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Theoretical adlayer surface morphology of wurtzite 2×2 reconstructions of the GaN(0001) surface

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Abstract

In the first-principles calculations presented here we employ a density functional formalism using a pseudopotential plane-wave basis set in order to obtain the minimum energy configurations of various GaN(0001) 2×2 surfaces involving N atoms. The calculated formation energies of the 2×2 ideal model are compared with a previously proposed laterally contracted Ga bilayer model. We show how the order and stability of the different reconstructions are influenced by the choice of the standard 2×2 ideal or contracted bilayer model. On the basis of these results, we have characterized the effect on the adlayer surface of N segregation on the top of the surface, and the stability dependence on the number of substitutions for the different models employed. Our results predict that not all the adlayer structures containing nitrogen are unstable relative to the commonly considered N (H3) adatom configuration.

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

1. Introduction

The III–V nitrides GaN, AlN and InN are important materials due to their potential optoelectronic device applications [1] and are the subject of enormous current research interest. Applications are mainly in the blue and ultraviolet spectral region [2], with recent progress in the industrial fabrication of wurtzite GaN-based light-emitting diodes (LEDs) [3] having made the nitride semiconductors major competitors in the optoelectronics market. This is mainly a consequence of the size of their electronic band gaps, which are thought to range up to 6.2 eV [4]. However, good quality epitaxial material is difficult to produce due to growth problems and this has limited the development of GaN-based technology. In view of these difficulties, a fundamental understanding of the deposition processes in nitride growth is required if better quality material is to be achieved, and this is an objective where both experimental investigations and theoretical studies such us *ab initio* simulations play an important role [5].

Under ambient conditions GaN crystallizes in the hexagonal wurtzite phase [6] but can also be grown in the cubic zinc-blende phase. Here we will be concerned with the wurtzite form because this is the equilibrium crystal phase when growth is on hexagonal substrates [7]. 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 polarities: 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 an N dangling bond orthogonal to the surface. For the cation Ga (anion N) each dangling bond is occupied with 3/4 (5/4) electrons. Although epitaxial growth is possible in both directions, some experiments have shown that growth on (0001) is superior to that on $(000\bar{1})$ [8], and in practice the (0001) GaN surface exhibits 1×1, 2×2, 4×4, 5×5 and 6×4 surface unit cells [9, 5], while in the case of GaN$(000\bar{1})$ 1×1, 3×3, 6×6 and c(6×12) structures have been seen [10, 5].

A common feature of all polar surfaces that is independent of the chemical environment (Ga- or N-rich) is a tendency to form Ga-rich surface stoichiometry, indicating that the N adatoms are thermodynamically unstable in most cases [11]. This has important consequences for the reactivity of these surfaces and it is one of the main problems in understanding the mechanisms of GaN growth. A number of studies have been made to investigate the incorporation of Ga on the different GaN surface reconstructions in both cubic and wurtzite phases with adatom and adlayer configurations [12–14]. In the case of N incorporation, there have been few studies of this process due to the general instability of the reconstructions [5].

In this work we have examined the fundamental mechanisms governing the GaN(0001) surface when different numbers of N atoms are incorporated into a single 2×2 overlying adlayer or in a second layer in the case of the contracted bilayer model described by Northrup *et al* [14]. The GaN $(000\bar{1})$ surface has not been investigated due to the strong N–N molecular bond with a binding energy of 9.8 eV [15]. This favours the formation of N molecules on the top of the surface, independently of the number of Ga atoms substituted. The relevant surfaces have been examined and their formation energies compared as a function of chemical potential with different numbers of N atoms substituting for Ga in the top layer.

2. Theoretical model

The computational study of the total energy and atomic structures are performed in the framework of density functional theory (DFT) using the generalized gradient approximation (GGA) of Perdew and Wang (PW91) [16]. For structural studies of polar surfaces, the GGA [17] has been shown to be more effective than the local density approximation (LDA) [18] scheme. In order to carry out the work we employed the CASTEP code [19]. The ions are described by norm-conserving, nonlocal atomic pseudopotentials in the Kleinman–Bylander form, which are generated using the optimization scheme of Lin *et al* [20] and include the Ga 3d electrons as part of the valence band. Wavefunctions are expanded in a plane-wave basis set up to an energy cut-off 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 sampling point scheme [21] for the surface unit cell, which gave two special k points.

The surface modelling is carried out using a supercell approach with each supercell containing six GaN bilayers and a vacuum region equivalent to six GaN bilayers with an overall length of approximately 13 Å. The energy and structural test calculations performed show that four bilayers are sufficient to describe the individual growth surface. Hence 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

any additional adatoms and adlayers on the surface, are allowed to relax to the lowest energy configuration commensurate with the initial symmetry of the surface. The geometry of the surface is optimized by calculating the forces at every atom site and then allowing the structure to relax until all forces are reduced below a threshold value of 5×10^{-2} eV Å^{-1}. The dangling bonds on the opposite surface are saturated with H atoms to reduce finite fields that could otherwise be produced across the supercell.

In order to study the modified surfaces, which have a different number of atoms, the formation energy has been calculated using the formula [5]

$$E_{\text{form}} = E_{\text{tot}} - E_{\text{bare}} - \Delta n_{\text{Ga}}\mu_{\text{Ga}} - \Delta n_{\text{N}}\mu_{\text{N}}$$

where E_{tot} and E_{bare} are the total energies of the adlayer covered 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 numbers of atoms of each atomic species per unit cell. The 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 [22]:

$$\mu_{\text{Ga}}^{\text{bulk}} - \Delta H_{\text{f}} < \mu_{\text{Ga}} < \mu_{\text{Ga}}^{\text{bulk}}.$$

Here $\mu_{\text{Ga}}^{\text{bulk}}$ is the chemical potential of Ga in its bulk phase and H_{f} is 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 gallium structure [23], implying that $\mu_{\text{Ga}} < E(\text{Ga}_\alpha)$. $E(\text{Ga}_\alpha)$ denotes the energy per atom of the α-gallium structure which is the low temperature stable phase of bulk gallium at ambient pressure where each atom has only one nearest neighbour at 2.4 Å, and the next six nearest neighbours lie within a shell with radius between 2.71 and 2.80 Å [24]. In the case of the N adatom the maximum chemical potential is equal to the energy per atom of molecular nitrogen; we therefore have $\mu_{\text{N}} < E(\text{N}_2)$.

3. Results and discussion

Before building the surfaces, it is important to calculate the bulk properties with sufficient accuracy because the optimized unit cell for the bulk will define the slab in the surface supercell used to build the geometrical surface and for formation energy calculations with the α-gallium structure and nitrogen molecule. The main geometrical parameters and cohesive energies calculated from a full geometric structural relaxation for α-gallium, bulk GaN and a nitrogen molecule are shown in table 1. We find that there is good agreement of the calculations with the experimental values and, in particular, the calculated heat of formation (ΔH_{f}) for bulk GaN is 1.14 eV, which is very close to the experimental value of 1.1 eV [25].

The GaN surfaces have been modelled in two ways. The energy calculations were performed for a standard 2 × 2 reconstruction containing one extra layer of atoms, as shown in figure 1(a), and the laterally contracted $\sqrt{3} \times \sqrt{3}$ adlayer structure [14], with two extra layers (a bilayer) of atoms, as shown in figure 1(b). We first performed calculations with only Ga atoms in the top layer and then we replaced some or all of the atoms in the top layer with N atoms. In order to compare the relative formation energies, we give results for the allowed range of the Ga chemical potential. The results are compared with those for the N adatom (H3) 2 × 2 configuration [10]. The Ga chemical potential $\Delta\mu_{\text{Ga}} = \mu_{\text{Ga}} - \mu_{\text{Ga,bulk}}$ varies between $\Delta\mu_{\text{Ga}} = 0$ (Ga-rich conditions) and $\Delta\mu_{\text{Ga}} = -\Delta H_{\text{f}}$ for GaN (N-rich). In general, most of the surfaces with N substitutions are metallic and do not satisfy the electron counting rule (ECR) [26].

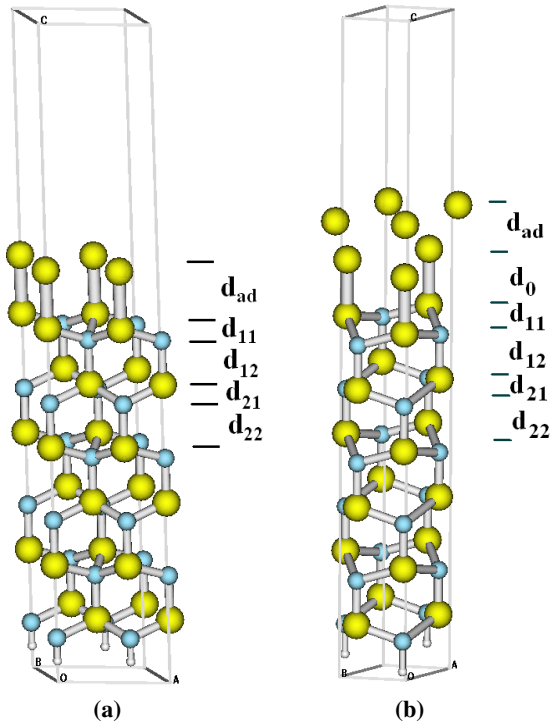


Figure 1. A side view defining the notation used for the interlayer distances and the substitution sites for (a) the ideal 2 × 2 and (b) the contracted bilayer GaN(0001) surface covered by one and two extra layers of atoms.

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

	a (Å)		b (Å)		c (Å)		Distances (Å)		Cohesive energy (eV)	
Structure	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
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]

[a] Reference [34].
[b] Reference [35].
[c] Reference [5].
[d] Reference [4].
[e] Reference [36].
[f] Reference [10].
[g] Reference [15].
[h] Reference [37].

3.1. The ideal 2 × 2 *reconstruction*

According to Northrup *et al* [14], the simple 2 × 2 structure is not the most stable of the adlayer configurations. Nevertheless, we carried out a series of initial calculations with this structure to provide a comparison with the more favourable laterally contracted arrangement.

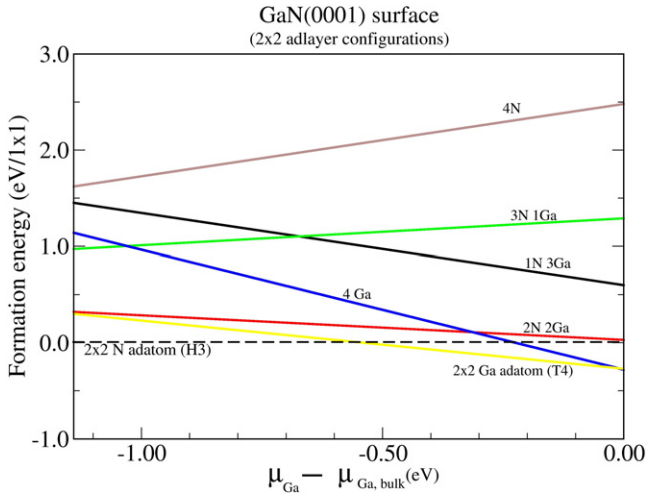
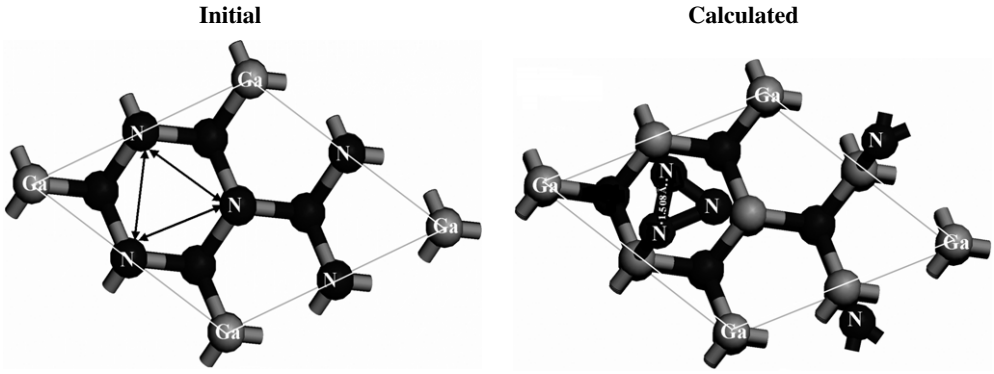


Figure 2. Comparison of the formation energies, relative to that of the 2 × 2 N adatom surface, for different models of the adlayer GaN(0001) 2 × 2 surface as a function of the chemical potential μ_{Ga} for the allowed range.

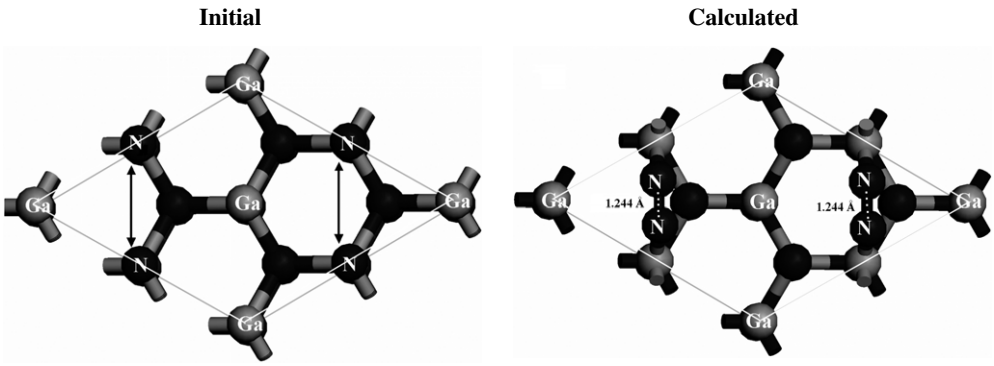
Figure 2 shows the relative formation energies calculated for seven configurations, including the N (H3) and Ga (T4) adatoms on the 2 × 2 GaN(0001) surface. For purposes of comparison, we plot the formation energy normalized to a 1 × 1 unit cell. The only stable structures relative to the N (H3) adatom configuration correspond to the Ga adlayer and Ga adatom in the Ga-rich limit. Structures with N substituting for Ga in the adlayer configuration are unstable over the complete range of allowed chemical potential. These results are in good agreement with the available experimental data and similar calculations [27, 28], which show that the GaN surfaces in thermodynamic equilibrium prefer Ga-rich conditions to N-rich conditions. According to the graph, there is a tendency for the surface to become more unstable as the number of N atoms increases. However, we note that the 2N–2Ga surface is the lowest energy configuration.

The instabilities on the top surfaces are due to the rearrangement of the nitrogen atoms. In the case of an N adlayer model, a trimer of N atoms forms which is similar to that shown in figure 3(a), with the fourth N atom directly above the Ga atom in the layer below. The distance between the N atoms in the 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 [29]. The same sort of behaviour is seen in the case of three nitrogen atoms and one gallium atom in the adlayer, which is shown in figure 3(a), but the structure of the trimer formed is slightly different, due to an increase to 1.51 Å in the bond length between N atoms. The elongation is due to the presence of the cation Ga that changes the atom coordination [30] and decreases the strength of bonds between the nitrogen atoms.

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 1.24 Å, compared to the N_2 molecule bond length of 1.09 Å. The strength of this particular bond leads to the relatively low calculated energy of the 2N–2Ga overlayer compared to the other configurations. The arrangement is shown in figure 3(b) and is such that vertical lines of equally spaced Ga atoms lie between lines of N dimers. 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



(a) Top layer composed by 1Ga, 3N atoms.



(b) Top layer composed by 2Ga, 2N atoms.

Figure 3. Top views of the initial and reconstructed (2 × 2) GaN surfaces with different numbers of N and Ga atoms on the top of the adlayer surface. For clarity several 2 × 2 unit cells are displayed. A trimer such as shown in (a) also appears in the case of the N adlayer.

configuration each N atom is surrounded by Ga atoms, with the N atom in a restricted area, directly bonded to the underlying Ga atom. The Ga atoms are also directly above Ga atoms in the layer below.

We denote the vertical distance between a top layer atom and its nearest neighbour in the underlying layer by d_{ad}, as for example in figure 1(a). In the case of Ga atoms, d_{ad} is coincident with the Ga–Ga bond length because in all the optimized configurations the top Ga atoms remain directly above the underlying Ga atoms. According to the data shown in table 2, on average, the distance between Ga atoms on the surface is close to that of the nearest neighbour separation in bulk α-gallium, $\sim$2.71 Å [31]. However, due to the horizontal movement of the nitrogen atoms in configurations with two, three and four nitrogen atoms in the top layer d_{ad} can have rather different values. For example, in the case of the 4N configuration, the vertical distance between the three nitrogens which form the trimer and their nearest underlying Ga atoms is 1.82 Å, while the remaining nitrogen is directly bonded to its nearest underlying Ga atom with a vertical separation of 1.89 Å. In the case of 1Ga–3N, the nitrogen atoms form a trimer where d_{ad} has the value 1.84 Å, while in the dimer formed in the case of 2Ga–2N the nitrogen atoms are separated vertically from their nearest Ga underlying neighbours by 1.91 Å. In the case of 3Ga–1N the single N atom is directly bonded over the underlying Ga atoms with

Table 2. Calculated structural parameters of the surface relaxation corresponding to figure 1(a) (lengths in ångströms).

Surface type	d_{ad} [a]	d_{11}	d_{12}	d_{21}	d_{22}	Obs.
2 × 2 N adatom	∼1.15	∼0.63	∼2.06	∼0.61	∼1.97	
2 × 2 Ga adatom	∼1.48	∼0.73	∼1.94	0.70	1.96	
Adlayers						
4Ga	2.58(Ga–Ga)	0.72	1.96	0.67	1.95	
3Ga–1N	1.92 (N–Ga)	∼0.76				
	2.61 (Ga–Ga)		1.98	0.70	1.96	
2Ga–2N	1.91(N–Ga)	∼0.71	∼1.97	∼0.69	1.96	N dimer 1.21
	2.63 (Ga–Ga)					
1Ga–3N	1.84 (N–Ga)	∼0.62	∼1.97	∼0.72	∼1.95	N trimer 1.51
	2.80 (Ga–Ga)					
4N	1.82 (N–Ga)	∼0.64	∼2.01	∼0.72	∼1.96	N trimer 1.46
	1.89 (N–Ga)					

[a] Vertical distance between top and nearest underlying atom. d_{ad}(exp) (Ga–Ga) ≈ 2.44 Å [37] and 2.71 Å [10]. d_{11}, d_{21} (calculated bulk) ≈ 0.64 Å (table 1). d_{12}, d_{22} (calculated bulk) ≈ 1.97 Å (table 1) ∼ average distance.

$d_{ad} = 1.92$ Å, not far from the value 1.97 Å calculated for the bulk material. The interlayer distances d_{11}, d_{12} and d_{21}, d_{22} defined in figure 1(a) are all very similar to their values in bulk GaN. In particular, the value of d_{22} is 1.95–1.96 Å for all surface configurations, which is close to the calculated bulk value of 1.968 Å and the measured bulk value of 1.96 Å.

3.2. The contracted bilayer model

The structure of the $\sqrt{3} \times \sqrt{3}$ laterally contracted bilayer structure [14] that we have considered is shown in figure 1(b). The bilayer is composed of two layers of Ga above the GaN substrate where the top layer has four atoms in the $\sqrt{3} \times \sqrt{3}$ surface unit cell above only three Ga atoms in the underlying layer. Northrup *et al* [14] have shown that there is more than one possible low energy arrangement of the top layer atoms, but in our calculations their registry B has been employed. They report that, in practice, the formation energy is largely independent of the arrangement chosen.

The calculated structural parameters of the relaxed surfaces are shown in table 3 where the interlayer distances are given according to the notation in figure 1(b), and a comparison is made with the calculated bulk values.

In the completely Ga covered top layer, there is some vertical corrugation as a consequence of the distortion from an ideal hexagonal adlayer, due to the asymmetry of the underlayer. This means that the atoms in the top layer are not coplanar. The value d_{ad} is the average vertical distance between the top two layers. The calculations show an average vertical separation between the layers of $d_{ad} = 2.52$ Å, and for the layer below $d_0 = 2.35$ Å, which agrees well with the previously calculated [14] values $d_{ad} = 2.54$ Å and $d_0 = 2.37$ Å.

In addition to the fully Ga covered top surface, we have also considered situations in which one or more Ga atoms are replaced by N atoms. The interlayer separations d_{12} and d_{22} are very similar in all cases, and very close to the values in bulk GaN. The values of d_{21} are fairly similar and close to the bulk value while d_{11} is consistently larger than the bulk value.

Figure 4, shows the calculated formation energies relative to the 2 × 2 N adatom structure for the seven configurations studied, including the laterally contracted Ga monolayer surface. In the case of the all Ga configurations (these were studied by Northrup *et al* [14]), our

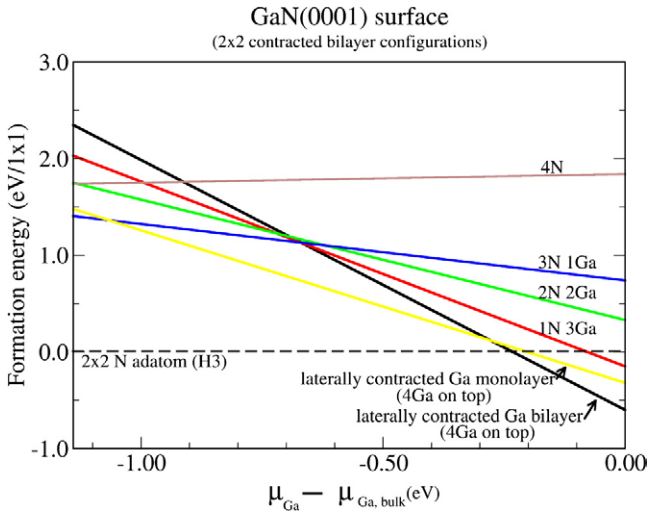


Figure 4. Comparison of the formation energies, relative to that of the 2×2 N adatom surface, for different models of the laterally contracted bilayer and monolayer GaN(0001) surface as a function of the chemical potential μ_{Ga} for the allowed range.

Table 3. Calculated structural parameters of the surface relaxation corresponding to figure 1(b) (lengths in ångströms).

Surface type	d_{ad} [a]	d_0 (Ga–Ga)	d_{11}	d_{12}	d_{21}	d_{22}	Obs.
Cont. monolayer		∼2.49	∼0.73	∼1.95	∼0.64	1.95	
Cont. bilayer	∼2.52 (Ga–Ga)	∼2.35	∼0.71	∼1.96	0.67	1.96	
Adlayers							
3Ga–1N	∼1.87 (N–Ga)	∼2.55	∼0.73				
	∼2.35 (Ga–Ga)			1.96	0.67	1.96	
2Ga–2N	∼1.86 (N–Ga)	∼2.61	∼0.76	∼1.97	0.69	1.95	
	∼2.19 (Ga–Ga)						
1Ga–3N	∼1.96 (N–Ga)	∼2.48	∼0.70	∼1.97	0.69	1.95	N dimer 1.12
	∼2.48 (Ga–Ga)						
4N	∼1.08 (N–Ga)	∼2.51	∼0.73	∼1.96	0.67	1.96	N trimer 1.34
	∼1.81 (N–Ga)						

[a] Vertical distance between top and nearest underlying atom. d_{ad}(exp) (Ga–Ga) ≈ 2.44 Å [37] and 2.71 Å [10]. d_{11}, d_{21} (calculated bulk) ≈ 0.64 Å (table 1). d_{12}, d_{22} (calculated bulk) ≈ 1.97 Å (table 1) ∼ average distance.

results are in quite good agreement with that work. The most thermodynamically stable surfaces are obtained under Ga-rich conditions, which is the natural tendency in the case of GaN surfaces [32]. In contrast with our results in the previous section, we note that not all N-containing surfaces are unstable relative to the N adatom (H3) configuration. In fact we observe that the 1N3–Ga surface is marginally more stable under Ga-rich conditions. This stability may arise because for the GaN(0001) surface in the Ga-rich limit a 1×1 Ga fluid structure is reported [9] while the 2×2 structure appears during growth under conditions of excess nitrogen. The borders between these two regimes correspond to the re-evaporation of excess Ga during growth. If, as according to Northrup *et al* [14], the contracted bilayer model shows a better description of the pseudo-1×1 structure, this result could describe the transition between the two reconstructions and the 1×1 RHEED pattern observed where the 2×2 reconstruction could be seen [33].

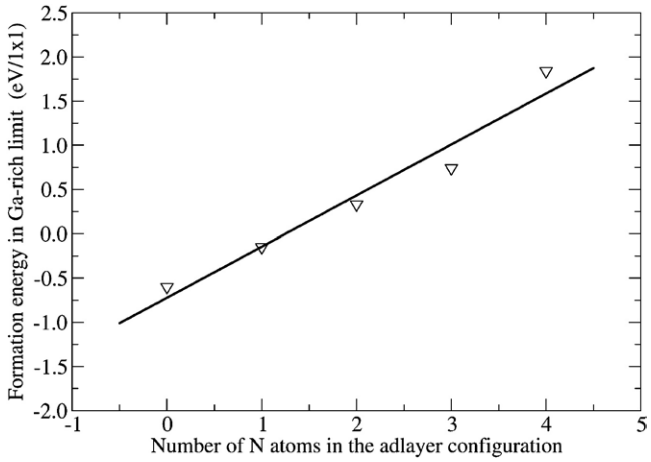


Figure 5. Energy stability for different models of a laterally contracted GaN bilayer (0001) surface as a function of the number of N atoms in the adlayer configuration in the Ga-rich limit ($\mu_{\mathrm{Ga}} - \mu_{\mathrm{Ga}}^{\mathrm{bulk}} = 0$).

Figure 5 clearly shows that as the number of N atoms is increased in the sequence 2N–2Ga, 3N–1Ga, 4N, the surfaces become increasingly unstable, which is as expected. In the Ga-rich limit we have approximately

$$E_{\mathrm{f}} \approx -0.72 + 0.58n \qquad 0 \leqslant n \leqslant 4 \tag{1}$$

where E_{f} is the formation energy in electronvolts.

4. Conclusions

Using first-principles methods we have studied the structure and stability of the GaN(0001) surface with one and two additional layers. The top layer was either entirely Ga or contained a variable number of N atoms substituting for Ga. In the case of a standard 2×2 surface under Ga- and N-rich conditions, the surfaces are all unstable relative to the N adatom (H3) configuration, independent of the number of N substitutions in the top layer. In the case of the laterally contracted bilayer model there is a near linear relationship between the formation energy and the number of N atoms in the top layer in the Ga-rich limit. Under these circumstances we have found that there is an adlayer configuration containing a single N atom with a lower energy than that of the N adatom (H3) configuration.

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