and experimental data. The lattice mismatch between wz-AlN and wz-GaN is 2.88% for $a$ and 4.90% for $c$, compared to the corresponding experimental values 2.41% and 3.92%, respectively. For the zb-phase, the in-plane lattice mismatch between AlN and GaN is 3.6% compared to experimental one 2.67%. The internal parameter $u$, describing the relative atomic position, is sensitive to both piezoelectric and spontaneous polarization. For both wz-AlN and GaN, this value is slightly larger than the ideal value of $3/8=0.375$. The ideal

![FIG. 1. (Color online) Geometry of different types of GaN/AlN superlattices.](image)

**TABLE I.** Lattice constants $a$, $c$, and $c/a$ ratio, internal parameter, $u$, cohesive energy, $E_c$, and band gap, $E_g$, of wz and zinc-blende bulk AlN and GaN.

<table>
<thead>
<tr>
<th>Method</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>$u$</th>
<th>$E_c$ (eV)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present GGA</td>
<td>3.134</td>
<td>5.001</td>
<td>1.596</td>
<td>0.3825</td>
<td>10.547</td>
<td>4.21</td>
</tr>
<tr>
<td>GGA$^a$</td>
<td>3.113</td>
<td>5.041</td>
<td>1.6193</td>
<td>0.3798</td>
<td>11.403</td>
<td>4.245</td>
</tr>
<tr>
<td>GGA$^b$</td>
<td>3.1095</td>
<td>4.9938</td>
<td>1.606</td>
<td>0.3819</td>
<td>12.071</td>
<td></td>
</tr>
<tr>
<td>Exp.$^c,d$</td>
<td>3.112</td>
<td>4.982</td>
<td>1.601</td>
<td>0.385</td>
<td>11.669</td>
<td>6.25</td>
</tr>
<tr>
<td>Present GGA</td>
<td>3.227</td>
<td>5.260</td>
<td>1.630</td>
<td>0.3768</td>
<td>8.784</td>
<td>1.81</td>
</tr>
<tr>
<td>GGA$^a$</td>
<td>3.245</td>
<td>5.296</td>
<td>1.632</td>
<td>0.3762</td>
<td>8.265</td>
<td>1.45</td>
</tr>
<tr>
<td>GGA$^b$</td>
<td>3.1986</td>
<td>5.2262</td>
<td>1.634</td>
<td>0.3772</td>
<td>9.265</td>
<td></td>
</tr>
<tr>
<td>Exp.$^c,d$</td>
<td>3.189</td>
<td>5.185</td>
<td>1.626</td>
<td>0.3755</td>
<td>9.058</td>
<td>3.51</td>
</tr>
<tr>
<td>Present GGA</td>
<td>4.399</td>
<td>4.390</td>
<td>11.361</td>
<td>4.13 (indirect)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GGA$^a$</td>
<td>4.394</td>
<td>11.907</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GGA$^b$</td>
<td>4.38</td>
<td>11.52</td>
<td>5.34 (indirect)$^f$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exp.$^c$</td>
<td>8.770</td>
<td>1.66</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present GGA</td>
<td>4.565</td>
<td>4.538</td>
<td>9.249</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GGA$^a$</td>
<td>4.590</td>
<td>8.253</td>
<td>1.28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GGA$^b$</td>
<td>4.50</td>
<td>8.96</td>
<td>3.299</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference 40.
$^b$Reference 41.
$^c$Reference 42.
$^d$Reference 12.
$^e$Reference 43.
$^f$Reference 44.
c/a ratio for the wz structure is $c/a = \sqrt{8/3} \approx 1.633$. For wz-AlN, the theoretical $c/a$ value is smaller than the ideal value by 0.037, compared for wz-GaN by 0.003. The larger the deviation from the ideal wz structure (namely $a$ being larger while $c/a$ being smaller), the larger the spontaneous polarization parameter (GaN: $-0.034$ C/m$^2$ and AlN: $-0.090$ C/m$^2$).\(^{39}\)

For both wz- and zb-phases, AlN has larger cohesive energy than GaN. This is related to the larger electronegativity difference between the cation and anion (Al: 1.61, Ga: 1.81, and N: 3.04). The ground wz structure is calculated to be more stable than the corresponding metastable zb phase by 51 meV for AlN and 14 meV for GaN, which compares well with other DFT-GGA results using pseudopotential plane-wave methods, namely, 42 and 12 meV in Ref. 40 and 164 and 16 meV in Ref. 41. As expected, the DFT-GGA leads to an underestimation of the band gap values for semiconductors. Our calculated direct band gap values are 4.21 eV, 1.81 eV, and 1.66 eV for wz-AlN, wz-GaN, and zb-GaN, respectively. In agreement with previous experimental\(^{12}\) and theoretical\(^{40}\) results, zb-AlN is predicted to be an indirect semiconductor with a band gap of 3.48 eV, in excellent agreement with 4.13 eV in Ref. 40.

We find that all the studied wz- and zb-GaN/AlN superlattices are direct band gap semiconductors.

**B. wz-(0001) and zb-(111) superlattices**

We first study the free-standing (fully relaxed) wz-(GaN)$_n$/(AlN)$_m$ (0001) and zb-(GaN)$_n$/(AlN)$_m$ (111) superlattices. The fully optimized lattice constants $a$ and $c/n$ are shown in Fig. 2. For both systems, the relaxed in-plane lattice constant $a$ lies between the corresponding in-plane lattice constants $a_{\text{wz}}^m$ and $a_{\text{zb}}^m/\sqrt{2}$ of the parent semiconductors. The free-standing $c/n$ values (as well as those obtained for fixed in-plane lattice constants) converge rather well from 10+10 for the wz-(0001) systems and from 9+9 for the zb-(111) systems.

The presence of a built-in electric field can be demonstrated by using the core-levels as reference energies to determine the relative alignment of the valence band edges.\(^{44,45}\) Here, we use the N 1$s$ orbital binding energy, $E_b^{\text{CL}}$, in different layers, as shown in Fig. 3, for the various sized superlattices. The obtained results allow the following important conclusions. First, our calculations demonstrate the presence of spontaneous polarization in wz-GaN/AlN(0001), as well as in the zb-GaN/AlN(111) superlattices. While spontaneous polarization has been well documented in wz-(0001) superlattices, to the best of our knowledge, this is the first demonstration of the presence of spontaneous polarization in zb-(111) superlattices. Second, both systems show similar trends of the core-level shift. In each semiconductor region (GaN or AlN), there is a different slope of the curves, corresponding to opposite sign of the electric fields, in the well GaN (negative) and barrier AlN (positive) regions, exhibiting V-shaped profiles. The similar core-level shift profiles of the zb or wz systems also indicate that the direction of spontaneous polarization is the same in these two systems, namely, in the well region, from the nitrogen (anion) atom to the nearest neigh-

**FIG. 2.** Lattice constants $a$ and $c/n$ for various polar superlattices, (a) $a$ and (b) $c/n$ for wz-GaN/AlN(0001), and (c) $a$ and (d) $c/n$ for zb- GaN/AlN(111) superlattices.

**FIG. 3.** (Color online) Calculated variation in the N 1$s$ core-level binding energy for (a) wz-GaN/AlN(0001) and (b) zb-GaN/AlN(111) free-standing (fully relaxed) superlattices.
bor metal (cation) atom along the c axis, i.e., the [0001] direction. Third, the slopes of the linear regions correspond to the absolute values of the electric fields $E = \Delta E_{\text{CL}}^{\text{CL}}/\Delta z$, where $\Delta E_{\text{CL}}^{\text{CL}}$ is the difference of $E_{\text{CL}}^{\text{CL}}$ of the N atoms with a distance of $\Delta z$ along the [0001] or [111] direction. With different thickness superlattices, the core-level shifts in the linear region are nearly parallel to one another, showing the strength of electric field is nearly a constant with respective to thickness. It is evident that the strength of electric field in the wz-(0001) superlattices is much stronger than that in zb-(111) systems. The calculated absolute built-in electric field values in the well regions are about $5.1 \pm 0.3$ and $1.4 \pm 0.4$ MV/cm for the freestanding wz-(0001) and zb-(111) superlattices, respectively (see Fig. 4).

The presence of spontaneous polarization of the built-in electric fields in wz-(0001) and zb-(111) superlattices are closely related to the symmetry of the bulk and the superlattice systems. For the wz structure, since the four tetrahedral bonds are nonequivalent, bond-to-bond charge transfer, and ionic relaxation will cause spontaneous polarization. As a result, it is expected to possess an intrinsic polarization along the [0001] direction. After forming a heterostructure wz-GaN/AlN, because AlN has a higher cation-anion electronegativity difference to that of GaN, the net component of the polarization vector in the [0001] direction in triply bonded N with Al is larger in amplitude compared to in the GaN tetrahedron, thus it is known there is spontaneous polarization across the heterostructures. For zb systems, spontaneous polarization is absent in an infinite bulk zb crystal. In the zb-GaN/AlN(111) systems, forming a heterostructure will introduce symmetry breaking, perpendicular to the [111] direction and thus lead to atomic displacement. Similar to the case of the wz-(0001) superlattices, this will induce a spontaneous polarization field along the [111] growth direction due to the difference of polarization between GaN and AlN regions.

The difference in the magnitude of the electric-fields in wz-GaN/AlN(0001) and zb-GaN/AlN(111) superlattices is a combined effect of charge redistribution and specific atomic arrangement, in particular, around the interface regions. To demonstrate the charge transfer, we calculate the effective total Mulliken charge (defined as the difference of the total Mulliken charge in the superlattice and the corresponding bulk AlN or GaN) for each DL (containing one N atom and one Al or Ga atom) for the 6+6 wz-(0001) and zb-(111) superlattices, as shown in Fig. 5. It can be seen that around the interface regions the AlN DL has positive Mulliken charge and the GaN DL has negative charge, showing charge transfers from the AlN region to the GaN region. As expected, charge accumulation is a local effect, forming large opposite interface dipole at the interfaces, and resulting in strong built-in electric field throughout the superlattices. Interestingly, such an effect is pronounced in two DLs at each interface for wz-GaN/AlN(0001) superlattice and three DLs at each interface for zb-GaN/AlN(111) superlattices. Such a difference is due to the different stacking sequences in these two systems. The magnitude of charge accumulation in wz-GaN/AlN(0001) superlattices is significantly larger than that in zb-GaN/AlN(111) superlattices. On the other hand, there is a close relationship between the bulk wz and zb structures. In fact, for $u = 3/8$ and the ideal $c/a$, the tetrahedron formed by the cation and its four N neighbors is exactly the same as that formed in the zb structure. However, there is a significant difference (by 13%) in the position of the second nearest neighbors. After forming heterostructures, these relative atomic positions in the zb superlattice do not change much. Taking the 6+6 superlattice as an example, the first and second nearest neighbors at the type A and B interfaces in the wz-6+6(0001) and zb-6+6(111) superlattices are listed in Table II. One can see that for the first neighbor distance differences at the type A and type B interfaces, both systems undergo a distortion with a similar magnitude, namely 0.084 Å and 0.089 Å for wz- and zb-superlattices, respectively. By contrast, the second neighboring distance change at the two interfaces are 0.062 Å and $-0.001$ Å. So, we attribute the large difference of the electric fields in wz-(0001) and zb-(111) superlattices to the difference of Mulliken charge distribution around the interfaces and associated structural distortions, mainly with regard to the second nearest neighboring distances.
TABLE II. The first and second nearest neighbor cation-anion distances at the type A and B interfaces in the free-standing wz-6+6 GaN/AlN(0001) and zb-6+6 GaN/AlN(111) superlattices, units in Å. The atom labels are as those in Fig. 1.

<table>
<thead>
<tr>
<th>Nearest neighbor (nn)</th>
<th>Interface</th>
<th>wz-6+6(0001)</th>
<th>zb-6+6(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First nn</td>
<td>Type A (N1–Ga1)</td>
<td>1.995</td>
<td>1.988</td>
</tr>
<tr>
<td></td>
<td>Type B (N2–Al1)</td>
<td>1.911</td>
<td>1.899</td>
</tr>
<tr>
<td>Second nn</td>
<td>Type A (N1–Ga2)</td>
<td>3.219</td>
<td>3.168</td>
</tr>
<tr>
<td></td>
<td>Type B (N2–Al2)</td>
<td>3.157</td>
<td>3.169</td>
</tr>
</tbody>
</table>

Such strong electric fields have significant effects on the total band structure and layer-resolved [each “layer” containing one metal (Ga or Al) and one N atom] density of states (DOS), as shown in Fig. 6 for the 12+12 wz-(0001) and zb-(111) superlattices. First, the presence of the electric field leads to a bending of the conduction and valence band proﬁles across the superlattice and associated localization of electron and hole gases on the two opposite interfaces of the quantum well. The resulting valence band maximum (VBM) is located around interface A and the conduction band minimum (CBM) around interface B. As a consequence, with increasing well and barrier thickness, the strong built-in electric field in the AlN/GaN superlattices gives rise to a marked reduction in the band gap with increasing thickness. Second, the presence of the electric field produces a progressive separation of the energy density of states (DS) on the two interfaces of the quantum well. The resulting valence band maximum (VBM) is located around interface A and the conduction band minimum (CBM) around interface B. As a consequence, with increasing well and barrier thickness, the strong built-in electric field in the AlN/GaN superlattices gives rise to a marked reduction in the band gap with increasing thickness. Further, the built-in electric field produces a progressive separation of the electron and hole wave functions with increasing well width, resulting in a decrease in emission strength (and eventually in the increase in the decay time) and in the strong redshift of the quantum confined Stark effect (QCSE).

Owing to the smaller electric field in the zb-(111) superlattices, the QCSE is weaker than in the wz-(0001) systems, resulting in a modest decrease in the band gap with increasing thickness. Second, the built-in field produces a progressive separation of the electron and hole wave functions with increasing well width, resulting in a decrease in emission strength (and eventually in the increase in the decay time) and in the strong reduction in the exciton binding energy.

Given the similarity of the wz-(0001) and zb-(111) superlattices, it is interesting to compare strain effects on the built-in electric field (Fig. 4) and band gap (Fig. 7) in these two systems. The binding energy of the N 1s core-level as a function of position for the selected wz-(0001) and zb-(111) superlattices under different strain conditions is shown in Fig. 8. For the band gap, the presence of strain induces a similar effect in these two systems—namely, compressive strain (fix-AlN) leads to larger band gaps, and tensile strain (fix-GaN) leads to smaller band gaps compared to the free-standing (fully optimized) ones. In agreement with Ref. 33, both wz-(0001) and zb-(111) superlattices are type I heterostructure systems, i.e., the VBM (CBM) of GaN is higher (lower) than that of AlN. Thus the band gap values of the GaN/AlN superlattices are mainly determined by the well (GaN) region. We confirm a similar behavior of the band gap change in bulk GaN under the same various strain conditions.

In contrast, strain plays the reverse role in affecting the built-in electric field in the wz-(0001) and zb-(111) superlattice systems (see Figs. 4 and 8). That is, compressive strain decreases the electric field in wz-(0001) but increases it in zb-(111) superlattices. For the wz-GaN/AlN(0001) superlattices, Ambacher et al. derived that the alignment of the piezoelectric and spontaneous polarization is parallel in the case of tensile strain and antiparallel for compressive strain. This is in agreement with our results showing that compressive strain (fix-AlN) leads to a smaller electric field, and tensile strain (fix-GaN) leads to a larger electric field compared to the free-standing one. It is found that the spontaneous polarization dominates the contribution to the electric field, and strain-induced piezoelectric polarization is esti-

\[ \text{Energy [eV]} \]

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\[ \text{K} \]

\[ \text{A} \]

\[ \text{B} \]

\[ \text{G} \]

\[ \text{N} \]

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FIG. 8. (Color online) Calculated variation in the N 1s core-level binding energy in left, wz-(0001), and right, zb-(111) superlattices under different strain growth conditions for different sized superlattices.

FIG. 9. Lattice constants $a$ and $c/n$ for various nonpolar superlattices (a) $a$ and (b) $c/n$ for zb-(100) and (c) $a$ and (d) $c/n$ for zb-(110) superlattices.

FIG. 10. (Color online) Calculated variation in the N 1s core-level binding energy in various (a) zb-(100) superlattices and (b) zb-(110) superlattices.
mated to contribute only about 5% for the wz-GaN/ AlN(0001) superlattice. Our calculated electric field values for the wz-GaN/AlN(0001) superlattice, around 4.8–5.4 MV/cm, are significantly lower than the 10±1 MV/cm (Ref. 25) deduced by fitting spectra. However, they are in much better agreement with recent experimental results,27 namely, 6.07 and 5.04 MV/cm for the 20 period 2.3 nm/1.9 nm and 1.4 nm/1.9 nm [corresponding to (8–10)+8 and (5–6)+8] superlattice systems wz-GaN/AlN(0001) MQWs.

For the zb-(111) systems, Smith derived that tensile strain (fix-GaN) results in the piezoelectric polarization vector pointing from cation to anion ([0001]), i.e., antiparallel to the spontaneous polarization,28 resulting in a reduced electric field. Similarly, compressive strain (fix-AlN) results in a piezoelectric polarization vector in the [001] direction, which is parallel to the spontaneous polarization, giving an increased electric field. This is in agreement with our calculated magnitudes of the electric fields under different strain conditions (Fig. 4). Compared to the wz-(0001) systems, piezoelectric polarization contributes a notably larger ratio in the zb-(111) superlattices, namely, about 30% to the total polarization or electric field.

C. zb-(100) and (110) superlattices

The fully relaxed lattice constant a and c/n values for the zb-(100) and zb-(110) superlattices are shown in Fig. 9. Similarly to as was found for the two previous systems, the relaxed in-plane lattice constants, a, lies between the corresponding in-plane lattice constants, a0/√2, of the parent semiconductors (being 3.111 Å and 3.228 Å for zb-AlN and zb-GaN, respectively), with zb-(110) superlattices having slightly larger a values than zb-(100).

For both zb-(100) and (110) superlattices, owing to the existence of a mirror plane, the position of the N 1s core-level binding energy does not change significantly within the well or barrier region, i.e., there is no built-in electric field in the well (GaN) or barrier (AlN) regions, as shown in Fig. 10. Here, quantum confinement effects govern the electronic properties of the zb-GaN/AlN superlattices. The corresponding N 1s binding energy is −375.60 eV and −376.42 eV in bulk zb-AlN and zb-GaN, respectively. Interestingly, in both systems, the N 1s core-level of well region (GaN) are pushed downward by 0.15 eV compared to the bulk. However, for the barrier region, while in zb-(100) the core-level values do not change significantly, those in zb-(110) superlattices are also pushed downward by about 0.32 eV compared to that of bulk AlN. The core-level values are sensitive to the atomic environment. In the ideal (unrelaxed) zb-(110) superlattices, each atomic plane parallel to the interface contains both a cation and an anion and is therefore “neutral” or “nonpolar.” However, we find atomic relaxation will break such neutrality. The N atomic displacements are shown in Fig. 1(d). This leads to the zb-(100) superlattices has a stronger electron confinement (well depth 0.95 eV) than zb-(110) superlattices (well depth 0.65 eV). Another notable difference between these two systems concerns the structural distortion around the interfaces. For the zb-(100) superlattices, there is one common bridging N atom. By contrast, in the zb-(110) systems, there are two N atoms along the [110] direction after internal relaxation. This is reflected in the core-levels shift (see Fig. 10). That is, there is one, and two N-atoms core-levels located between those of the barrier and well regions in zb-(100) and zb-(110) superlattice, respectively.

As expected, such quantum confinement effects will affect the band gap values of these superlattices. In agreement with Ref. 33, both zb-(110) and (110) superlattices are found to be type I, meaning that the band gap values of superlattices are dominated by the GaN region. Decreasing the thickness of the superlattice period leads to stronger quantum confinement. For both zb-(100) and zb-(110) systems, the short 4+4 superlattices have the lowest N 1s eigenvalues in the well (GaN) region. Thus, shorter period superlattices have a lower global VBM (and a higher CBM), thus larger band gap values. It can be also seen that the band gap decrease in the short superlattices change less significantly in zb-(110) than in zb-(100) due to the weaker confinement in the former systems. The band gap as a function of the layer thickness number, n, is shown in Fig. 11 for these two systems. Our all-electron results are in contrast with the LMTO-ASA re-

**FIG. 11.** Calculated band gap values as a function of layer thickness under different strains. (a) zb-(100) and (b) zb-(110) superlattices.

**FIG. 12.** (Color online) Total bandstructure (left) and layer-resolved DOS (right) for the zb-(100)-12+12 (upper panel) and zb-(110)-12+12 superlattices (below panel). Dark (black) represents the s orbital, light (green) the p orbitals, and gray the d orbitals. The dashed lines indicate the interface. Note the difference of atomic orders in c direction in these two systems.
sults of Ref. 33, in which the band gap is predicted to be independent of the thickness for zb-GaN/AlN (100) superlattices. Note in Ref. 33, besides the ASA, the internal parameter $u$ is treated as various constants.

With increasing layer number, one might expect that the band gap will converge to the band gap of the bulk well, i.e., zb-GaN (1.66 eV). In the short superlattice region $n \leq 8$, the band gap values increase rapidly with decreasing the thickness due to strong quantum confinement effects. For $n > 8$, the change in band gap becomes modest with the changes in thickness. For example, for the “fix-GaN” zb-16+16 (110) superlattice, the band gap is 1.90 eV, still sizably larger than the band gap of bulk zb-GaN. We confirm that in thick (such as 16+16) superlattices, the bond distances in the middle of GaN region are almost identical to bulk GaN. By using same calculational parameters (such as $k$-points and basis set cutoff value) for pure bulk GaN calculations in the same sized supercell, we obtained the expected bulk band gap of 1.66 eV, thus ruling out a possible reason for this deviation as being due to computational errors. Figure 12 shows the atom-resolved DOS along the $c$-direction for the 12+12 zb-(100) and zb-(110) superlattice. One can see that around the interface region, there is not an abrupt, but a gradual change in both CBM and VBM at the interface. Moreover, it can be seen that the CBM has the lowest energy at the center of the well region and simultaneously, the VBM has the highest energy, reflecting the quantum confinement.

For a zb superlattice under biaxial strain, Smith and Mailhiot demonstrated that for a [111] growth axis, the strain-induced polarization is along the growth axis, for a [110] growth axis, it is in the superlattice plane, and for a [100] growth axis, such polarization vanished. Although for the [110] and [100] growth axes, the strain does not generate electric fields along the growth direction, it does affect the core-level profile—for both systems, tensile (compressive) strain shifts the $N\,1s$ binding energy upwards (downwards) compared to the free-standing superlattices (see Fig. 13), keeping the shape of the diagrams ($N\,1s$ core-level position versus distance) unchanged. This leads to smaller (larger) band gap values for the fix-GaN (fix-AlN) superlattices, as shown in Fig. 11.

IV. SUMMARY AND CONCLUSION

Over the past two decades, GaN/AlN superlattices have represented prototypical heterointerface systems, where the electronic polarization has profound consequences on the electrostatics and electrodynamics of epitaxial films and heterostructures. Based on all-electron DFT calculations, we systematically investigate the electronic structure of the (0001)-oriented wz and (111)-, (100)-, and (110)-oriented zb-GaN/AlN superlattices, where the band gap, the strength of the electric field, and their correlation with biaxial strain as a function of the superlattice thickness are investigated. For the wz-(0001) and zb-(111) systems, the band gap continuously decreases with increasing thickness of the superlattice due to the effect of the built-in electric field and the resulted band-bending effects. Through the $N\,1s$ core-level shift, we demonstrate the presence of spontaneous polarization in both wz-(0001) and zb-(111) superlattices. For the latter system, such an effect has been commonly neglected. The built-in electric field in the well region is calculated to be about $5.1 \pm 0.3$ and $1.4 \pm 0.4$ MV/cm in wz-(0001) and zb-(111) superlattices, respectively. This phenomenon leads to a remarkable electron-hole spatial separation. Interestingly, the strain-induced piezoelectric effect, which is mainly determined by the barrier region, plays a reverse role in affecting the strength of the electric field for wz-(0001) and zb-(111) superlattices. Spontaneous polarization dominates the contribution to the electric field in both systems, and the strain-induced piezoelectric polarizations are estimated to contribute only about 5% for the wz-(0001) superlattices and about 30% for the zb-(111) systems. Both zb-GaN/AlN(100) and zb-GaN/AlN(110) systems have virtually constant core-level $N\,1s$ binding energies in the well and barrier regions and, consequently, no internal electric fields in the growth direction. The zb-GaN/AlN(100) superlattices are predicted to exhibit stronger quantum confinement effects compared to zb-GaN/AlN(110). In both systems, confinement effects lead to a marked band gap increase with decreasing thickness of the superlattice period. Tensile (compressive) strain leads to smaller (larger) band gap values.

ACKNOWLEDGMENTS

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Note that the VBM and CBM are located around, but not exactly at the position of the interface due to the hybridization between these two conduction bands. In a recent study, we demonstrated the continuous tunability of the band gap and strength of the built-in electric field in GaN/AlN superlattices by control of the thickness of both the well and barrier.

This is only valid for superlattices with similar thickness of barrier and well. In a recent study, we demonstrated the continuous tunability of the band gap and strength of the built-in electric field in GaN/AlN superlattices by control of the thickness of both the well (GaN) and barrier (AlN) regions. For more details see, X. Y. Cui, D. J. Carter, M. Fuchs, B. Delley, S.-H. Wei, A. J. Freeman, and C. Stampfl, Phys. Rev. B 81, 155301 (2010).

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