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Theory of surfaces and interfaces of group III-nitrides

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Abstract

Employing first principles total energy calculations, we have studied the structure and energetics of surfaces and interfaces in group III-nitrides and their alloys. Consequences for the morphology and stability of epitaxial layers will be discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Group III-nitrides; First principles calculations

1. Introduction

A first step towards controlling and improving the quality and stability of semiconductor interfaces is a better understanding of the fundamental mechanisms during growth. First principles total energy calculations employing density-functional theory have emerged as a powerful and accurate tool to study various static properties of interfaces such as atomic geometry, stability and electronic structure. Improved methods now enable studies of the initial stages of the interface formation on an atomic scale. In the present paper, we will discuss how these methods can be used to obtain a very detailed insight into the structure, stability and formation of surfaces and interfaces in group III-nitrides.

We will focus on group III-nitrides for which segregation effects and the lack of lattice matched substrates make the formation of smooth 2D interfaces rather challenging (see, e.g., Ref. [1]). In the first part, we discuss our present understanding concerning the structure and adatom kinetics of *clean* GaN surfaces. In the second part, the effect of indium on surface and interface morphology will be discussed.

2. Methodological aspects

The morphology and structure of surfaces and interfaces can be described by employing two principal approaches: (i) thermodynamic equilibrium and (ii) kinetics. In the first case (thermodynamic equilibrium), the stable structure can be obtained by finding the structure with the minimum (Gibbs) free energy. This approach can be applied if all atoms of the system are sufficiently mobile and have sufficient time to find their energetically preferred site, i.e., at high growth temperatures and/or low particle fluxes. If these two conditions are not fulfilled, adatoms moving on the surface can be trapped in local minima rather than reaching their equilibrium configuration. In this case, the surface/interface structure depends also on the initial structure and the reaction path. While the first approach requires just

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the knowledge of surface and interface energies, a correct description of kinetic process requires the knowledge of diffusion barriers and migration paths of surface adatoms.

Both surface energies and adatom kinetics can be calculated by first principles total energy calculations employing density-functional theory. The exchange-correlation energy and potential have been described by the local density approximation (LDA). We have tested also the generalized gradient correction (GGA-PBE) but found it to significantly underestimate the formation enthalpy (for a more detailed discussion see Ref. [2]). The following results have been therefore calculated employing LDA. Details of the method can be found elsewhere [3,4].

3. Bare GaN surfaces

The relevant surfaces for growing GaN are the (0001) (Ga-face) and (000-1) (N-face) orientations for the wurtzite modification and the (001) surface for the cubic phase. The structure and energetics of these surfaces have been extensively studied both by first principles total energy calculations and experiment [5]. A remarkable and unexpected feature of all identified stable surfaces is the tendency to have excess Ga atoms in the top surface layer. In fact, most stable reconstructions exhibit exclusively Ga atoms in the surface layer (even under N-rich conditions) and under more Ga-rich conditions structures with two and more Ga layers can be formed [6,7]. This effect (which has not been observed on other semiconductor surfaces and which results in novel surface structures) is a result of two properties characteristic for group-III nitrides. First, there is a large difference between the binding energy of Ga-bulk (~ 3 eV) and the N_2 molecule (~ 5 eV) making it preferable for the system to add on the surface Ga atoms rather than N atoms. For most other semiconductors, the binding energy is roughly the same for both components, e.g., for GaAs the binding energies of As-bulk (2.9 eV) and Ga-bulk are similar. Second, the lattice constant of GaN is small ($\sim 20\%$ smaller than for GaAs) giving rise to strong Ga–Ga bonds at the surface.

The tendency to form mainly Ga-terminated surfaces has important consequences for the stability and properties of these surfaces. An immediate consequence is that GaN surfaces become *less stable* when going from Ga towards N-rich conditions: Under more N-rich conditions, a higher energy is required to remove Ga atoms from the chemical reservoir than under more Ga-rich conditions (where excess Ga atoms will be formed). Therefore, under conditions close to thermodynamic equilibrium Ga-rich conditions are preferred and optimum (flat) GaN surfaces should be formed. Indeed, recent experiments show that the best surface morphology can be achieved when growing at more Ga-rich conditions (close to the formation of Ga droplets) [9].

4. Growth kinetics

An important question is whether kinetic effects might change these conclusions. We have therefore also studied the diffusion barriers and migration paths of Ga and N adatoms on characteristic GaN surfaces. Both, diffusion barriers and possible migration paths can be obtained from the potential energy surface. One example (for the diffusion at the Ga-terminated (000–1) surface) is shown in Fig. 1. The total energy surface is obtained by calculating the energy when moving an adsorbate over the surface. At each position, the height of the adsorbate above the surface and the adsorbate induced surface relaxations are calculated. In this plot, the local minima correspond to the adsorption sites and the barrier between two adsorption sites defines the diffusion barrier. For the specific surface studied here, the barrier for Ga/N adatoms is 0.2/0.9 eV, i.e., under typical growth conditions the mobility of Ga atoms will be significantly faster than of N adatoms. This trend has been also found for other surfaces (see, e.g., Ref. [8]): diffusion barriers for Ga adatoms are in the range of 0.2–0.7 eV and between 0.9 and 1.5 eV for N adatoms.

The origin of the very different diffusion barriers is a direct consequence of the fact that in thermodynamic equilibrium GaN surfaces will be predominantly covered with Ga atoms. On those surfaces, Ga adatoms form weak Ga–Ga bonds (Ga melts already at ~ 30°C) while N atoms form strong Ga–N bonds (making it hard to move this atom over the surface). For example, a N adatom in the H3 site on the

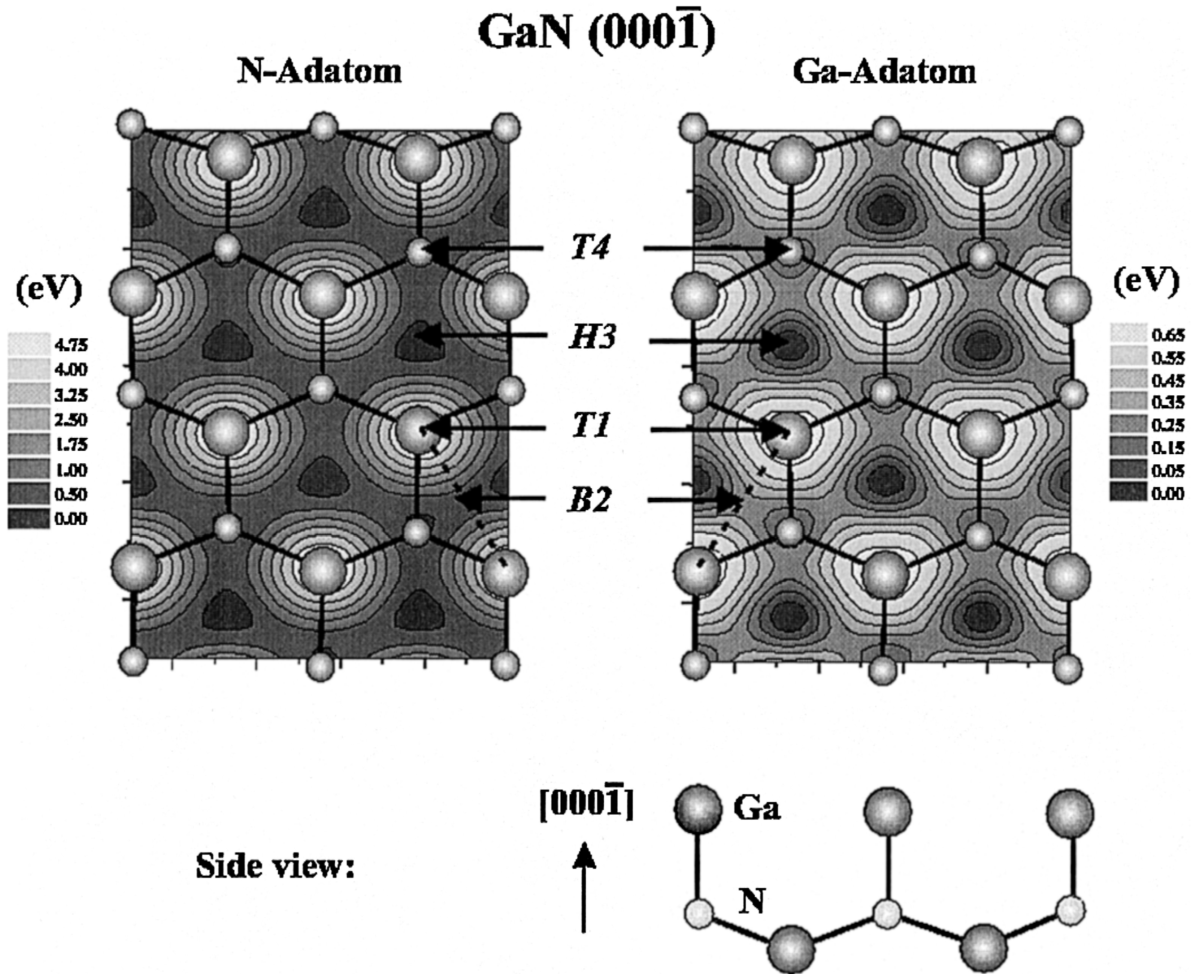

Fig. 1. Contour plot of the total energy surface of a N and a Ga adatom on the GaN (000$\bar{1}$) surface. Note the very different diffusion barriers for Ga and N adatoms.

GaN(0001) surface forms three bonds with the underlying Ga layer. The strength of each of these bonds is approximately ~ 2 eV. To migrate, the N atom must break one of these bonds as it moves from the H3 site to the B2 site. Consistent with this simple analysis, our calculations give a barrier of ~ 1.4 eV for this process.

The very different diffusivity of Ga and N adatoms has important implications for the existence of N-terminated surfaces. As has been argued in Section 3, equilibrium surfaces with N adatoms are typically unstable, which would make it hard to grow GaN. The assumption we made was that the system is in thermodynamic equilibrium, i.e., N adatoms at the surface have *sufficient time* to equilibrate with the N_2 partial pressure. From our calculations, we find that the only way to transfer N adatoms into the N_2 gas phase is by forming N_2 molecules on the surface. These molecules are physisorbed (binding energy of 70 meV) and can be easily desorbed. The alternative process — desorption of a single N adatom — can be neglected (desorption barrier. ~ 6 eV). The crucial step required to reach thermodynamic equilibrium is thus the formation of N_2 molecules: this process is however limited by the rather low mobility of the N atoms. When going

from Ga towards N-rich conditions, it is therefore expected that the incoming flux of N atoms is larger then the flux of desorbing N_2 molecules. Under these conditions, N atoms will be stabilized at the surface, thus making the concentration of N atoms on the surface during growth larger than what one would obtain assuming equilibrium conditions. The fact that N adatoms can be kinetically stabilized on the surface has important consequences. Our results show that the mobility of Ga adatoms is largely reduced (from 0.7 to 1.8 eV) implying a lower diffusivity and rougher surfaces [8]. We can therefore conclude that Ga-rich growth conditions are preferable both from a thermodynamic and kinetic point of view. This conclusion is consistent with recent experiments.

The tendency to form Ga-rich surfaces has also important consequences on the magnitude of surface energies. As has been shown in Ref. [10], the surface energies for stable structures at different orientations and at Ga-rich conditions are rather high. A comparison with surface energies of ''traditional'' semiconductors shows that the surface energy of GaN is by a factor of 2...3 larger. The reason is the large bond strength of GaN (making it hard to cut the bonds) and the constraint of forming Ga-terminated surfaces only (which strongly limits the number of possible surface structures). From the unusually large surface energy of GaN, one might expect that these surfaces are chemically very active. Indeed, recent theoretical studies showed that a variety of impurities (As [4], In [14], O [11]) bind very strongly at these surfaces significantly lowering the energy of adsorbate covered surfaces. This behavior results in high impurity concentrations (as characteristic for group-III nitrides) and is detrimental to device applications.

5. Adsorbate-covered GaN surfaces

In order to reduce the surface reactivity and thus the high impurity concentrations, a partial passivation of the surface might be beneficial. An attractive mechanism to achieve partial passivation is the use of surfactants. Generally, for an element to be used as surfactant, it should bind well to the surface (thus, significantly reducing the surface energy) and (ideally) have no miscibility in the bulk. Possible candidates discussed in the literature are, e.g., As and In [12,13]. Theoretical studies showed indeed that As significantly stabilizes the surface energy (particularly of the cubic (001) surface) [4] and has a low miscibility in bulk GaN [15]. Recent theoretical studies however, show that As (under *p*-type conditions) can be incorporated on the Ga site in significant concentrations [15]. On this site, As acts as a deep double donor, which can efficiently compensate acceptors.

In this respect, indium would be an ideal surfactant: indium is built in on the Ga site where it is an isoelectronic defect. Thus, incorporation of small amounts of indium in GaN will not affect carrier concentrations or luminescence efficiency adversely. Studying a large number of surfaces with In on and in the surface layer, we find it to significantly lower the surface energy. Also, the miscibility is found to be low. We have also calculated the diffusion and exchange barriers for adatoms on these surfaces. The results depend sensitively on the specific In-terminated structure and thus on the specific growth conditions. Details will be discussed elsewhere [14]. Here, we will focus on another aspect of In on surfaces: namely, its ability to cause the formation of pits at the termination of dislocations. As has been shown in Ref. [16], the replacement of Ga with In strongly reduces the surface energy of the (1–101) surface while the energy reduction of the (0001) surface is rather moderate. Therefore, at high In concentrations the formation of (1–101) facetted pits at the dislocations terminating on the (0001) surface is enhanced. At these defects (see, e.g., Ref. [17]), a hexagonal region of the (0001) surface is replaced by six sidewall facets having the (1–101) orientation. Since In aggregation lowers the energy of the (1–101) surface relative to that of the (0001) surface, formation of these defects is promoted. This effect is mainly driven by the very different atomic geometry of the two surfaces: At (0001) all cations are threefold coordinated (they have three nearest neighbor bonds) while at (1–101) cations are two- and one-fold coordinated. The very different coordination implies a strong chemical sensitivity: low coordinated atoms will be predominantly occupied by species forming strong bonds (like Ga–N bonds) while low coordinated sites will be mainly occupied with weak binding species (like In–N). Therefore, replacing Ga by

In atoms is more favorable for the (1–101) surface (where cations are under-coordinated) than on (0001). We note that the existence of low coordinated surface atoms is rather unusual and has never been observed on ''traditional'' semiconductors. The reason is again that the principle of forming predominantly Ga-terminated surfaces overrides all other principles. Instead of forming surfaces with triply coordinated N atoms, the system prefers to have Ga atoms in the surface (although these atoms are under-coordinated). Thus, the effect In has on the surface (and growth morphology) depends strongly on its concentration. Under growth conditions for which In incorporation is negligible (high temperatures and high Ga flux) In simply occupies adlayer sites on the (0001) surface [5] and may act as a surfactant. However, under conditions under which InGaN alloys are grown (reduced temperatures and reduced Ga flux) the preferential segregation of In to sites having reduced N coordination can lead to the formation of morphological instabilities, such as the formation of dislocation pits on the (0001) surface.

6. Conclusions

Based on first-principles calculations, we have shown that group-III nitride surfaces have a number of novel and unexpected features making this material system very different from traditional semiconductors. Implications for the stability and growth of surfaces have been discussed. Most of these effects could be related to a unique feature of group-III nitride surfaces: the tendency to stabilize Ga-rich surfaces.

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