Ab initio studies of strained wurtzite GaN surfaces

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Abstract
In GaN and other group III nitrides the considerable lattice mismatch with the
substrates normally employed during growth, such as sapphire, 6H-SiC and
ZnO, can lead to the presence of strain which may affect the surface properties.
Here we have studied the effect of biaxial strain on the structure, electronic
configuration and formation energy of various GaN(0001) and $(000\bar{1})$ 1×1
surfaces. In particular, we consider the Ga and N tetrahedral (T4), hexagonal
(H3) and asymmetric top (atop) configurations. The *ab initio* total energy
calculation studies presented here employ the density functional formalism
using a pseudopotential plane-wave basis set approach in order to obtain
the minimum energy configurations of the unstrained and biaxially strained
structures. We show in bulk GaN a good linearity between the biaxial strain
imposed and the calculated structural cell parameters. The calculated formation
energies of the GaN surfaces show that the most stable configuration for the
different reconstructions is not influenced by the biaxial strain.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The group III nitride semiconductors have undergone extremely rapid development resulting
in a large number of research publications during the past few years. The intense interest in
the nitrides is due to their important applications as optoelectronic materials for violet, blue
and green light-emitting devices [1] and high frequency/high power transistors [2, 3]. The
usefulness of the materials in device applications and behaviour is a consequence of the wide
range of electronic bandgaps which reaches up to 6.2 eV [4] and the high structural stability
under irradiation [5]. However, the important applications cannot always be realized due to
the difficulty of growing the material epitaxially. The deposition processes in nitride growth
have to be understood in much greater detail if better quality materials are to be achieved,
and this is an objective where both experimental investigation and theoretical studies play an
important role [6].

GaN crystals exist in two polymorphs; the wurtzite and zincblende structures. We shall be concerned with the wurtzite form which is the equilibrium crystal structure when epitaxial growth is on hexagonal substrates [7] along the [0001] or [000$\bar{1}$] axes. It should be noted that the [0001] and [000$\bar{1}$] directions of wurtzite GaN are inequivalent due to the different polarity: by convention the [0001] direction, or Ga face, has a Ga dangling bond pointing perpendicular to the surface in the [0001] direction in the ideal case, whereas the ideal [000$\bar{1}$], N face, is terminated by N dangling bonds. In practice the (0001) GaN surface exhibits 1×1, 2×2, 4×4, 5×5 and 6×4 surface unit cells [8, 6], and in the case of GaN(000$\bar{1}$)1×1, 3×3, 6×6 and c(6×12) structures have been seen [9, 6].

Significant problems encountered when growing and using GaN epitaxial films relate to the lattice mismatch with the substrate and the difference in the thermal expansion coefficients between epitaxial layers and substrate [10]. These will affect the surface properties due to the resultant biaxial stress. The lattice mismatch between wurtzite group III nitrides and, for example, hexagonal 6H-SiC and ZnO substrates is about 4%, while that of GaN with sapphire is ~15% [1]. As the temperature changes the mismatch can change and therefore it is important to find a high quality substrate in order to minimize these two effects.

In this work we have carried out an investigation of the effect of lattice strain on the structural and electronic properties of wurtzite GaN as this could potentially affect the deposition of Ga and N atoms during the growth process. In particular, we have examined the formation energy as a function of chemical potential with different biaxial strains. We report the results of *ab initio* density functional calculations used to investigate the effect of biaxial strain on the various 1×1 clean and adatom surface reconstructions of GaN(0001) and GaN(000$\bar{1}$).

2. Theoretical model

The calculations of the total energy and atomic structures were performed in the framework of density-functional theory (DFT) using the generalized gradient approximation (GGA) of Perdew and Wang (PW91) [11] as implemented in the CASTEP code [12]. More details of such calculations can be found in [12] and references therein but we present a brief summary below. The electron–ion interactions were described by norm-conserving, non-local atomic pseudopotentials generated using the optimization scheme of Lin *et al* [13] in the Kleinman–Bylander form. The Ga 3d states were included in the valence band because we have found that if they are considered as part of the frozen pseudopotential core the error in the surface energy calculation is significant. The valence electron wavefunctions were expanded in a plane-wave basis set up to a kinetic energy cut-off of 900 eV. This converges total energy differences to better than 1 meV/atom. The minimization of total energy was performed using a pre-conditioned conjugate gradient algorithm. Brillouin zone integrations were performed using a Monkhorst–Pack [14] sampling scheme dense enough to give a similar energy convergence to the basis set cut-off.

We used a plane-wave basis set (due to the high accuracy that can be achieved in electronic structure calculations since, when sufficiently converged, the basis set can also be considered complete) and therefore had to impose periodic boundary conditions in all three spatial directions. Therefore, to model a surface, we used a supercell approach in the direction perpendicular to the surface. The convergence with respect to supercell size has been tested and it was found that a supercell containing six GaN bilayers and 10 Å of vacuum was adequate. Furthermore, test calculations performed on the total energy and structural parameters showed that four bilayers are sufficient to describe the individual growth surface; hence the first four GaN bilayers are fixed in the strained and unstrained bulk optimized configurations. All of

Table 1. Calculated structural parameters and cohesive energies of bulk wurtzite GaN, α-gallium and the N_2 molecule are shown.

Structure	a (Å)		b (Å)		c (Å)		Distances (Å)		Cohesive energy (eV)	
	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp
GaN (bulk)	3.204	3.190[a]	3.204	3.190[a]	5.218	5.189[a]	d_{GaN}1.966	1.955/1.958[b]	9.69	9.058[d]
α-gallium	4.39	4.51[c]	4.52	4.52[c]	7.62	7.64[c]	d_{GaGa}2.46	2.44[c]	2.84	2.81[f]
N_2(molecule)	—		—		—		d_{NN}1.101	1.098[e]	5.70	4.91[f]

[a] Reference [29].
[b] Reference [30].
[c] Reference [31].
[d] Reference [4].
[e] Reference [32].
[f] Reference [33].

the other atoms including adatoms on the surface were allowed to relax to their lowest energy commensurate with the initial symmetry of the surface. The dangling bonds on the opposite surface were saturated with fractionally charged H atoms to reduce the electric field that could otherwise be introduced across the supercell. This approach significantly reduces the size of the supercell required to give satisfactory convergence of the total energy and structural parameters of the surface.

In order to study the modified surfaces, which have a different number of atoms, a consistent and meaningful definition of the formation energy E_{form} is required. Such a definition is [6]

$$E_{form} = E_{tot} - E_{bare} - \Delta n_{Ga}\mu_{Ga} - \Delta n_N\mu_N$$

where E_{tot} and E_{bare} are the total energies of the 1×1 covered adlayer and bare surfaces, μ_{Ga} and μ_N are the chemical potentials of Ga and N respectively and Δn_{Ga} and Δn_N represent the differences in the number of atoms of each atomic species per unit cell. This formation energy has been calculated as a function of the chemical potential of one of the constituents (Ga) in the thermodynamically allowed range of the Ga chemical potential [15]

$$\mu_{Ga}^{bulk} - \Delta H_f < \mu_{Ga} < \mu_{Ga}^{bulk}$$

μ_{Ga}^{bulk} being the chemical potential of Ga in its bulk phase and ΔH_f the heat of formation of GaN. The total energy per atom is calculated at zero temperature. The maximum chemical potential for Ga is equal to the energy per atom for the orthorhombic α-gallium structure [16], implying that $\mu_{Ga} < E(Ga_{\alpha\text{-gallium}})$. In the case of the N adatom the maximum chemical potential is equal to the energy per atom of molecular nitrogen; we therefore have $\mu_N < E(N_2)$.

3. Results and discussion

3.1. Bulk and surface reconstruction

The main geometrical parameters and cohesive energies calculated from a full geometric structural relaxation (atomic positions and lattice parameters) for the α-gallium structure, bulk GaN and the nitrogen molecule are shown in table 1. We find that there is good agreement in the calculations with the experimental values, and in particular, the calculated heat of formation (ΔH_f) for bulk GaN, 1.15 eV, being very close to the experimental value of 1.1 eV [17].

A range of calculations have been carried out on the strained bulk GaN unit cell including the evaluation of the internal parameter u, normalized volume V/V_0 (V_0 is the unstrained unit

Table 2. Calculated bulk GaN unstrained and strained unit cell parameters. Values in brackets are from [10].

Biaxial strain (%)	a, b (Å)	c (Å)	V (Å^3)	u	V/V_0	c/c_0	c/a
+4	3.332	5.110	49.149	0.388	1.06	0.98	1.5334
+2	3.268	5.164	47.771	0.382	1.03	0.99	1.5800
				($\sim$0.382)	(1.03)	(0.99)	($\sim$1.575)
0	3.204	5.218	46.403	0.377	1.00	1.00	1.6286
	(3.145)	(5.111)	(43.780)	(0.377)	(1.00)	(1.00)	(1.6252)
−2	3.140	5.268	44.988	0.373	0.97	1.01	1.6776
				($\sim$0.372)	(0.97)	(1.01)	($\sim$1.675)
−4	3.076	5.333	43.713	0.368	0.94	1.02	1.7335

cell volume and V the strained unit cell volume), normalized lattice constant c/c_0 (c is the strained c lattice constant and c_0 the unstrained c lattice constant) and the ratio of the lattice constants c/a. The results of these calculations are presented in table 2, which can be seen to be in good agreement with the previous bulk results [10]. The bulk unit cell results are also in good agreement with respect to the experimental values shown in table 1. This is important for later calculations because the optimized unit cell results calculated for the bulk are used in the creation of the supercells in the surface calculations.

We now consider the GaN surfaces. The electron counting rule (ECR) [18] is a useful concept in the study of semiconductor surfaces. It is an empirical rule which states that the equilibrium surface is that in which the number of available electrons in the surface layer will exactly fill all dangling-bond states in or near the valence band and leave all states in or close to the conduction band empty. Although exceptions to this principle have been reported [19, 20], the main consequence is that a surface satisfying the ECR should be semiconducting. Using the ECR, the surfaces considered in the present work for the [0001] and [000$\bar{1}$] directions are expected to be metallic due to the presence of dangling bonds. The surfaces have N and Ga atoms which are sp^3 hybridized, such that each N atom contributes $5/4e$ to each of the four neighbouring Ga bonds and in the Ga layer each Ga atom contributes $3/4e$ to each of the four neighbouring bonds. The Ga top layer of atoms in 1×1 GaN(0001) or the N top layer atom in the GaN(000$\bar{1}$) surface each remains with one dangling bond and three back bonds connecting them with their three nearest neighbours (N or Ga respectively) on the second substrate layer. A dangling-bond band is easily identified in the energy gap region of the associated bandstructure, as discussed below, and thus we have a metallic surface [6].

Figure 1 shows the top (a) and side (b) views of the surface reconstruction with the p(1×1) symmetry structure employed in this study. The adsorption sites considered in this symmetry are the T4, H3 and atop position adlayers. All of these surface reconstructions are studied for both anion (000$\bar{1}$) structures and cation (0001) terminated surfaces.

3.2. Cation terminated surface

The positions of the Ga and N atoms were allowed to relax to their lowest symmetry-constrained energy configuration for each of the different scenarios. The most stable configurations of the Ga adlayers studied in the unstrained and strained GaN(0001) surfaces are shown in table 3 where the interlayer distances are given (according to the notation in figure 1) and where a comparison can be made with the calculated bulk values. The value of the adlayer distance d_{ad} in the unstrained and strained surfaces in the atop position is $\sim$2.50 Å. This value is similar to the distance between Ga atoms in the α-gallium structure, the Ga-dimer distance

(a)

dark grey = adatom
dark = Ga atom
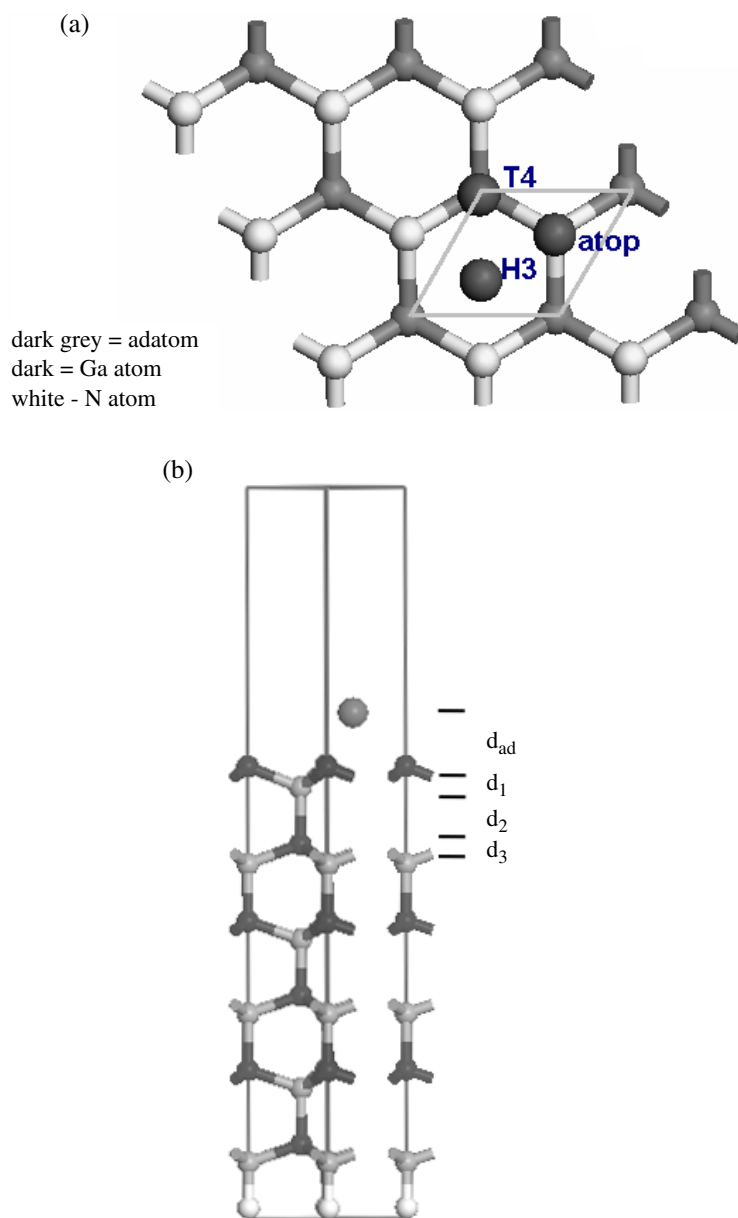white - N atom

(b)

Figure 1. (a) A top view of the T4, H3 and atop adsorption sites; the H3 site is also shown in (b), side view with the notation used for the interlayer distances.

being 2.44 Å [21] and slightly greater (0.04 Å) than the distance in a previous calculation realized in a laterally contracted Ga monolayer structure [22] due to DTF formalism [23] our GGA calculation overestimates the distance with respect to the LDA reference calculation. In the case of the H3 and T4 configurations, the value of d_{ad} is smaller. In the H3 case the adatom sits with a 'hole' beneath it in which there are no directly underlying atoms. In the T4 case the nearest directly underlying atom is nitrogen in the subsurface layer, so the Ga

Table 3. Distances (in Å) of the structural parameters calculated for unstrained and strained bulk GaN and for the relaxed (0001) surface relaxation. An explanation of the definitions of the parameters is shown in figure 1(b).

System	Surface unstrained				Surface strained +4%				Surface strained −4%			
	d_{ad}	D_1	d_2	d_3	d_{ad}	d_1	d_2	d_3	d_{ad}	d_1	d_2	d_3
Clean		0.72	1.98	0.67		0.51	1.97	0.45		0.75	1.92	0.66
Ga(H3)	2.29	0.71	1.94	0.63	2.11	0.60	1.91	0.48	2.22	0.75	1.90	0.65
Ga(T4)	2.35	0.72	1.95	0.65	2.11	0.61	1.92	0.46	2.24	0.76	1.89	0.64
Ga(atop)	2.56[a]	0.70	1.93	0.64	2.51[a]	0.56	1.92	0.46	2.49[a]	0.71	1.87	0.63
Bulk		0.64	1.97	0.64		0.57	1.98	0.57		0.70	1.96	0.70

[a] d_{ad}(exp): (Ga–Ga)$_{bulk}$ ∼ 2.7 Å [9], (α-gallium) ∼ 2.44 Å [31]. d_1, d_3(exp) ∼ 0.65 Å [6]. d_2(exp) ∼ 1.96 Å [30].

adatom is found closer to the Ga surface layer in both cases. When positive or negative strain is applied, the value of d_{ad} is less than the corresponding value for the unstrained structure for all adatom configurations. We note that there is a decrease of the value of the distance between the surface and first subsurface atoms, d_1, with positive strain and an increase with negative strain for all adatom configurations, which is consistent with a simple Poisson effect response. In all strained and unstrained configurations we find that d_3 is less than d_1 whereas these, of course, have the same value in the bulk material.

Figure 2 shows the relative formation energies calculated for seven configurations, including the bare surface and the Ga-covered and N-covered GaN(0001) surfaces in the unstrained and strained configurations. The most stable structures for both strained and unstrained surfaces are those with the Ga-covered adsorbate while the N-covered surfaces are unstable. These results are in good agreement with experimental data where the 1×1 hexagonal surface is obtained in Ga-rich growth, and also in good agreement with theoretical studies in a bilayer and monolayer model [22] and previous calculations in unstrained 1×1 reconstructions [6]. The clean strained surfaces have formation energies which are less stable by about 0.5 eV with +4% of biaxial strain, and 1 eV with −4% of biaxial strain compared to the unstrained surface. In Ga-covered or Ga-rich conditions in the unstrained surface we find that the three configurations have very similar formation energies (within 0.06 eV per 1×1 unit cell) with the Ga adatom preferring the T4 position, the H3 position being slightly less stable, and finally, the atop position having the highest formation energy. In the case of strained surfaces with +4% biaxial strain the most stable arrangement has the Ga adatom in the T4 position followed by H3 with a similar formation energy (within 0.04 eV per 1×1 unit cell) and separated from the atop position configuration by 0.08 eV; this is the same ordering as in the unstrained case. With −4% biaxial strain the atop position remained the least stable with a difference in energy of 0.02 eV higher than the atop, while H3 is the lowest energy configuration structure, being 0.03 eV below the calculated energy for the T4 position. In practice the energy difference in the latter case is rather small and therefore is not a strong indicator of a change in the stability of the different configurations due to the strain. Thus these results reveal no significant change in the ordering of the different reconstructions with strain.

To consider that the interactions of the adatoms with the surface can, at least in part, be described by Coulombic interactions with the surrounding atoms it is a useful exercise to perform a Mulliken-type analysis on the system. There is no unique method to partition the electronic charge density into atomic charges, but here we expand the electronic wavefunctions in an atomic orbital basis set (as used in the pseudopotential generation), which at least gives
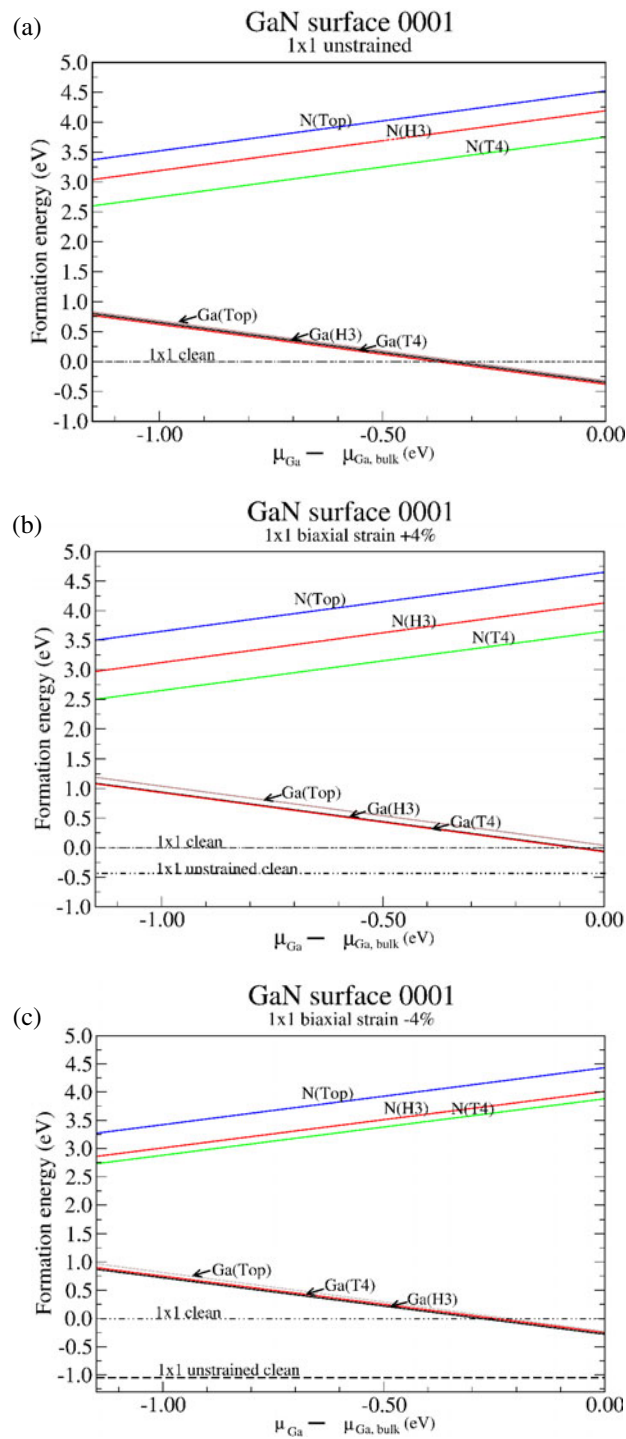
Figure 2. Comparison of formation energies, relative to that of the relaxed clean surface, for different models of strained and unstrained GaN(0001) surfaces as a function of the chemical potential μ_{Ga} for the allowed range: (a) the results for the unstrained surface; (b), (c) the results with a strain of +4% and −4%.

Table 4. Distances (in Å) of the structural parameters calculated in bulk GaN and for $(000\bar{1})$ surface relaxation corresponding to figure 1(b).

System	Surface unstrained				Surface strained +4%				Surface strained −4%			
	d_{ad}	d_1	d_2	d_3	d_{ad}	d_1	d_2	d_3	d_{ad}	d_1	d_2	d_3
Clean		0.41	2.10	0.66		0.35	1.97	0.48		0.53	2.02	0.71
Ga(H3)	1.90	0.73	2.00	0.69	1.80	0.65	1.93	0.57	1.71	0.78	1.89	0.68
Ga(T4)	2.04	0.73	2.00	0.70	1.97	0.66	1.92	0.54	1.80	0.81	1.87	0.67
Ga(atop)	2.05[a]	0.67	2.02	0.69	2.03[a]	0.59	1.95	0.56	1.99[a]	0.73	1.96	0.72
Bulk		0.64	1.97	0.64		0.57	1.98	0.57		0.70	1.96	0.70

[a] d_{ad}(exp)(Ga–N) $\sim d_2$(exp) ~ 1.96 Å [30]. d_1, d_3(exp) ~ 0.65 Å [6].

a well defined methodology [24, 25]. There exist other methods (fitting potentials etc) but in general each method tends to give the same trends, if not exactly the same numerical value of atomic charge. The Mulliken charge on the Ga adatom is $-0.06e$ in both the unstrained and strained (4%) configurations; the Ga top surface atom charge values are 0.82 and 0.83 and for the N subsurface atom we obtain -1.05 and -1.04 respectively in the unstrained and strained (4%) situations. In figure 3 we show the electronic charge density for the atop reconstruction along the $[11\bar{2}0]$ direction for the unstrained and 4% strained GaN(0001) surfaces. It can be seen that the electronic charge density decreases near the Ga adatom due to the electropositive character of this atom, and there is transfer of electron charge to the N atom. This is due to the strong ionic bonding between Ga and N in GaN where the charge is transferred from Ga to the N atom in agreement with similar calculations [26]. In both figures there is an accumulation of charge between the surface Ga atoms. This increase in the Ga–Ga interaction is clearly one indication of the presence of a metallic bond which is confirmed in the bandstructure calculation shown in figure 4. In this figure we can see in the middle of the bandgap one partially occupied band (labelled M) induced by the adatom which appears in the unstrained and strained surfaces. It can be seen that the characteristics of this band are not significantly altered by the existence of a 4% strain, indicating that the electronic properties of the surface remain similar to the unstrained case.

3.3. Anion terminated surface

Comparing the total energy results that have been obtained for the $(000\bar{1})$ and (0001) surfaces shows that the $(000\bar{1})$ surfaces are energetically less stable than the (0001) surfaces. The calculated difference in energy between the cation surface (Ga face) with respect to the anion surface (N face) is approximately 1.15 eV in the unstrained and strained systems, which is in agreement with previous calculations in the case of unstrained surfaces [27]. Due to the difference in binding energy between the Ga bulk and the N_2 molecule (the strength of the N–N molecular bond is 9.76 eV [28], which is much bigger than the case of Ga bulk), the combination of clean N surfaces with N adlayer atoms leads to the formation of N_2 molecules [6]. Thus it is only necessary to consider surface reconstructions with adsorbed Ga atoms on an N-terminated surface. The calculated structural parameters of unstrained and strained GaN(000$\bar{1}$) surfaces are shown in table 4.

Figure 5 shows the relative formation energies of the four configurations involving bare and Ga-covered $(000\bar{1})$ surfaces in the unstrained and strained structures. The energies of the +4% and −4% biaxially strained clean surfaces are about 0.5 and 1 eV respectively above that of the unstrained surface; this is similar to the results for the (0001) surfaces. In both the unstrained and strained systems the differences between the H3, T4 and atop formation
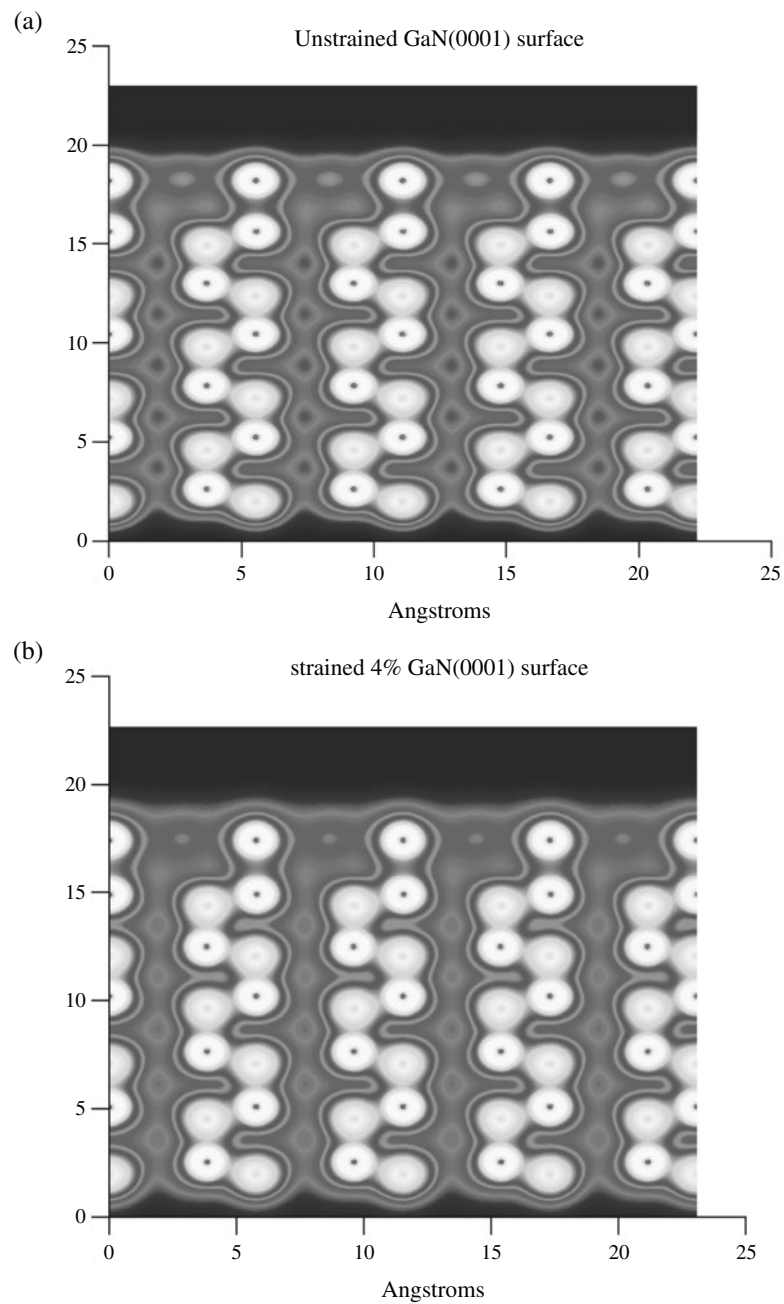
(a)

(b)

Figure 3. Here we show the total valence electron charge density in the $(11\bar{2}0)$ plane for the wurtzite GaN(0001) surfaces, Ga adlayer in atop position: (a) unstrained; (b) with a biaxial strain of +4%.

energies are greater than in the case of the (0001) surfaces. In all cases the Ga adatom in the atop position is more stable than either the H3 or T4 configurations, which is in good agreement with previous calculations [6] for unstrained systems. The differences in formation energy between the more stable atop configuration and the H3 and T4 configurations are about
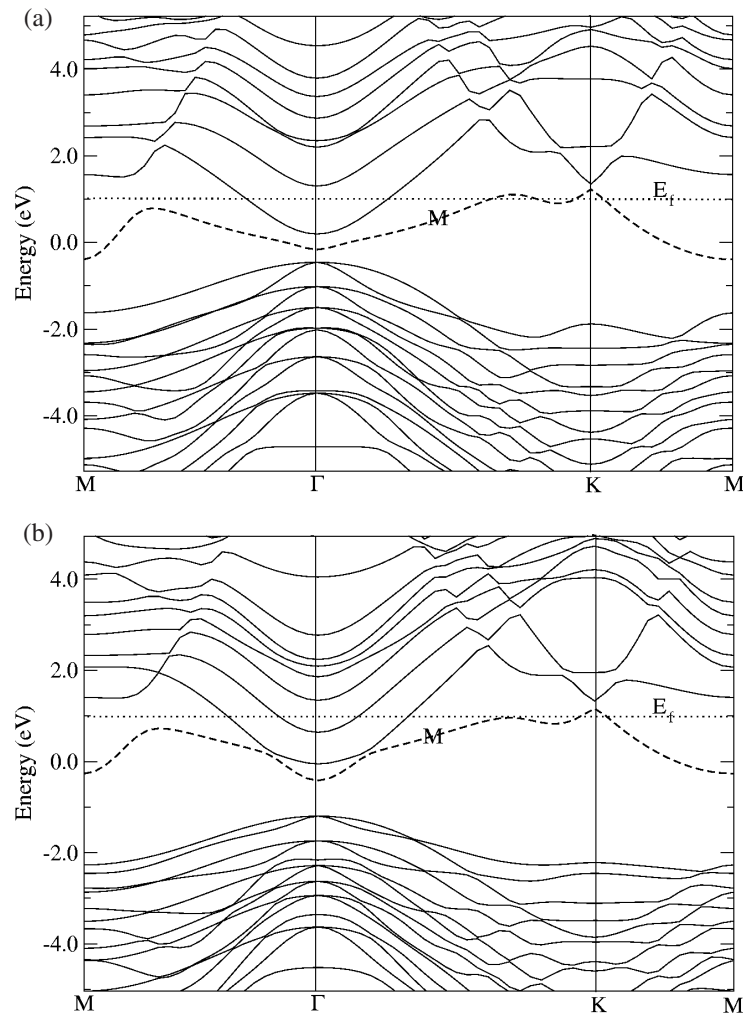
Figure 4. The surface band structure of the relaxed adlayer (atop) GaN(0001): (a) for the unstrained case; (b) with biaxial strain of +4%.

0.6 and 0.8 eV respectively for the unstrained surfaces. This difference in the ordering of the three Ga adlayer configurations is preserved in the strained surfaces, indicating that strain has no significant influence on the ordering.

The Mulliken charge analysis of the unstrained GaN($000\bar{1}$) surface for each of the Ga adatom configurations shows an atomic charge of $0.29e$ for the T4 Ga adatom, 0.31 for H3 and 0.26 for the atop position. No substantial changes in charge take place in the strained structures where the calculated atomic charges shows values of $0.29e$ and $0.33e$ for the T4 Ga adatom, 0.32 and 0.34 for H3 and 0.27 and 0.28 in the atop configuration for +4% and −4% strained surfaces respectively. The value of the charge of the Ga adatom in the H3 position leads to the strongest Ga–N bond which would lead us to expect a reduced value for d_{ad} and this is confirmed by the data shown in table 4. On the other hand, as in the stressed and unstressed surfaces the Mulliken values of the N surface atom and the subsurface Ga remain near the calculated values for bulk material with $1e$ for Ga and $−1e$ for N, with a maximum difference of $0.1e$.
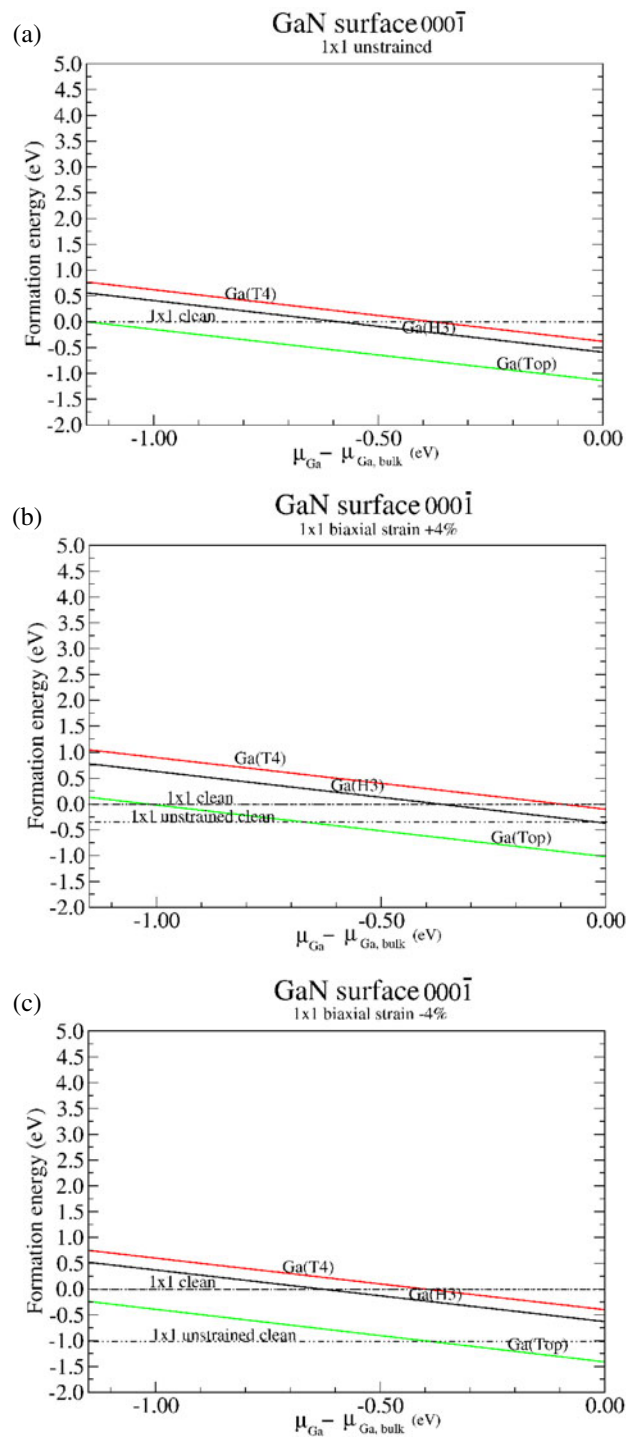
(a)

(b)

(c)

Figure 5. The adatom formation energies, relative to that of the relaxed clean surface, for different models of the strained and unstrained GaN(000$\bar{1}$) surface as a function of the chemical potential μ_{Ga} for the allowed range: (a) the results for the unstrained surface; (b), (c) the results with a strain of +4% and −4%.

4. Conclusions

We have studied the energetics of the GaN(0001) and GaN(000$\bar{1}$) surfaces under the influence of biaxial strain using first principles calculations. Application of surface biaxial strain under N-rich conditions results in surfaces that are completely unstable. The ordering of the different surface reconstructions is the same except for that of the −4% GaN(0001) surface. In practice the energy difference in the latter case is so small that we can conclude that strain does not cause any appreciable change in the ordering of the different reconstructions for either surface.

Acknowledgment

References

[1] Jain S C, Willander M, Narayan J and Van Overstraeten R 2000 *J. Appl. Phys.* **87** 965
[2] Feenstra R M, Northrup J E and Neugebauer J 2002 *MRS Internet J. Nitride Semicond. Res.* **7** 3
[3] Monemar B and Pozina G 2000 *Prog. Quantum Electron.* **24** 239
[4] Stampfl C and Van de Walle C G 1999 *Phys. Rev.* B **59** 5521
[5] Ferhat M and Bechstedt F 2002 *Phys. Rev.* B **65** 075213
[6] Wang F-H, Krüger P and Pollmann J 2001 *Phys. Rev.* B **64** 035305
[7] Smith D J, Chandrasekhar D, Sverdlov B, Botchkarev A, Salvador A and Morkoc H 1995 *Appl. Phys. Lett.* **67** 1830
[8] Xue Q K, Xue Q Z, Bakhtizin R Z, Hasegawa Y, Tsong I S T, Sakurai T and Ohno T 1999 *Phys. Rev. Lett.* **82** 3074
[9] Smith A R, Feenstra R M, Greve D W, Neugebauer J and Northrup J E 1997 *Phys. Rev. Lett.* **79** 3934
[10] Wagner J M and Bechstedt F 2002 *Phys. Rev.* B **66** 115202
[11] Perdew J P and Wang Y 1992 *Phys. Rev.* B **45** 13244
[12] Segall M D, Lindan P J D, Probert M J, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 *J. Phys.: Condens. Matter* **14** 2717
[13] Lin J S, Qtiesh A, Payne M and Heine V 1993 *Phys. Rev.* B **47** 4174
[14] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
[15] Qian G X, Martin R M and Chadi D J 1988 *Phys. Rev.* B **38** 7649
[16] Northrup J E 1989 *Phys. Rev. Lett.* **62** 2487
[17] Smith A R, Feenstra R M, Greve D W, Shin M S, Skowronski M, Neugebauer J and Northrup J E 1999 *Surf. Sci.* **423** 70
[18] Pashley M D 1989 *Phys. Rev.* B **40** 10481
[19] Whitman L J, Thibado P M, Erwin S C, Bennett B R and Shanabrook B V 1997 *Phys. Rev. Lett.* **79** 693
[20] Biegelsen D K, Bringans R D, Northrup J E and Swartz L E 1990 *Phys. Rev. Lett.* **65** 452
[21] Bernasconi M, Chiarotti G L and Tosatti E 1995 *Phys. Rev.* B **52** 9988
[22] Northrup J E, Neugebauer J, Feenstra R M and Smith A R 2000 *Phys. Rev.* B **61** 9932
[23] Jones R O and Gunnarsson O 1989 *Rev. Mod. Phys.* **61** 689
[24] Segall M D, Pickard C J, Shah R and Payne M C 1996 *Mol. Phys.* **89** 571
[25] Segall M D, Shah R, Pickard C J and Payne M C 1996 *Phys. Rev.* B **54** 16317
[26] Rapcewicz K, Buongiorno Nardelli M and Bernholc J 1997 *Phys. Rev.* B (RC) **56** R12725
[27] Neugebauer J, Zywietz T, Scheffler M and Northrup J 2000 *Appl. Surf. Sci.* **159/160** 355–9
[28] Fuchs M, Da Silva J L F, Stampfl C, Neugebauer J and Scheffler M 2002 *Phys. Rev.* B **65** 245212
[29] Schulz H and Thieman K H 1977 *Solid State Commun.* **23** 815
[30] Grosse F and Neugebauer J 2001 *Phys. Rev.* B **63** 085207
[31] Gong X G, Chiarotti G L, Parrinello M and Tosatti E 1991 *Phys. Rev.* B (RC) **43** 14277
[32] Northrup J E, Di Felice R and Neugebauer J 1997 *Phys. Rev.* B **55** 13878
[33] Lide D R and Frederikse H P R (ed) 1996 *CRC Handbook of Chemistry and Physics: a Ready-Reference Book of Chemical and Physical Data* (student edn) (Boca Raton, FL: CRC Press)