

Surface Structures, Surfactants and Diffusion at Cubic and Wurtzite GaN

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Clean and As covered zinc-blende and wurtzite GaN surfaces have been investigated employing density-functional theory calculations. For clean GaN surfaces our calculations indicate the stability of several novel surface structures that are very different from those found on traditional III-V semiconductors. Adding impurities commonly present in significant concentrations during growth strongly modifies surface reconstructions and energies. In particular, we find that arsenic has a low solubility and significantly stabilizes the cubic GaN (001) surface making it interesting as a potential surfactant. Finally, we have studied the diffusion of Ga and N adatoms on both the equilibrium and non-equilibrium surfaces. Our calculations reveal a very different diffusivity for Ga and N adatoms: While Ga adatoms are very mobile at typical growth temperatures, the diffusion of N adatoms is slower by several orders of magnitude. These results give insight into the fundamental growth mechanisms and allow conclusions concerning optimum growth conditions.

1 Introduction

Despite progress in growing high quality material for device fabrication, an understanding of the fundamental growth mechanisms of GaN is still in its infancy. Knowledge of the structure of clean and adsorbate covered surfaces and the mechanisms of incorporation and diffusion of adatoms is still incomplete. However, an understanding of these mechanisms is crucial to gain a deeper insight into the relevant growth mechanisms on an atomic scale and to improve growth in a controlled fashion.

First-principles density functional theory (DFT) calculations have been applied successfully to understand defects, impurities, doping, and surface reconstructions of non-polar and polar III-nitride surfaces [1] [2] [3] [4]. In this work we review the application of DFT calculations to model the behavior of surfactants (e.g. As) and to determine the energetics of adatom migration on GaN surfaces. We summarize the results obtained for the (001) surface of cubic GaN and the (0001) and (000 $\bar{1}$) surfaces of wurtzite GaN.

The outline of the paper is as follows: In the first part the computational method is described. We then discuss the properties and structure of cubic and wurtzite equilibrium GaN surfaces and the effect of surfactants on the reconstructions and energies of these surfaces. Finally,

the migration paths and diffusion barriers of N and Ga adatoms on selected surfaces are described. Based on these results we discuss consequences for the growth of GaN in a thermodynamic and kinetic context.

2 Formalism

The energy necessary to create a surface is called the *surface energy*. This energy depends on the specific thermodynamic conditions. Specifically, the chemical potentials of Ga and N, which are related to the reservoirs they are taken from, determine the surface reconstruction and energy. The surface energy is defined as

$$E^{surf} = \frac{1}{2} \left\{ E^{tot} - n_{Ga} \mu_{Ga} - n_N \mu_N \right\}$$

where N_{Ga} and N_N are the numbers of Ga and N atoms in the cell, and E^{tot} is the total energy for the slab. The factor 1/2 takes into account that there are two equivalent surfaces per slab.

The total energy has been calculated employing local density-functional theory in combination with a plane wave basis set and first principles pseudopotentials. The strongly localized character of the N 2s and 2p electrons and of the Ga 3d electrons make such an

approach rather challenging. We therefore use soft Troullier-Martins [5] pseudopotentials and an efficient scheme to construct the initial wave functions [6]. The pseudopotentials were constructed in the fully separable form of Kleinman and Bylander [7]. An explicit treatment of the Ga 3d electrons as valence electrons is crucial to calculate accurate surface energies. The exchange and correlation energy functionals are those derived from the homogeneous electron gas calculations of Ceperley and Alder [8] by Perdew and Zunger [9]. The wave functions are expanded in a plane wave basis set with a cutoff energy of 60 Ry. A 2x2x1 Monkhorst-Pack mesh has been used to sample the Brillouin zone [10]. The surfaces are described in a repeated slab geometry. For all calculations the atoms in the two top surface layers were allowed to relax. We used both symmetric slabs consisting of 9 layers GaN (to obtain the absolute value of the surface energy) and asymmetric slabs consisting of 4 layers GaN where one side has been saturated with pseudo-hydrogen. The resulting electric field is compensated by introducing a dipole layer in the vacuum region [11]. A detailed analysis of the local density of states (LDOS) showed that the H^{*}-passivated side is electrically inactive: no surface states within the band-gap exist and the surface is electrically neutral. The use of an asymmetric slab has two advantages. First, the saturated surface atoms stay in their ideal positions with respect to the bulk material. Therefore, strain effects due to relaxation are minimized and the slab thickness can be reduced, resulting in improved numerical performance. Second, the surface band structure can be directly calculated. Symmetric slabs give rise to two distinct problems in calculating the surface bandstructure: (i) the electronic states on the two surfaces couple to each other to produce an unphysical splitting of the surface bands and (ii) for zinc-blende (001) slabs the surfaces are twisted by 90° relative to each other (giving an inseparable combination of two surface band structures).

Total energy surfaces (TES) have been mapped on a (2x2) surface unit cell with a grid of $\sim 1\text{\AA}$ spacing. The upper two layers and the adatom height were fully relaxed. We started from the ideal clean Ga-terminated surface and an adatom height of $\sim 1\text{\AA}$ (N) and $\sim 2\text{\AA}$ (Ga). Having mapped out the total energy surface on the grid the minima are explicitly calculated by removing all constraints on the adatom, i.e., by fully relaxing the adatom and the surface layers. The TES were then interpolated using both energies and forces on the grid by combining symmetrized plane waves with a singular value decomposition-scheme [12].

3 Polar GaN Surfaces

3.1 The cubic (001) surface

Surface reconstructions on GaN (001) have been intensively studied using RHEED measurements. Brandt *et al.* observed a reversible sequence of RHEED-patterns indicating (1x1), (2x2), and c(2x2) symmetries for GaN grown on GaAs (001) by changing from very N-rich conditions to Ga-rich conditions [13] [14]. Identical reconstructions have also been reported by Lischka *et al.* [15] and Feuillet *et al.* for GaN grown on GaAs (001) [16]. For GaN on SiC, however, Feuillet *et al.* reported a very different pattern: a (4x1) structure (under N-rich conditions) and a (1x1) reconstruction (under Ga-rich conditions) [16].

First principles total-energy calculations have been employed in Ref. [3] on clean and adsorbate covered GaN (001) surfaces and it has been concluded that all energetically favored surfaces are Ga-stabilized. Even under extreme N-rich conditions a Ga-terminated surface is energetically most stable. First principles calculations predict that the equilibrium surface is a (4x1) reconstructed surface consisting of linear tetramers lining up along the (110) direction [3]. This model is also an excellent candidate to explain the observed (4x1) RHEED patterns [15 einsetzen!!]. To explain the c(2x2) and 2x2 RHEED patterns observed for GaN grown on GaAs, a large number of models with c(2x2) and 2x2 symmetry have been investigated [3]. However, all such structures are found to be energetically *less* stable than the (4x1) structure. Therefore, it has been concluded that the (2x2) and c(2x2) surface reconstructions are not intrinsic reconstructions of the clean GaN(001) surface, but result instead from impurities on the surface [3]. We will elucidate this issue in Sec. 4.

3.2 The wurtzite (0001) and (0001 $\bar{1}$) surfaces

Recently, surface reconstructions on GaN (0001) and (0001 $\bar{1}$) surfaces have been investigated combining RHEED, STM and first-principles calculations by Smith *et al.* [4]. STM observations showed a large number of different reconstructions. For the GaN (0001 $\bar{1}$) surface, reconstructions having (1x1), (3x3), (6x6) and c(6x12) symmetry have been observed [4]. GaN (0001) reconstructions include a (2x2), (5x5), (6x4) and a pseudo (incommensurate) (1x1) structure [17]. First principles calculations [4] identified the (1x1) structure observed on GaN (0001 $\bar{1}$) to be a Ga-adlayer structure. For the (0001) surface these calculations [4] predicted that Ga and N adatom structures are preferred: Under Ga-rich conditions a (2x2)-T4 Ga-adatom structure is most stable while under N-rich conditions a (2x2)-H3 N-adatom structure is lowest in energy.

3.3 Cation stabilized surfaces and metallic bonding

A rather general feature of the stable surfaces that have been studied up until now is the absence of threefold coordinated N atoms. Exceptions include the stoichiometric GaN(10 $\bar{1}$ 0) surface [2] and the 2x2 H3 N-adatom reconstruction of the GaN(0001) surface [4]. The latter surface is only stable under extreme N-rich conditions. In most cases N adatoms appear to be unstable with respect to the formation of N₂ molecules. The trend towards Ga-stabilized surfaces can be understood in terms of the unique properties of GaN: the pronounced ionicity, the large mismatch in the covalent radii and the very different chemical properties of Ga and N. Due to the small radius of the N atoms, the spacing between Ga atoms in GaN is only slightly larger than in Ga bulk. Therefore, Ga atoms in the surface layer can form metallic bonds even without any relaxation, and the strength of these bonds is only slightly weaker than those formed in bulk Ga. This behavior has not been observed on traditional semiconductor surfaces where dimers or trimers between surface atoms are commonly formed. An analysis of the electron density for the GaN(000 $\bar{1}$) Ga-adlayer structure (Figure 1) shows an accumulation of charge between the surface Ga atoms. The p-orbitals of the surface Ga atoms overlap strongly with their neighbors and give rise to a highly disperse metallic band of surface states in the band gap [4] [17]. The additional metallic bonds stabilize excess Ga on the surface and explain why Ga terminated surfaces are so stable. Ga-terminated surfaces are also stabilized by the fact that N₂ molecules (which limit the chemical potential of N) exhibit one of the strongest chemical bonds in nature. Therefore, for N to be stable it has to be incorporated on a site where it can form strong bonds as e.g. in bulk GaN. On the surface, however, the N adatoms are under-coordinated and can form only two or three bonds making N in these configurations less stable than in a N₂ molecule.

3.4 Adsorbate covered polar GaN surfaces

The fact that N atoms are thermodynamically unstable on GaN surfaces has important consequences for the reactivity of these surfaces. On “traditional” III-V semiconductors (e.g. GaAs) a nearly chemically inert surface can be achieved by going towards very anion-rich conditions. We will call this mechanism *self-passivation*, which means that the surfaces can be stabilized by one of the constituents of the material (typically the anion). However, as pointed out above such a mechanism would not work for GaN; the surface consists always of a thin Ga-film, which is high in energy and can easily react with impurities present in the growth chamber. The very different character of the surfaces also becomes evident

when comparing absolute surface energies. For GaN the surface energy is lowest under Ga-rich conditions with values between 110 and 130 meV/Å² [18]. For traditional semiconductors the surface energy is generally about 2 times smaller, e.g. for GaAs it is between 45 and 65 meV/Å² [19].

Let us now consider how arsenic, an element that may be present in significant concentrations when growing on a GaAs substrate, affects the Ga terminated surfaces. We have studied how the surface energy and geometry are influenced when As is incorporated in the first and second surface layer. Figure 2 depicts several models of cubic GaN (001) surfaces having various amounts of As in the top two layers.

The energetically lowest surface structure is a (2x2)-reconstructed surface consisting of As₂ dimers lining up along the (110) direction on a Ga-terminated surface (Figure 2 fuse captions a...e). This structure is consistent with recent STM measurements of Wassermeier et al. where one dimer per (2x2) unit cell has been observed [20]. An analysis of the surface energies revealed that the As dimer structure is more stable than the lowest clean GaN surface [the (4x1) tetramer structure] over the entire thermodynamically allowed range. We therefore propose that the (2x2) reconstruction observed when growing cubic GaN on GaAs is mediated by As in the surface layer. The stability of the As covered surface also explains the experimentally observed irreversible transition from the (4x1) (i.e. clean GaN surface) to the (2x2) reconstruction (i.e. As covered surface) when exposing the surface with an additional As background pressure [16].

In Figure 2 also a representative set of our investigated structures and their corresponding surface energies have been included. There are configurations like mixed dimer structures (Figure 2a, buse captions a...e

) which are close in energy to the (2x2) As dimer reconstruction. All of the structures that contain As in the second or deeper surface layers (Figure 2e) are significantly higher in energy than the structures with As on the surface. This indicates that As prefers to stay on top of the surface and that As is nearly immiscible in GaN consistent with previous experimental [21] and theoretical [22] studies. Both the significant lowering of the surface energy and the low miscibility (preventing As from being incorporated in bulk GaN) make arsenic an interesting candidate as a surfactant. However, to fully understand the effect of As it is also necessary to consider the influence of As on the Ga and N diffusion barriers, which is work under progress. Ausfuhrlicher!!!

To our knowledge, experimental investigations of the influence of As on GaN surfaces have been made (at

least intentionally) only for cubic GaN. In order to understand and predict the effect on the wurtzite surfaces, we have also calculated the surface energies of As covered (0001) and (000 $\bar{1}$) surfaces. Figure 3 shows the surface energies relative to the clean GaN surfaces as a function of the As coverage for both the wurtzite and cubic material. The behaviors of the (0001) and (000 $\bar{1}$) surfaces are qualitatively similar: the surface energy reaches a minimum for an As coverage of 0.25 monolayer (ML) and increases for higher coverages. While the surface energy, relative to the clean GaN surface, is reduced by only 0.2 eV per 1x1 unit cell for the (0001) surface, it is reduced by 0.8 eV for the (000 $\bar{1}$) surface. The quantitative difference between the two orientations is due to the specific atomic configurations (see Figure 4). On the (0001) surface, each surface atom has only one dangling bond while on the (000 $\bar{1}$) surface the atoms have three dangling bonds [4]. Consequently, the chemical reactivity of the (000 $\bar{1}$) surface is greater, and the binding energy of As (and probably most other impurities) is larger on the (000 $\bar{1}$) surface than on the (0001) surface. This suggests that impurity concentrations are *higher* when growing on (000 $\bar{1}$) than on (0001).

The cubic (001) surface exhibits a *qualitatively* very different behavior: The surface energy is *always* reduced, even at a *full ML* of coverage. The minimum at 0.5 ML corresponds to the (2x2) As dimer structure. Since the surface energy is independent of the coverage always reduced and the solubility of As in GaN is small As should might be a good *surfactant* on the cubic (001) surface. However, in case of the wurtzite (0001) and (000 $\bar{1}$) surface, the energy is only reduced for specific coverages and we expect a less pronounced surfactant effect. However, a surfactant behavior cannot be excluded and it would be very interesting to *experimentally* investigate the effect of As on the reconstructions and surface properties also for wurtzite GaN.

4 Diffusion at Polar GaN Surfaces

Based on the calculated equilibrium structures the diffusion barriers for Ga and N adatoms have been calculated by mapping the 2-dimensional total energy surface. We will focus here on the “ideal” Ga-terminated cubic GaN surface. Calculations performed for other polar cubic and wurtzite GaN surfaces exhibit a qualitatively very similar behavior [23]. Figure 5 shows the total energy surface along a path through high-symmetry points for both Ga and N adatoms. The global minimum (i.e. the adsorption site) for a N adatom is the epitaxial site between two Ga atoms where it bonds to the two dangling bond states ($B_{||}$). A Ga adatom prefers the 4-fold coordinated hollow site (H_4), i.e. the same site a Ga atom would occupy in bulk GaN (although there are no

N-atoms between the surface and the adatom). From Figure 5 we also obtain the diffusion barriers. A qualitatively and quantitatively very different diffusivity for Ga and N adatoms is found. While Ga adatoms are very mobile – the diffusion barrier is ~ 0.2 eV – the mobility of the N adatom is lower by orders of magnitude (diffusion barrier ~ 1.5 eV).

The very different diffusion barriers for Ga and N adatoms are a direct consequence of the fact that only Ga-rich surfaces are stable. On Ga-rich surfaces, a Ga adatom bonds to the surface by forming Ga-Ga bonds. An analysis showed that these bonds are weak undirected metallic bonds. This is also consistent with the fact that bulk Ga is a soft metal which melts already at $\sim 30^\circ\text{C}$. It also explains e.g. why for a Ga adatom the barriers over the inequivalent bridge positions (B_{\perp} , $B_{||}$) are almost identical and why diffusion barriers for cations are significantly smaller than e.g. for GaAs. For a N adatom, on the other hand, strong and directed Ga-N bonds are formed. Compared to the Ga adatom, the diffusion barrier increases by an order of magnitude.

5 Conclusions and consequences for the MBE growth

The very different diffusivity of the two species provides new insight into the stability and residence time of N adatoms on the GaN surface. Although N atoms are thermodynamically unstable against desorption as N_2 molecules (as pointed out in the Section 3.3) the low mobility of this species implies that desorption of N adatoms is kinetically hindered. In order to desorb, the N adatoms have to form molecules. Since the diffusion barrier for N is high, the migration is slow and consequently the residence time of N should be reasonably large. On the other hand, since Ga adatoms are very mobile, the probability that Ga atoms capture N atoms is much higher than the other process where N atoms form molecules and desorb from the surface. Thus, *if* there are enough Ga atoms present (which is the case under more Ga-rich conditions) the incorporation probability of N atoms is enhanced.

The kinetic barrier for the desorption of N also means that under N-rich growth conditions regions can be formed which are primarily covered with N. Further, recent calculations have shown that excess N strongly increases the diffusion barrier of Ga adatoms [23]. From a kinetic point of view we therefore expect *optimum growth under slightly Ga-rich conditions*, where the Ga diffusion is fast. Under these conditions a more two dimensional growth can be expected leading for example to a lower density of stacking faults and a smoother surface morphology.

Another advantage of growing under slightly Ga-rich conditions is the higher stability of the surface

against surface roughening and faceting. Experimental observations [13] [16] confirm these conclusions: Optimum surface morphology is achieved under more Ga-rich conditions while under N-rich conditions surface roughening and inferior material quality has been observed. Finally, it should be mentioned that the extreme binding energy of N_2 and the large mismatch in atomic radii, which drive polar surfaces to be Ga rich, are general features of the III-nitride semiconductors. For AlN, InN and its alloys with GaN we expect therefore a similar behavior.

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FIGURES

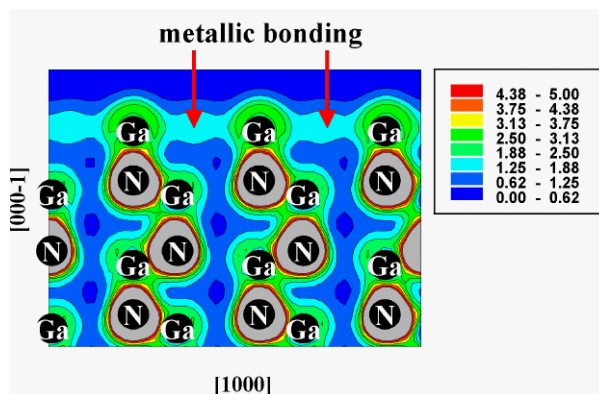


Figure 1. Contour plot of the valence-electron density for the (1x1) Ga-terminated (000 $\bar{1}$) surface in the (1-210) plane. The units are in [10^{-3} e/bohr $^{-3}$]. Note the clear enhancement of the charge density in the top surface layer which is characteristic for the strong Ga-Ga interaction and the metallic bonding in the surface. The plane plotted contains the [000 $\bar{1}$] and the [10 $\bar{1}$ 0] directions.

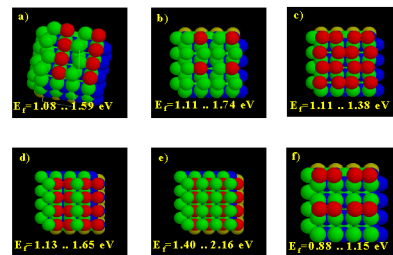


Figure 2. Examples of surface structures containing As in the first and second layer for the cubic (001) surface. The surface energies are given for Ga (left number) and N-rich (right number) conditions.

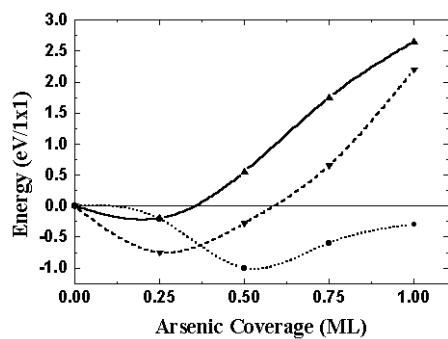


Figure 3. Surface energies [in eV/(1x1) cell] for the (0001), the (000 $\bar{1}$) and the (001) surfaces [solid, dashed, dotted line] as a function of the As coverage. The energies are relative to the energy of the corresponding equilibrium surfaces for each orientation.

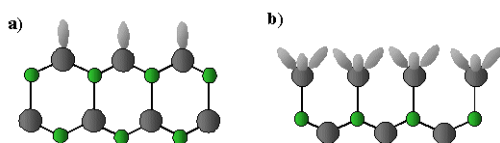


Figure 4. Atomic structures of the wurtzite [(0001), a)] and [(000 $\bar{1}$), b)] surfaces. Large (grey) balls mark Ga atoms, small (green) balls N atoms.

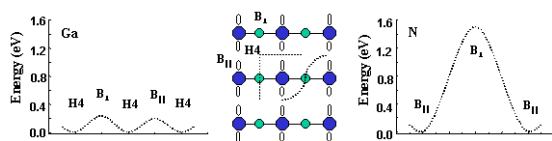


Figure 5. Diffusion pathways and diffusion barriers for isolated Ga (left) and N (right) adatoms on the Ga-terminated (1x1) GaN (001) surface. A top view of the surface is shown in the center. The large balls mark the Ga atoms, the smaller the N atoms in the second layer. The diffusion path is marked as dotted line. Note that for the Ga adatom two inequivalent paths with almost degenerate barriers exist.