First-principles calculations of 2×2 reconstructions of GaN(0001) surfaces involving N, Al, Ga, In, and As atoms

V. Timon, S. Brand, S. J. Clark, M. C. Gibson, and R. A. Abram

Department of Physics, University of Durham, South Road, Durham DH1 3LE, United Kingdom

The *ab initio* studies presented here employed a pseudopotential-plane-wave method in order to obtain the minimum-energy configurations of various 2×2 GaN(0001) surfaces involving N, Al, Ga, In, and As atoms. Comparison of the various possible reconstructions allows predictions to be made regarding the most energetically favorable configurations. Such comparisons depend on the value of the effective chemical potential of each atomic species, which can be related directly to experimental growth conditions. The most stable structure as a function of chemical potentials is determined. Based on these results we have characterized the effect of N in the adlayer surface and the stability dependence with number of substitutions as a function of the model employed and the possible surfactant character of some of the added atoms. Surface phase diagrams as a function of the chemical potential have been calculated to show the phase transition between the different reconstructions.

PACS number(s): 68.35.Bs, 68.35.Rh, 71.20.Nr, 31.15.Ar

I. INTRODUCTION

When a crystal is cleaved to expose a surface, the surface atoms are left with unsaturated chemical bonds. In an effort to reduce the density of these dangling bonds, the atoms in the top few layers rearrange, giving rise to a surface reconstruction. The study of such surface reconstructions, particularly in the case of the nitrides, is attracting considerable attention due to their importance from both a technological and fundamental point of view. For the development of device fabrication processes it is essential to achieve a good understanding of the atomic-scale structural, electronic, and chemical properties of semiconductor surfaces, and that is the motivation of the current work.

In recent years the III-V nitrides GaN, AlN, and InN have emerged as important materials due to their potential optoelectronic device applications[1] and are now the subject of enormous interest. Applications are mainly in the blue and ultraviolet spectral region,[2] with recent successful progress in the industrial fabrication of wurtzite GaN-based light-emitting diodes[3] (LED's) having made the nitride semiconductors major competitors in the optoelectronic market. The electronic band gaps of the nitrides range up to 6.2 eV (Ref. 4) and hence span the entire visible region and beyond into the UV.

Under ambient conditions GaN crystallizes in the hexagonal wurtzite phase[5] but can also be grown in the cubic zincblende phase. Here we shall be concerned with the wurtzite phase, which is the equilibrium crystal structure when growth is on hexagonal substrates.[6] It should be noted that the relevant surfaces for growing wurtzite GaN are the polar (0001) and (000$\bar{1}$) orientations which are inequivalent due to their different polarity. For the cation Ga (0001) and anion N (000$\bar{1}$) surfaces each dangling bond is occupied with 3/4 or 5/4 electrons, respectively, as indicated in Fig. 1. Although epitaxial growth is possible in both directions, experiments[7] have shown that growth on (0001) is generally superior to (000$\bar{1}$) and in practice the (0001) GaN surface exhibits 1

×1, 2×2, 4×4, 5×5, and 6×4 surface unit cells,[8,9] while in the case of GaN (000$\bar{1}$), 1×1, 3×3, 6×6, and c(6 ×12) structures have been seen.[9,10]

Of all III-V semiconductors produced by crystal growth, GaN is one of the most difficult to grow in good-quality epitaxial form because there is no ideal substrate for such growth. Moreover, due to the extremely low chemical reactivity of N_2 on GaN surfaces, growth of GaN in a nitrogen atmosphere does not occur. External flow of nitrogen-containing reactive species is required to initiate the growth process. A common feature of all polar surfaces, independent of the chemical environment (Ga or N rich), is a tendency to form Ga-rich surface stoichiometry and the N adatoms are thermodynamically unstable in most cases.[11] This has important consequences for the reactivity of these surfaces. A number of studies have been made to describe the incorporation of Ga in the different GaN surface reconstructions in both cubic and wurtzite phases with adatom and adlayer configurations.[12–14] However, there are few reports of the role of N on GaN surfaces, due to the instability of these reconstructions.[9] In view of these difficulties a better fundamental understanding of the N deposition processes in GaN growth is required if higher-quality material is to be achieved. In addition to experimental methods, *ab initio* simulations[15] can provide accurate theoretical predictions of surface geometries, electronic structure, and behavior and such an approach is the subject of this paper.

In this work we have studied the mechanisms governing the GaN (0001) surface N-induced reconstruction. The GaN (000$\bar{1}$) surface has not been investigated due to the strong N-N molecular bond of 9.8 eV,[16] which will tend to lead to the formation of N molecules on the top of the surface, independent of the number of Ga atoms substituted. We have focused our attention on the 2×2 surface in the N- and Ga-rich limits in which the most stable reconstruction observed corresponds to a N-adatom (H3) structure.[17] After altering the surface energetics with regards to surfactants like arsenic, we have examined the influence of nitrogen on the

3/4 (0001 cation terminated)   **5/4** (000$\bar{1}$ anion terminated)
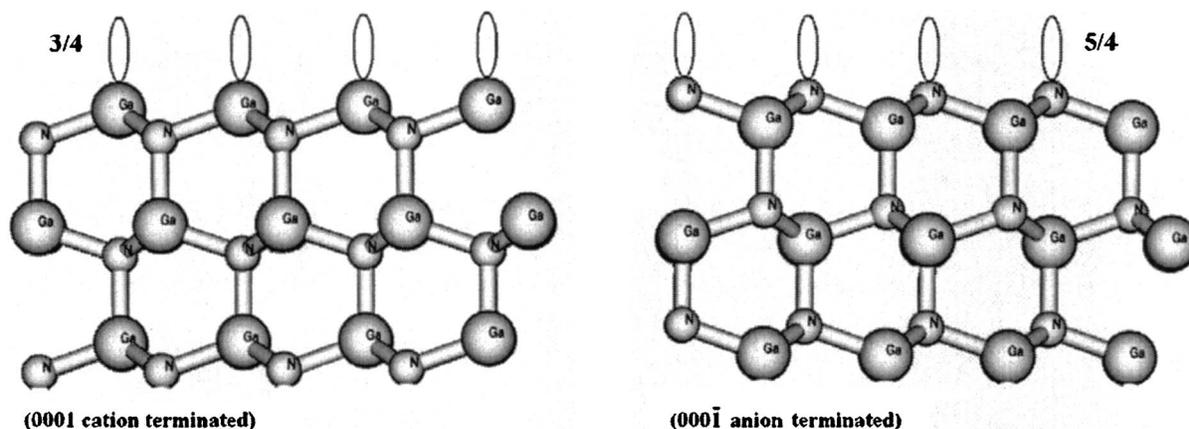
FIG. 1. Atomic structures of wurtzite (0001) and (000) GaN surfaces. The number indicates the nominal number of electrons per dangling bond.

GaN surface and compared this with the experimental results of nitrogen-rich GaNAs alloys.[18]

II. THEORETICAL MODEL

The phase diagram for the adlayer model in the GaN (0001) 2×2 reconstruction is based on density functional theory (DFT) calculations in combination with an appropriate thermodynamic model. The DFT surface calculations carried out made use of the CASTEP code[19] using the generalized gradient approximation (GGA) of Perdew and Wang (PW91).[20] The ions are described by norm-conserving, nonlocal atomic pseudopotentials in the Kleinman-Bylander form generated using the optimization scheme of Lin *et al.*,[21] except in the case of the In atom, where the ultrasoft pseudopotential proposed by Vanderbilt[22] has been used. The Ga 3d states are included within the valence band because of the demonstrable improvements in structural properties and enthalpy of formation.[23] Wave functions are expanded in a plane-wave basis set up to an energy cutoff of 800 eV and the total energy is converged to better than 0.01 eV/atom. Integrations over the Brillouin zone were performed using a $2 \times 2 \times 1$ Monkhorst-Pack set[24] sampling-point scheme for the surface supercell, which gave two special k points.

Convergence in k points and the necessary extent of the vacuum region above the surface were investigated as a preliminary to our main calculations where the total energy convergence with respect to k-point sampling and surface structure was checked by repeating the calculation with a larger $4 \times 4 \times 1$ sampling set which did not appreciably affect the results. Our calculations indicated that a supercell containing six GaN bilayers and a vacuum region equivalent to six GaN bilayers with overall approximate length of 13 Å was required. Both the energy and structural test calculations performed show that six bilayers are sufficient to describe the individual growth surface. The first four GaN bilayers are fixed in the appropriate bulk-optimized configuration in order to simulate the growth surface. The atoms in the two bilayers above the constrained layers, together with the additional adatoms and adlayer on the surface, are allowed to relax to the lowest-energy configuration commensurate with

the initial symmetry of the surface. The geometry of the surfaces is optimized by calculating the forces using the Hellmann-Feynmann theorem at every atom site and then allowing the structure to relax until all forces are reduced below a threshold of 5×10^{-2} eV/Å. The dangling bonds on the opposite surface are saturated with H atoms to reduce the finite fields that could otherwise be produced across the supercell.

The thermodynamics formalism employed follows the scheme of Quian *et al.*[25] and Northrup[26] where, to study surfaces having a varying number of atoms, the relative formation energies depend on the chemical potential of the excess atomic species. We define the formation energy[27] as

$$E_f = E_{tot} - E_{ref} - \Delta n_{Ga}\mu_{Ga} - \Delta n_N\mu_N - \Delta n_i\mu_i,$$

where E_{tot} and E_{ref} are the total energies of the adlayer covered and reference surfaces and μ_{Ga}, μ_N, and μ_i are the chemical potentials of Ga and N and the foreign chemical species (Al, In, or As atoms) introduced in the adlayer. Δn_{Ga}, Δn_N, and Δn_i represent the differences in the number of atoms of each atomic species with respect to the reference surface. In equilibrium the chemical potential of a given species is equal in all the phases that are in contact and the phase is in equilibrium with the GaN bulk so that $\mu_{Ga} + \mu_N = \mu_{GaN}$.[27] In order to avoid the formation of undesirable phases $\mu_{Ga} < E(Ga_{\alpha\text{-}gallium})$ (prevents the formation of bulk Ga), $\mu_N < E(N_2)$ (prevents N_2 molecule formation), $\mu_{Al} < E(Al_{fcc})$ (prevents the formation of bulk Al), $\mu_{In} < E(In_{bct})$ (prevents the formation of bulk In), and $\mu_{As} < E(As_{A7})$ (prevents the formation of bulk As). Al_{fcc}, In_{bct}, and As_{A7} represent the bulk phases of Al fcc, In bct, and As trigonal $A7$ metallic structures, respectively.

III. RESULTS AND DISCUSSION

We first focused our attention on bulk calculations of the crystalline structure and cohesive properties of GaN, and also of the Al fcc, α-gallium, In bct, and As trigonal $A7$ metallic structures and the N_2 molecule. This was done because the optimized GaN unit cell for the bulk will define the slab in the surface supercell used to build the geometrical

TABLE I. Calculated structural parameters and cohesive energies of bulk wurtzite GaN, α-gallium, N_2 molecule, Al fcc, In bct, and As trigonal $A7$ structures (GaN, α-gallium, and N_2 results are reproduced from our previous work in Ref. 32).

Structure	a (Å)		b (Å)		c (Å)		Distances (Å)		Cohesive energy (eV)	
	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
GaN (bulk)	3.205	3.190[a]	3.205	3.190[a]	5.222	5.189[a]	d_{GaN} 1.968 d_{GaN} 0.643	1.955/1.958[b] ≈0.65[c]	8.74	9.058[d]
α-gallium	4.43	4.51[e]	4.51	4.52[e]	7.61	7.64[e]	d_{GaGa} 2.47 d_{GaGa} 2.68	2.44[e] 2.71[f]	2.84	2.81[g]
N_2 (molecule)	—		—		—		d_{NN} 1.100	1.098[h]	4.76	4.91[g]
Al (fcc)	4.02	4.05[i]	4.02	4.05[i]	4.02	4.05[i]	d_{AlAl} 2.84 d_{AlAl} 4.02	2.86 4.05[i]	3.44	3.39[i]
In (bct)	3.30	3.24[i]	3.30	3.24[i]	5.03	4.94[i]	d_{InIn} 3.30 d_{InIn} 3.43	3.25 3.38	2.25	2.52[k]
As (Trigonal A7)	3.75	3.76[j]	3.75	3.76[j]	10.56	10.55[j]	d_{AsAs} 2.52	2.50	3.04	2.96[l]

[a]Reference 40.
[b]Reference 41.
[c]Reference 9.
[d]Reference 4.
[e]Reference 42.
[f]Reference 10.
[g]Reference 16.
[h]Reference 43.
[i]Reference 44.
[j]Reference 45.
[k]Reference 28.
[l]Reference 46.

surface, and accurate total energies are important in the comparison of surface energies to identify the most stable structure through the chemical potentials of the surface constituents. The results of a full geometric structural relaxation (atomic positions and lattice parameters) and cohesive energies of the various bulk and N_2 molecule systems are presented in Table I. The set of results for the cell parameters obtained shows good agreement with experiment (to within 1%). The cohesive energies of the solids and nitrogen molecule are very close to the experimental data (within ~0.2 eV/atom) as are the results of similar calculations.[28]

Starting from the bare GaN (0001) surface (see Fig. 2) and systematically adding N atoms and/or substituting a complete N adlayer configuration by Al, Ga, In, and As, the equilibrium geometry and formation energy for the different reconstructions have been investigated. In the case of the Ga-adlayer surface, N atoms have been replaced by Ga atoms on the top of the surface while in the Ga-adatom and N-adatom configurations only one Ga or N atom is added on the top of the bare surface in order to calculate the relative formation energies for the most energetically favorable configuration in comparison with the bare surface. The Ga chemical potential $\Delta\mu_{Ga}=\mu_{Ga}-\mu_{Ga,bulk}$ varies between $\Delta\mu_{Ga}=0$ (Ga-rich conditions) and $\Delta\mu_{Ga}=-\Delta H_f=1.15$ for GaN (N-rich conditions). In general, most of the surfaces with these substitutions are metallic and do not satisfy the electron counting rule (ECR).[29]

Figure 3 shows the relative formation energies calculated for 14 configurations, including the N (H3) and Ga (T4) adatoms on the 2×2 GaN (0001) surface. In the case of the
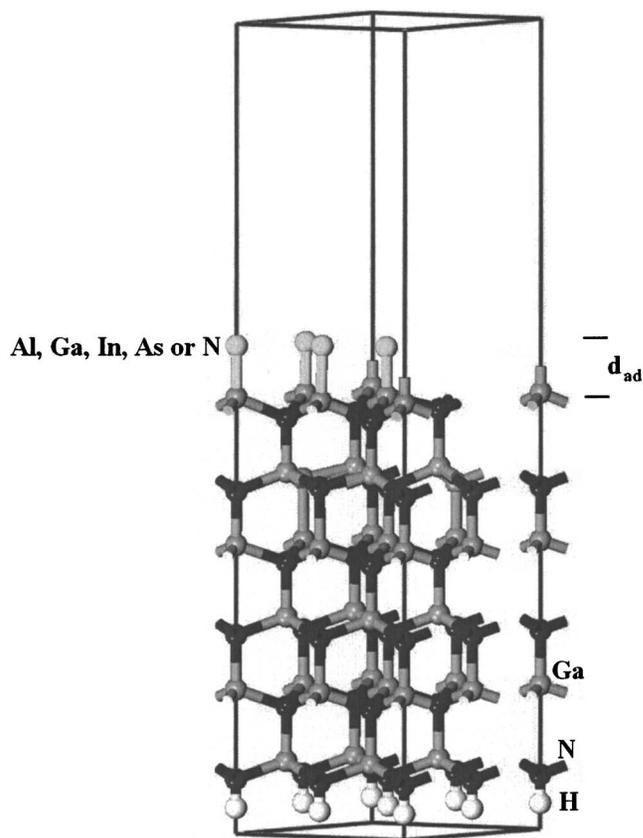
FIG. 2. (Color online) Basic 2×2 GaN (0001) wurtzite surface studied with one extra layer of atoms.

GaN 2x2 adlayer surfaces (0001)

(a)

GaN 2x2 adlayer surfaces (0001)

(b)
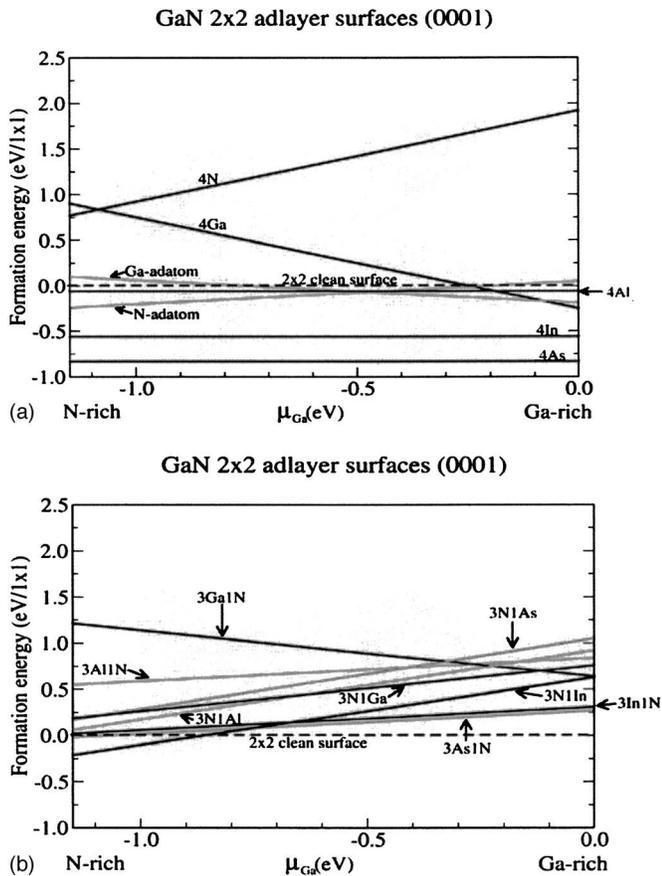
FIG. 3. (Color online) Comparison of formation energies (relative to that of the relaxed clean surface) for different 2×2 reconstructions for GaN (0001) surfaces as a function of the Ga chemical potential. (a) Formation energy of surfaces with the adlayer completely covered with N, Ga, Al, In and As. The Ga and N adatom results from our previous work (Ref. 32) are shown for comparison. (b) Formation energy of surfaces with one and three N substitutions over the completely covered adlayer surface.

results shown for Al, In, and As, the conditions are chosen corresponding to a situation in which the Al, In, and As chemical potentials are equal to their values in the bulk. Our calculations show that surface incorporation of N in the GaN adlayer is highly unfavorable, suggesting that N tends to segregate on the surface. This is because, with the introduction of small atoms (N) over a surface with bigger atoms (Ga), the system prefers to break the symmetry, thus forming low-symmetry configurations.[30] This phenomenon has been observed on the top of the GaN(0001) surface, where N atoms bind to other N atoms, forming trimers with almost similar strengths for the N-N bonds, as shown in Fig. 4. This behavior is repeated in the case of structures with three N atoms and one Al, Ga, In, or As atom in the adlayer configuration, and is independent of the kind of substituted atom. It is noted that with four N atoms the bond distance between the N atoms in the formed trimer is 1.46 Å, very close to the typical value of 1.457 Å for the N-N separation in compounds containing nitrogen and gallium.[31,32] In the case of three nitrogen atoms and one Ga, Al, or In atom in the adlayer, the nitrogen atoms join together, forming trimers on the top of
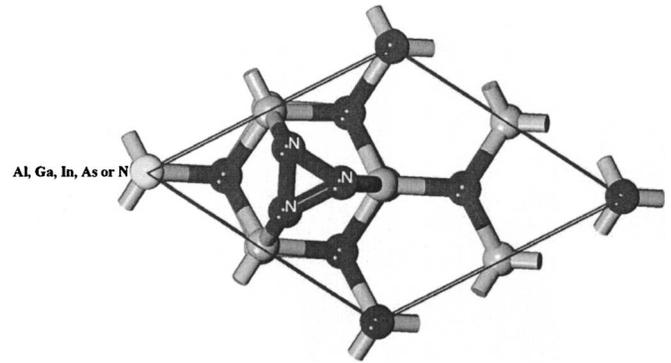
FIG. 4. (Color online) Top view of the 2×2 GaN (0001) surface with 3N atoms forming a trimer on the top of the surface.

the surface, Table II. The distance between the N atoms in the trimer formed depends on the nature of the fourth atom. In the case of group-III atoms Al, Ga, and In the N-N bond length in the trimer has a consistent value of about 1.51 Å while in the case of the As atoms it decreases to a value of

TABLE II. Calculated structural parameters of the adlayer surface relaxation corresponding with Fig. 2 (lengths in angstroms).

Surface type	d_{ad}[a]	Obs
4Ga	2.58 (Ga-Ga)	
4Al	2.60 (Al-Ga)	
4In	2.78 (In-Ga)	
4As	~2.48 (As-Ga)	As trimer 2.61
4N	1.82 (N-Ga)	N trimer 1.46
	1.89 (N-Ga)	
1N3Ga	2.61 (Ga-Ga)	
	1.92 (N-Ga)	
1N3Al	2.58 (Al-Ga)	
	1.95 (N-Ga)	
1N3In	2.75 (In-Ga)	
	1.91 (N-Ga)	
1N3As	2.46 (As-Ga)	As trimer 2.49
	1.94 (N-Ga)	
2N2Ga	2.63 (Ga-Ga)	N dimer 1.21
	1.91 (N-Ga)	
2N2Al	2.60 (Al-Ga)	N dimer 1.21
	2.10 (N-Ga)	
2N2In	2.83 (In-Ga)	N dimer ~1.21
	2.03 (N-Ga)	
2N2As	2.43 (As—Ga)	N dimer 1.17
	1.87 (N-Ga)	
3N1Ga	2.80 (Ga-Ga)	N trimer 1.51
	1.84 (N-Ga)	
3N1Al	2.75 (Al-Ga)	N trimer 1.51
	1.86 (N-Ga)	
3N1In	2.99 (In-Ga)	N trimer 1.51
	1.86 (N-Ga)	
3N1As	2.47 (As-Ga)	N trimer 1.48
	1.80 (N-Ga)	

[a]Vertical distance between top and nearest underlying atom.

1.48 Å, indicating a strengthening of the nitrogen bonds.[33] The large difference in electronegativity (Pauling scale) of nitrogen (3.04) with respect to arsenic (2.18) (Ref. 34) favors electron localization around the nitrogen atom, leading to a decreased interatomic distance between the N atoms in the trimer.

With two substitutions, the Ga atoms remain directly above the underlying Ga atoms and the two N atoms form a dimer with a separation of 1.21 Å, which is to be compared to the N_2 molecule bond length of 1.09 Å.[32] The same behavior is observed in the case of the adlayer structures 2Al2N and 2In2N with a dimer separation similar to that for 2Ga2N whereas in the case of 2As2N the dimer separation is 1.17 Å. With only one N substitution in the 2×2 unit cell, all the Ga and N atoms remain directly above the underlying Ga atoms. The N atoms do not move because in the 2×2 configuration each N atom is surrounded by Al, Ga, In, and As atoms, respectively, with the N atom in a restricted area, directly bonded to the underlying Ga atom. In the case of the group-III elements (Al, Ga, and In) the atoms remain over the underlying Ga atom with bond distances of 2.58 Å in the case of Ga-Al, 2.61 Å for Ga-Ga, and 2.75 Å for Ga-In as shown in Table II. For the arsenic 3As1N structure, the three As atoms are bonded to form an equilateral triangle with As-As bond of lengths 2.49 Å, in good agreement with similar calculations.[35]

In the optimized final surface structure for the cases of the Al, Ga, and In adlayers, the atomic positions of the adlayer atoms are always above the underlying Ga atoms. In the case of the arsenic adlayer three of the arsenic atoms form a trimer with bond lengths of 2.61 Å, similar to the trimer structure shown in Fig. 4 for the N trimer. This value is somewhat different from the 2.48 Å calculated by Ramachandran *et al.*[35] This may be due to the presence of the nearby fourth As atom affecting the trimer bond strength. The excess electron charge leads to a change in the character of the surface (the surface with an As trimer satisfies electron counting but an adlayer with four As atoms does not) and their interaction with the As fourth atom causes an increase in the bond distance between the As trimer atoms.

Returning to the calculated formation energies, we consider the 2×2 bare structure as a reference. Starting from the most unstable structure, the N adlayer, we modified this by systematically replacing all the N atoms by Al, Ga, In, and As, Fig. 3(a). The formation energies are shown in Fig. 3(a), where for purposes of comparison they are normalized to a 1×1 unit cell. For the surfaces involving Ga atoms (which can be compared with the results of Northrup *et al.*[14]), there is good agreement and similarly the In adlayer results are in good agreement with other recent work.[36] In the case of the Ga-adlayer surface the most thermodynamically stable surface is obtained under Ga-rich conditions, which is the natural tendency in the case of GaN surfaces.[37] With the Al, In, and As atoms the energies are independent of Ga chemical potential because the stoichiometry of these surfaces differs from the bare surface by the addition of four atoms of Al, In, or As alone. The Al-adlayer structure is stable by 0.07 eV compared to the clean surface, which is one explanation for the poor quality of growth in the first layer in the epitaxy of Al films over clean GaN (0001) surfaces reported by Liu *et*
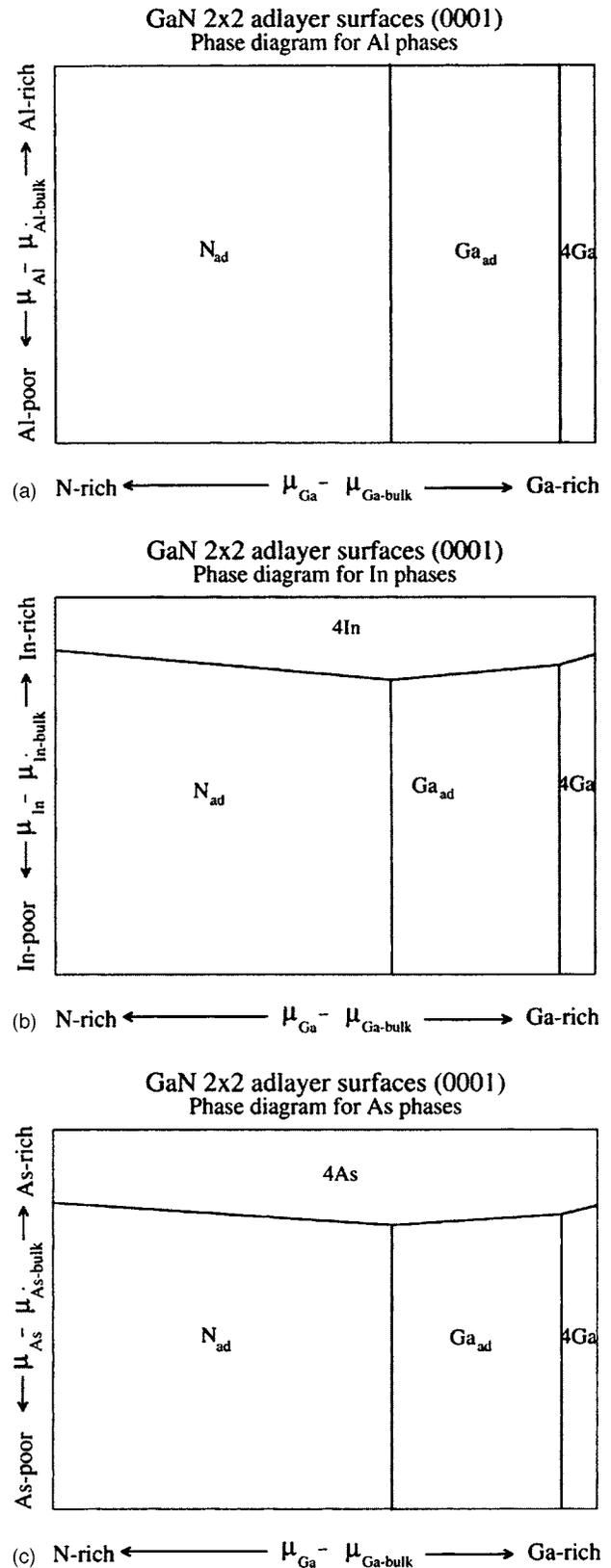
FIG. 5. Phase diagrams for the GaN (0001) surface as a function of Al and Ga, In and Ga, and As and Ga, respectively, chemical potentials. (a) Al phases. (b) In phases. (c) As phases.

al.[38] Due to the surfactant behavior of the In and As (Ref. 36) atoms these adlayer structures are the most stable of all, which is in accordance with the strong 2×2 reflection high-energy electron diffraction (RHEED) pattern[35] of As on GaN surfaces.

Figure 3(b) shows the relative formation energy of adlayer surfaces with one or three N atoms on the top of the 2×2 GaN (0001) surface. In principle it should be the case that structures with N in the adlayer configuration should be energetically highly unfavorable over the complete range of allowed chemical potentials. According to the graph, there is a tendency for the surface to be unstable as the number of N atoms increases except in the case of the 3N1In structure under N-rich conditions. All the other structures with N are unstable, independent of the kind of atom in the adlayer, and no surfactant behavior is observed. In the case of 3As1N under N-rich conditions the structure is close to being stable, but this difference is not considered significant because the energy difference is similar to the numerical errors in our calculations.

From the phase diagram and the relations between the different structures a number of conclusions may be drawn. Using the results obtained for the energetically more stable surfaces according to Fig. 3, Fig. 5 shows the phase diagrams as a function of a given Al, Ga, In, and As set of chemical potentials for the different reconstructions. Surfaces with higher energies have not been considered due to their instability.

In the case of Al substitutions, to which Fig. 5(a) refers, the incorporation of Al atoms is energetically less stable than the N- and Ga-adatom and Ga-adlayer models over the entire range of the Ga chemical potential independent of the Al concentration. This result may explain the low Al surface mobility with respect to Ga in growth over (0001) planes[39] and in the difficulty in growing good-quality Al films on GaN.[38]

Also, independent of the Al concentration and going from Ga- to N-rich conditions, the phase diagram reproduces the previously predicted surface structures (Ga monolayer, Ga adatom, and N adatom) for clean GaN surfaces with no impurities on the surface. For In substitutions, Fig. 5(b), the diagram is consistent with previous calculations made by Neugebauer *et al.*[37] It is notable that under N-rich conditions the adlayer surface corresponding to 3N1In is stable with respect to the clean surface but it does not appear in the phase diagram because it is less stable than the N-adatom, Ga-adatom, or Ga-adlayer surfaces depending on the value of chemical potential. Only if we go beyond the allowed range of the chemical potential would it appear. Thus we would not expect to observe this surface in practice.

Figure 5(c) shows the results for As substitutions. Under As-rich conditions, a stable phase is found, which is in agreement with experiment and previous theoretical results,[35] and under As-poor conditions the behavior is similar to the clean GaN (0001) surface. The As-adlayer configuration has a lower surface energy than that of the Ga adlayer, consistent with the slightly larger cohesive energy of bulk As (2.86 eV/atom) compared to that of Ga (2.81 eV/atom).

IV. CONCLUSIONS

In summary, using first-principles methods we have studied the structure and stability of the adlayer 2×2 model of the GaN (0001) surface with foreign or impurity-covered atoms. The top layer was either entirely Al, Ga, In, or As or contained a variable number of N atoms. In the case of a surface completely covered by In or As atoms, a surfactant effect of these atoms has been observed. For most of the surfaces, independent of the number of N substitutions in the top layer under Ga- and N-rich conditions, the surfaces are unstable relative to the bare Ga-terminated surface. However, we have found an N-substituted configuration containing three N atoms and one In atom with a lower energy than the bare surface configuration.

We have constructed phase diagrams for the GaN (0001) surface exposed to Al, In, and As, which shows the condition required for the existence of different phases and the relationship between the different reconstructions.

[1] *Properties of Advanced Semiconductor Materials: GaN, AlN, InN, BN, and SiGe*, edited by M. E. Levinshtein, S. L. Rumyantsev, and M. S. Shur (Wiley, New York, 2001).

[2] S. C. Jain, M. Willander, J. Narayan, and R. Van Overstraeten, J. Appl. Phys. **87**, 965 (2000).

[3] D. Xiao, K. W. Kim, S. M. Bedair, and J. M. Zavada, Appl. Phys. Lett. **84**, 672 (2004).

[4] C. Stampfl and C. G. Van de Walle, Phys. Rev. B **59**, 5521 (1999).

[5] *Properties of Group-III Nitrides*, edited by J. H. Edgar (ISPEC, London, 1994).

[6] David J. Smith, D. Chandrasekhar, B. Sverdlov, A. Botchkarev, A. Salvador, and H. Morkoc, Appl. Phys. Lett. **67**, 1830 (1995).

[7] J. Neugebauer, Phys. Status Solidi C **6**, 1651 (2003).

[8] Q. K. Xue, Q. Z. Xue, R. Z. Bakhtizin, Y. Hasegawa, I. S. T. Tsong, T. Sakurai, and T. Ohno, Phys. Rev. Lett. **82**, 3074 (1999).

[9] Fu-He Wang, P. Krüger, and J. Pollmann, Phys. Rev. B **64**, 035305 (2001).

[10] A. R. Smith, R. M. Feenstra, D. W. Greve, J. Neugebauer, and J. E. Northrup, Phys. Rev. Lett. **79**, 3934 (1997).

[11] T. K. Zywietz, J. Neugebauer, and M. Scheffler, Appl. Phys. Lett. **74**, 1695 (1999).

[12] R. Miotto, G. P. Srivastava, and A. C. Ferraz, Physica B **292**, 97 (2000).

[13] R. M. Feenstra, J. E. Northrup, and Jörg Neugebauer, MRS Internet J. Nitride Semicond. Res. **7**, 3 (2002).

[14] J. E. Northrup, J. Neugebauer, R. M. Feenstra, and A. R. Smith,

Phys. Rev. B **61**, 9932 (2000).

[15] Fu-He Wang, P. Krüger, and J. Pollmann, Phys. Rev. B **64**, 035305 (2001).

[16] J. R. Fuhr and W. L. Wiese in *CRC Handbook of Chemistry and Physics*, 77th ed., edited by D. R. Lide and H. P. R. Frederikse (CRC Press, Boca Raton, 1996).

[17] A. R. Smith, R. M. Feenstra, D. W. Greve, M. S. Shin, M. Skowronski, J. Neugebauer, and J. E. Northrup, Surf. Sci. **423**, 70 (1999).

[18] M. Gherasimova, B. Gaffey, P. Mitev, L. J. Guido, K. L. Chang, K. C. Hsieh, S. Mitha, and J. Spear, MRS Internet J. Nitride Semicond. Res. **4S1**, G3.44 (1999).

[19] M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, and M. C. Payne, J. Phys.: Condens. Matter **14**, 2717 (2002).

[20] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[21] J. S. Lin, A. Qteish, M. C. Payne, and V. Heine, Phys. Rev. B **47**, 4174 (1993).

[22] D. Vanderbilt, Phys. Rev. B **41**, R7892 (1990).

[23] C. G. Van de Walle and J. Neugebauer, J. Appl. Phys. **95**, 3851 (2004).

[24] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[25] Guo-Xin Qian, R. M. Martin, and D. J. Chadi, Phys. Rev. B **38**, 7649 (1988).

[26] J. E. Northrup, Phys. Rev. Lett. **62**, 2487 (1989).

[27] C. Bungaro, K. Rapcewicz, and J. Bernholc, Phys. Rev. B **59**, 9771 (1999).

[28] M. Fuchs, J. L. F. Da Silva, C. Stampfl, J. Neugebauer, and M. Scheffler, Phys. Rev. B **65**, 245212 (2002).

[29] M. D. Pashley, Phys. Rev. B **40**, 10481 (1989).

[30] C. G. Van de Walle and J. Neugebauer, J. Appl. Phys. **95**, 3851 (2004).

[31] D. A. Neumayer, A. H. Cowley, A. Decken, R. A. Jones, V. Lakhotia, and J. G. Ekerdt, Inorg. Chem. **34**, 4698 (1995).

[32] V. Timon, S. Brand, S. J. Clark, and R. A. Abram, J. Phys.: Condens. Matter **17**, 17 (2005).

[33] A. Costales, A. K. Kandalam, and R. J. Pandey, J. Phys. Chem. B **107**, 4508 (2003).

[34] http://environmentalchemistry.com/yogi/periodic/electronegativity.html

[35] V. Ramachandran, C. D. Lee, R. M. Feenstra, A. R. Smith, J. E. Northrup, and D. W. Greve, J. Cryst. Growth **209**, 355 (2000).

[36] J. E. Northrup and C. G. Van de Walle, Appl. Phys. Lett. **84**, 4322 (2004).

[37] J. Neugebauer, T. K. Zywietz, M. Scheffler, J. E. Northrup, H. Chen, and R. M. Feenstra, Phys. Rev. Lett. **90**, 056101 (2003).

[38] Q. Z. Liu, L. Shen, K. V. Smith, C. W. Tu, E. T. Yu, S. S. Lau, N. R. Perkins, and T. F. Kuech, Appl. Phys. Lett. **70**, 990 (1997).

[39] S. Ruffenach-Clur, Olivier Briot, Bernard Gil, Roger-Louis Aulombard, and J. L. Rouviere, MRS Internet J. Nitride Semicond. Res. **2**, 27 (1997).

[40] H. Schulz and K. H. Thieman, Solid State Commun. **23** 815 (1997).

[41] F. Grosse and J. Neugebauer, Phys. Rev. B **63**, 085207 (2001).

[42] X. G. Gong, G. L. Chiarotti, M. Parrinello, and E. Tosatti, Phys. Rev. B **43**, 14277 (1991).

[43] J. E. Northrup, R. Di Felice, and J. Neugebauer, Phys. Rev. B **55**, 13878 (1997).

[44] A. Zoroddu, F. Bernardini, P. Ruggerone, and V. Fiorentini, Phys. Rev. B **64**, 045208 (2001).

[45] D. Schiferl and C. S. Barrett, J. Appl. Crystallogr. **2**, 30 (1969).

[46] G. Zollo, J. Tarus, and R. M. Nieminen, J. Phys.: Condens. Matter **16**, 3923 (2004).