

# Surface segregation and interface stability of AlN/GaN, GaN/InN, and AlN/InN {0001} epitaxial systems

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(Received 29 July 1999)*

Surface segregation in wide band-gap nitride alloys was studied using *ab initio* calculations. In agreement with recent experiments we find that  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  {0001} surfaces prefer Ga termination, and  $\text{Ga}_x\text{In}_{1-x}\text{N}$  and  $\text{Al}_x\text{In}_{1-x}\text{N}$  {0001} prefer In termination. The segregation energy is found to depend critically on the type of surface reconstruction. For cation-terminated reconstructions on both the (0001) and (000 $\bar{1}$ ) surfaces the segregation energies are similar and an order of magnitude larger than in the arsenides or Si/Ge systems. The largest segregation energy of about 3.6 eV is found for the AlN/InN surface. In contrast, segregation effects for the N-adatom  $2 \times 2$  reconstruction on the (0001) surfaces are strongly suppressed. At AlN/GaN and GaN/InN interfaces the segregation effects are very weak and should not affect their morphology. Our results suggest the choice of optimal conditions of growth that lead to sharp interfaces and longer lifetimes of carriers in III-nitride heterosystems.

## I. INTRODUCTION

Semiconductor-based optical and microelectronic devices rely on the controlled epitaxial growth of heterostructures. In turn, the quality of these heterostructures reflects the atomic-scale morphology of the interfaces of which they are comprised. Interfacial roughness may strongly influence the properties of the electrons and holes confined to quantum wells and, in particular, affect carrier mobilities and recombination lifetimes. For this reason, the interface profiles of  $\text{Ga}_x\text{In}_{1-x}\text{N}/\text{GaN}$  (Ref. 1) and  $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$  (Ref. 2) heterostructures have recently been examined experimentally. In both cases, these studies revealed strongly asymmetric interfaces, with one being more abrupt than the other. This effect has previously been observed in Si/Ge (Ref. 3) and III-V (Refs. 4–7) heterosystems, and has been explained on the basis of surface segregation, i.e., the tendency of an alloy surface to be preferentially terminated by one of its components. The similarity of the chemical profiles of the quantum wells observed in the nitrides to those of the above systems suggests that surface segregation is the main mechanism responsible for the formation of the smeared interfaces. This conjecture is strongly supported by the recent observation of pronounced In segregation on the GaInN (000 $\bar{1}$ ) surface by Chen *et al.*<sup>8</sup> using Scanning Tunneling Microscope. Importantly, the usage of segregating In as a surfactant during GaN or  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  epitaxy leads to improved surface morphology, crystalline quality, and optical properties.<sup>9–11</sup>

The present paper investigates the energetics of surface segregation in AlN/GaN, GaN/InN and AlN/InN heterosystems. We analyze the technologically important {0001} surfaces of the wurtzite phase and concentrate on the segregation process that occurs between the free surface and the first two subsurface layers. This assumption will not hold for very

low growth rates, when thermodynamic equilibrium between the surface and the bulk may be achieved.<sup>12</sup> Furthermore, we observe that the actual morphology of interfaces is determined not only during growth, but may also change during annealing,<sup>13</sup> which in general is a necessary phase in the post-growth processing of devices. For this reason, the second part of the paper analyzes the thermodynamic stability of interfaces against interdiffusion. A comparison of the segregation processes at a free surface and an interface reveals the surface-specific effects that drive surface segregation.

The III-nitrides differ from other previously studied systems in two important respects. Firstly, due to a very large electronegativity of nitrogen, the chemical bonds in the nitrides are significantly more ionic in character than in the phosphides, arsenides, or antimonides. Secondly, the mismatch between the atomic radii of cations and anions is much larger in nitrides. These factors result in surface reconstructions of GaN{0001} that are qualitatively different from those observed for {111} surfaces of zinc-blende semiconductors,<sup>14,15</sup> which are the analog of the {0001} orientation in wurtzite. Another important aspect is the fact that there are two nonequivalent {0001} surfaces, the cation-terminated (0001) and the nitrogen-terminated (000 $\bar{1}$ ), or surfaces of cation and nitrogen polarity, respectively. Their properties differ in terms of reconstructions, chemical activity, and growth modes. As we show here, the segregation effects for the two surface polarities may also drastically differ, especially in the N-rich conditions of growth. An intimately related issue, characteristic of the III-nitrides, is the presence of an electric field in heterostructures, which may be both of pyroelectric and piezoelectric origin.<sup>16–18</sup> This field in, e.g., a  $\text{Ga}_x\text{In}_{1-x}\text{N}$  quantum well buried in GaN may have two orientations, and its actual direction is determined by the surface polarity of the film during epitaxy. The im-

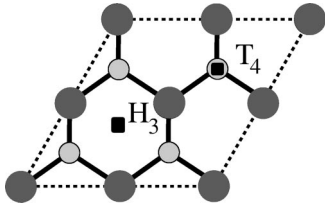


FIG. 1. Schematic top view of the (0001) GaN surface. On the Ga-polar (0001) surface, the dark atoms are gallium atoms, while the light atoms are nitrogen atoms. An adatom in the  $T_4$  site (represented by a black square inside of a light circle) sits above a subsurface atom (a light circle), while an adatom in the  $H_3$  site (represented by a black square) sits in the hollow site as shown. The dashed line outlines the  $2 \times 2$  cell.

portance of this point stems from the fact that the orientation of the field drastically affects the electronic states, and thus the properties of heterostructures<sup>19</sup> and the operation of devices.<sup>20,21,18</sup> The interplay between the surface roughness, electric field, and carrier properties is discussed in Sec. V.

Given the issues above, a study of surface segregation must take into account the reconstructions that may appear during epitaxy and both surface polarities should be considered. We carried out extensive calculations within the framework of a multigrid-based total-energy method that uses a real-space grid as the basis.<sup>22</sup> The Ceperley-Alder exchange-correlation energy<sup>23</sup> was used. Nonlocal, norm-conserving pseudopotentials<sup>24</sup> were included through the Kleinman-Bylander formalism.<sup>25</sup> A repeated slab geometry was used with a thickness of four bilayers of which the three bottom layers were kept fixed at the ideal lattice sites. For calculations of the reconstructions of the Ga-polarity surface, pseudohydrogen atoms of charge 0.75 passivated the N-terminated face, while for the study of the N-polarity face, pseudohydrogen atoms of charge 1.25 passivated the Ga-terminated surface.<sup>26</sup> A supercell with grid spacing of 0.27 a.u. was employed after a careful convergence study.<sup>27</sup> Further discussion of the calculations is given elsewhere.<sup>16,14</sup> For all studied systems the GaN substrate was assumed, and the relaxed lattice constants of AlN and InN in the  $c$  direction were found using the elastic constants calculated in Ref. 28.

## II. CATION-POLARITY SURFACES

We first analyze the cation-polarity (0001) surfaces. Previous calculations<sup>15,14</sup> have examined various  $1 \times 1$  and  $2 \times 2$  reconstructions of GaN(0001) and identified the lowest energy structures under Ga- and N-rich conditions of growth. A top view of the  $2 \times 2$  unit cell is shown in Fig. 1. There are two non-equivalent adsorption sites with hexagonal symmetry. The  $T_4$  site is on top of a nitrogen atom of the first anion layer, while the  $H_3$  is not. In the Ga-rich conditions, the reconstruction consists of a Ga adatom bonded to three surface Ga atoms at the  $T_4$  site, while in the N-rich conditions the reconstruction consists of a N adatom occupying the  $H_3$  site. This difference between the adsorption sites for cations and anions is explained by the Coulomb interaction between the adatom and the nitrogen of the first anion layer.<sup>14</sup> A very similar surface phase diagram has been calculated for AlN(0001).<sup>29</sup>

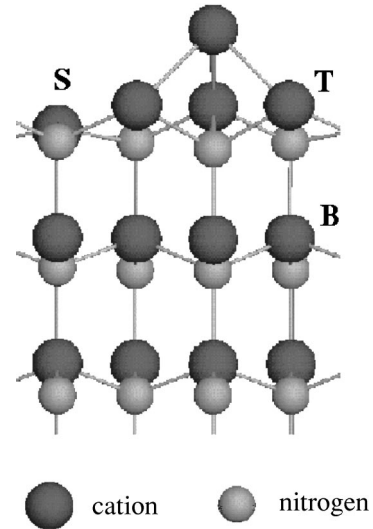


FIG. 2. Side view of the  $2 \times 2$  cell with an adatom. The dark atoms are cations, while the light atoms are nitrogen atoms.

Experimentally, even for the most investigated case of GaN the situation is quite complex, as has been comprehensively discussed by Smith *et al.*<sup>30</sup> A variety of reconstructions have been observed both during and after the growth by molecular-beam epitaxy. The best crystalline quality has been obtained in fairly Ga-rich conditions of growth. In this case many groups observe  $2 \times 2$  periodicity, sometimes considered as an indicator of optimal growth conditions, while others see only  $1 \times 1$  periodicity. The former reconstruction may be tentatively ascribed to the presence of Ga adatoms at the surface. This assignment is consistent with the recent observation of the  $2 \times 2$  and  $4 \times 4$  Ga-adatom reconstructions by scanning tunneling microscopy (STM).<sup>31</sup> On the other hand, however, Smith *et al.*<sup>30</sup> argue that the  $2 \times 2$  periodicity observed during the molecular-beam epitaxy (MBE) growth may arise from the unintentional presence of surface contaminants. For the progressively richer Ga conditions, Ga droplets form at the surface<sup>32</sup> [or In droplets on InN (Ref. 33)], the reconstruction is  $1 \times 1$ , and it possibly consists of a Ga adlayer,<sup>34,30</sup> which is in accordance with the greater density of Ga adatoms than in the  $2 \times 2$  Ga-adatom reconstruction. For the opposite N-rich limit, Smith *et al.*<sup>30</sup> argue that the  $2 \times 2$  surface seen during the growth in very N-rich conditions, or formed by nitridation,<sup>35,30</sup> may actually correspond to the N-adatom reconstruction. Finally, we mention that the sometimes observed very large surface periodicities, e.g.,  $6 \times 4$  or  $5 \times 5$ , are too large to be studied by *ab initio* methods at present.

### A. Cation-rich conditions

The side view of the adatom reconstruction preferred under cation-rich conditions is shown in Fig. 2. The surface segregation tendencies for, e.g., AlN/GaN may be characterized by the segregation energy  $E_{seg}$ , the change in the total energy upon the interchange of an Al in the surface layer and a Ga in the first subsurface layer. To calculate the segregation energy, the initial and final atomic configurations must be specified. Although the number of possible configurations that can occur at the surface during heteroepitaxy is imprac-

TABLE I. Segregation energies (in eV) for an Al adatom on GaN, an In atom on GaN, and an In atom on AlN for both surface polarities.

Site	GaN:Al	GaN:In	AlN:In
Cation polarity – cation adatom			
Adatom	0	0	0
<i>T</i>	-1.65	0.25	1.65
<i>S</i>	-2.1	0.9	2.35
<i>B</i>	-2.45	2.4	3.85
Cation polarity – nitrogen adatom			
<i>T</i>	0	0.53	0.95
<i>S</i>	-0.2	0.15	0.4
N polarity			
Surface layer	0	0	0
Buried site	-1.7	1.5	3.65

tically large, the value of the segregation energy is determined mainly by the chemical identity of the atoms participating in the segregation, and is less sensitive to other factors such as the lattice constant of the substrate, or the chemical identity of the distant neighbors. Accordingly, the energetics of segregation is analyzed in the following way: Consider, e.g., the GaN/AlN interface. We simulate the onset of the deposition of AlN on GaN(0001) by replacing a Ga adatom by an Al atom (actually, due to the  $2 \times 2$  symmetry of the unit cell, this corresponds to  $1/4$  monolayer of Al). The energy of this configuration is taken as the reference zero energy. Then, we exchange the sites of two atoms: the Al adatom and a Ga atom from the surface layer. We can continue this process by placing the Al atom in the first subsurface cation layer, etc. After the first step of segregation, Al may occupy one of two non-equivalent sites in the surface cation layer, i.e., either directly below the Ga adatom (*T* site in Fig. 2), or not (*S* site). The dangling bonds of the three cations located at the *T* sites are saturated by the Ga adatom, while the dangling bond of the cation at the *S* site is not.

In general, when a surface unit cell contains non-equivalent sites, the corresponding segregation energies should be different. In our case, the segregation energies  $E_{seg}^T$  and  $E_{seg}^S$  are 1.65 and 2.1 eV, respectively. The calculated sign of  $E_{seg}$  agrees with the experimentally observed trend: the chemically mixed  $\text{Al}_x\text{Ga}_{1-x}\text{N}(0001)$  surface prefers Ga termination. Placing Al at the buried *B* site in the second cation layer provides a further energy gain of 0.35 eV relative to the *S* site. The results for GaN:Al and for the remaining GaN:In and AlN:In configurations are summarized in Table I. The positive signs of the segregation energies in the two latter systems indicate that, in agreement with experiment, chemically mixed  $\text{Ga}_x\text{In}_{1-x}\text{N}(0001)$  and  $\text{Al}_x\text{In}_{1-x}\text{N}(0001)$  surfaces prefer In termination. Table I also shows that there is a qualitative similarity between the In configurations considered here: in all cases the segregation energy for the *S* site is higher than for the *T* site, and it increases for the second cation layer. For GaN:In, the calculated values are 0.25 eV for the *T* site and 0.9 eV for the *S* site; placing In atom in the first cation subsurface layer (*B* site) increases the total energy by 1.5 eV relative to the *S* site. The calculated segregation energies are the largest for

AlN:In(0001); we obtain  $E_{seg}^T = 1.65$ ,  $E_{seg}^S = 2.35$ , and  $E_{seg}^B = 3.85$  eV, which are one order of magnitude higher than the typical values in III-V and SiGe systems. Finally, the segregation of In on GaN and AlN affects the surface corrugation. For example, the height difference between the positions of Al adatom and the In atom at the *S* site is  $2.22 \text{ \AA}$ , while after the swap of these atoms the difference is reduced to  $1.24 \text{ \AA}$ . Such differences should be observable by scanning tunneling microscopy.

Considering the possible pathways of segregation at the (0001) surface, one intuitively expects that the exchange of sites between an Al adatom with a surface Ga at the *T* site located directly below it (i.e., the displacive adsorption of Al) is more probable than a swap with the more distant Ga at the *S* site. If this is the case, the initial energy gain is closer to  $E_{seg}^S = -1.65$  eV than to  $E_{seg}^T = -2.1$  eV. (This value should also be appropriate for the cation-rich conditions of growth, when the Ga adlayer forms and the dangling bonds of all surface atoms are saturated by adatoms.) However, after the site exchange, the segregated Ga adatom will hop to the adjacent surface site in order to denude the incorporated Al and gain thereby 0.45 eV (cf. Fig. 2). There is thus an effective repulsive interaction between Ga adatoms with the surface Al atoms, due to the difference between  $E_{seg}^T$  and  $E_{seg}^S$ . It follows from Table I that this repulsion is even stronger for InN:Ga and InN:Al surfaces. Based on this result we expect that a deposition of a fraction (close to  $1/4$ ) of monolayer of Al on GaN (or Ga on InN, etc.) may result in a chemically ordered surface with correlations between Ga adatoms and denuded Al atoms at *S* sites. An analogous chemical ordering has been observed for a  $1/2$  monolayer of Ge covering Si(001) surface,<sup>37</sup> where the surface dimers are chemically mixed and the Ge atoms occupy the ‘‘up’’ sites of the tilted dimers.

## B. Nitrogen-rich conditions

We now turn to the (0001) surfaces in the N-rich limit. Under these conditions, the  $2 \times 2$  reconstruction with the lowest energy is the N adatom located on top of three cations at the  $H_3$  site (see Fig. 1). As in the case of the Ga-adatom, each of the three sites below the adatom is denoted by *T*, while the remaining site is denoted by *S*.

To calculate the segregation energy for, e.g., GaN:Al, we compare, as above, the energies of two configurations: in the initial one, the Al atom is at the *T* site in the surface cation layer and the Ga atom is situated in the second cation layer, while in the final configuration their positions are swapped. For this segregation event we find that the segregation energy vanishes to within the precision of our calculations. For the Al atom located initially at the *S* site the segregation energy is  $-0.2$  eV. These values are one order of magnitude lower than those found for the Ga-adatom reconstruction. An analogous substantial reduction of the  $E_{seg}$  is also found for both GaN:In and AlN:In, see Table I. The physical origin of this effect is discussed in Sec. IV.

The strong decrease of the segregation energy induced by the presence of N adatoms implies that in order to effectively block the segregation the growth should occur under N-rich conditions. This procedure is expected to be particularly efficient for the deposition of a chemically pure overlayer, e.g.,



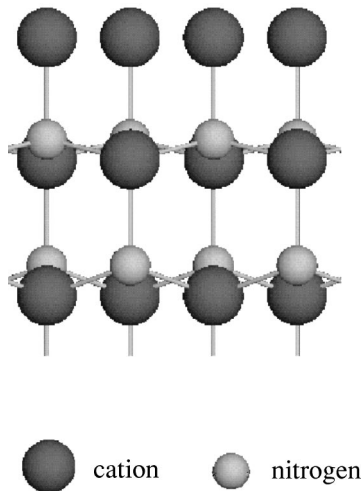


FIG. 3. Side view of the N-polarity surface with a cation adlayer. The dark atoms are cations, while the light atoms are nitrogen atoms.

GaN on InGaN, or AlN on GaN. In this case, only the onset of the deposition of the overlayer, corresponding to the formation of the GaN-on-GaN interface, should occur in the N-rich environment. For the deposition of a chemically mixed  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  layer, an elimination of the “leading edge” and “trailing edge” effects<sup>3,4,6</sup> resulting in a gradually changing composition close to interfaces would require the application of the N-rich conditions over a longer period, leading to a possible degradation of the film quality.<sup>36</sup>

### III. N-POLARITY SURFACES

We will now consider the N-terminated  $(000\bar{1})$  surfaces. The results are also given in Table I. The ground-state reconstruction of the  $\text{GaN}(000\bar{1})$  surface over a wide range of growth conditions is a  $1 \times 1$  cation adlayer,<sup>15</sup> shown in Fig. 3. We assume that this reconstruction holds for AlN and InN as well. Considering first GaN:Al, we take the configuration with one Al atom in the adlayer as the reference. A swap of Al with a Ga atom from the first subsurface cation layer provides an energy gain of 1.7 eV. A very similar value of 1.8 eV has been obtained for the  $\text{GaN}(000\bar{1})$  surface covered by one monolayer of Al, see Fig. 4(a) below; this demonstrates that the more distant neighbors have little impact on the segregation. For GaN:In and AlN:In we find 1.5 and 3.65 eV, respectively. Consequently, for this reconstruction as well as for the other cases, the segregation energies for AlN:In and GaN:In are consistently the highest and the lowest, respectively, see Table I. Moreover, In segregation for the  $(10\bar{1}1)$ -oriented GaN surface has been recently studied theoretically by Northrup *et al.*<sup>38</sup> The analyzed reconstruction consisted of a Ga adlayer on top of N atoms, in a configuration very similar to that of the Ga-adlayer on  $\text{GaN}(000\bar{1})$  surfaces. Their calculated values of the segregation energy for this orientation are 1.5 – 2.0 eV, which is very close to our value of 1.5 eV for In segregation at the Ga-adlayer on  $\text{GaN}(000\bar{1})$ . Finally, we note that these values are larger than the typical segregation energies measured for Si/Ge (Ref. 3) or other III-V (Refs. 4–6) heterosystems by as much as one order of magnitude.

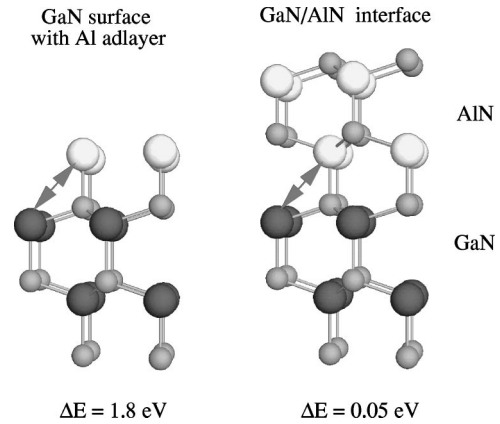


FIG. 4.  $\text{GaN}(000\bar{1})$  surface with an Al adlayer, and the corresponding GaN/AlN interface.

We now turn to the origin of these differences. In order to highlight the role of the free surface in the process of segregation, we compare segregation near a surface with that near an interface. Specifically, we analyze the  $(000\bar{1})$  surface of GaN and the GaN/AlN interface. The initial configurations of the atoms at the surface and at the interface are shown in Figs. 4(a) and 4(b), respectively. In both cases the  $(0001)$  atomic planes are chemically pure, i.e., we consider the  $\text{GaN}(000\bar{1})$  surface covered by one monolayer of Al and the ideal GaN/AlN interface, respectively. Each of the Al atoms at the surface has one broken bond, while all bonds of Al atoms at the interface are saturated. Next, we exchange the sites of two atoms, one Ga and one Al, as indicated by the arrows in Fig. 4, and allow all other atoms to relax towards a new equilibrium. Both before and after the swap the atomic configurations at the surface and at the interface are equivalent. However, the energy gain induced by the swap at the surface is 1.8 eV, while the swap at the interface provides a gain of 0.05 eV, i.e., almost two orders of magnitude less, clearly illustrating the role of broken bonds. The same explanation accounts for the large difference in segregation energies obtained for the Ga-adatom and N-adatom reconstructions of the  $(0001)$  surface. In the former case, the nature of the bonds of the segregating atoms changes and  $E_{seg}$  is large, while in the latter case the N adatom saturates the bonds of the cations lying below, which strongly reduces  $E_{seg}$ .

The large values of the segregation energies and the large differences between surface and interface segregation can be understood by considering various bond energies and their differences. The local-density-theory bond energies can be obtained from the cohesive energies  $E_{coh}$ , which are 2.31, 2.65, and 3.4 eV per bond for InN, GaN, and AlN, respectively.<sup>39</sup> In the case of surface segregation we observe that, e.g., the exchange of Al and Ga atoms between the first surface layers shown in Fig. 4(a) results not only in the change of the type of the dangling bond at the surface, but also in a change in the saturated bonds in the subsurface layers. This latter affects the total energy, since the energy of the Al-N bond is stronger than that of the Ga-N bond by 0.75 eV. Accordingly, after a swap shown in Fig. 4(a), three Ga-N bonds are replaced by three Al-N bonds, and the overall energy gain is 1.8 eV. The swap at the interface, on the other hand, does not change the number of Ga-N and Al-N bonds

in the system [cf. Fig. 4(b)], and thus the energy change is much smaller. We also note ordering of the differences between bond energies:  $\Delta E_{coh}(\text{InN-AlN}) > \Delta E_{coh}(\text{GaN-AlN}) > \Delta E_{coh}(\text{InN-GaN})$ , which is in agreement with the trend displayed by the segregation energies. Furthermore, both the cohesive energies and their differences are much larger in the nitrides than in the phosphides and arsenides, which explains why the segregation energies in the latter compounds are smaller by one order of magnitude. One should note, however, that these simple arguments are not sufficient to quantitatively explain the details of the results, since charge transfer effects accompanying surface reconstructions as well as the strain energy due to the mismatch of atomic radii play non-negligible roles.

#### IV. STABILITY OF INTERFACES

The segregation results for interfaces raise the question of stability of interfaces against intermixing. If unstable, interfaces may become broadened during growth at elevated temperatures and/or annealing.<sup>13</sup> The stability of interfaces was previously analyzed for III-V (Ref. 40) and II-VI (Ref. 41) heterojunctions. A broad interface may be regarded as an interlayer of an alloy between the two constituents of the heterostructure. Consequently, the stability of an alloy and that of a heterointerface are intimately related: a stable interface implies that the alloy is unstable and should segregate into pure constituents.

In general, lattice-mismatched III-V and II-VI alloys are unstable with respect to segregation into pure end compounds. In these systems, the dominant role is played by the excess elastic energy of distorted bonds, while the energy induced by electron transfer effects are typically smaller by one order of magnitude.<sup>42</sup> On the other hand, the instability of lattice-mismatched alloys is strongly reduced for pseudomorphic growth, when the overlayer lattice constant parallel to the interface is the same as that of the substrate.<sup>43</sup> Consequently, in spite of the fact that relaxation perpendicular to the surface may occur, one (or both) constituent of the alloy remains biaxially strained after the segregation, and its energy is appropriately higher. (For example, after a segregation within a layer of a GaInN alloy grown on a GaN substrate, the InN-rich regions are biaxially compressed.)

Turning back to interface stability, it was found that the choice of the substrate is critical: for example, the ZnSe/CdSe interface is stable when the growth is on ZnSe, but is unstable when the growth occurs on CdSe substrate.<sup>41</sup> We find here that the AlN/GaN interface is unstable when the GaN substrate is assumed: as is shown in Fig. 4, the first swap of Al and Ga across the interface lowers the energy by 56 meV. A similar value of 53 meV was found for the GaN/InN interface. The swap of the second pair of atoms lowers the total energy by another 56 meV. Finally, the exchange of the full layer of Ga with the one of Al lowers the energy by 20 meV per interface atom, which is less than for a single swap because the atoms at the interface can relax along the *c*-direction only.<sup>41</sup> These values are not large when compared to the growth temperatures of nitrides, and indicate that the main mechanism for interface broadening is surface segregation. Additional broadening of the interfaces may result from diffusion, usually mediated by native defects, during high-temperature annealing.

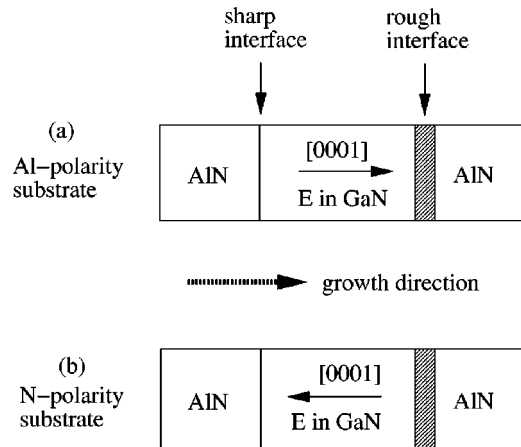


FIG. 5. Direction of the electric field in a GaN quantum well embedded in AlN after growth on Al-polarity and N-polarity substrates.

#### V. IMPACT OF THE SUBSTRATE ORIENTATION ON THE CARRIER LIFETIMES

As is well known, the scattering of free carriers by interface roughness is an important channel that limits carrier lifetimes in quantum structures. A high-quality interface is of particular importance in the wide band-gap nitrides, because alloy scattering (i.e., the scattering due to the chemical disorder in the alloy) may be dominant in these materials.<sup>19</sup>

In this section, we point out that the impact of interface roughness on electronic properties may be enhanced or diminished by the appropriate choice of substrate polarity. This possibility follows from the presence of a strong intrinsic electric field in III-N heterostructures, which is of both pyroelectric and piezoelectric origin.<sup>16,17</sup> In fact, the electric field present in a quantum well leads to localization of carriers close to one of the interfaces, depending on the direction of the field and the sign of the carrier's charge. The direction of the field is in turn determined by the polarity of the surface used for growth. On the other hand, our results show that surface segregation is largely independent of the surface orientation under cation-rich growth conditions. For both surface terminations, the deposition of AlN on GaN leads to interdiffusion and a rough interface. One may combine both factors and achieve localization of carriers close to the smooth interface by choosing an appropriate surface and growth sequence. This idea is illustrated in Fig. 5, where we show a GaN quantum well embedded in AlGaIn which is grown on Al-terminated [Fig. 5(a)] and N-terminated [Fig. 5(b)] substrate, respectively. Both the rough and the sharp interfaces are shown, together with the direction of the electric field. Longer electron lifetimes should be obtained for the case 5(a), when the field localizes electrons close to the smooth interface. The opposite geometry of Fig. 5(b) is advantageous for holes. One should stress that the actual magnitude and direction of the electric field in the GaN quantum well is the sum of the pyroelectric and piezoelectric contributions, and the latter depends on several factors, such as the lattice constant of the substrate, properties of the buffer layer, etc.,<sup>18</sup> and thus Fig. 5 serves only to illustrate the general idea.

## VI. SUMMARY

In summary, we have studied surface segregation in AlN/GaN, GaN/InN, and AlN/InN heterosystems for both (0001) and (000 $\bar{1}$ ) polarities. In agreement with experiment we find that mixed AlGaIn surfaces prefer Ga termination, and AlInN and GaInN surfaces prefer In termination. The calculated segregation energies for cation-rich conditions of growth of about 2–3 eV are unexpectedly large, being an order of magnitude higher than in III-V (Refs. 4–6) and Si/Ge (Ref. 3) systems. This large difference, and the trends in the calculated segregation energies, are explained by large cohesive energies of the nitrides. However, segregation effects on (0001) surfaces are strongly reduced in the N-rich conditions of growth. These results suggest the use of a N-rich environment to suppress segregation. A comparison with the energetics of interfaces reveals the origins of the surface-specific

effects that drive the segregation, namely the energetics of cation-N bonds and the relative energetics of dangling bonds. The AlN/GaN and GaN/InN interfaces are found to be weakly unstable with respect to interdiffusion. Finally, we point out that an appropriate choice of the substrate orientation and growth sequence may minimize the impact of interface roughness on lifetimes of free carriers confined in quantum structures. This possibility follows from the dependence of the direction of the electric field in the quantum well on the atomic scale details during growth.

## ACKNOWLEDGMENT

This work was supported in part by Grant Nos. KBN 2-P03B-093-14, ONR N00014-92-J-1477, and ONR Polaris program.

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