Atomic structure and energetics of the *c*-GaN(001) surface

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Density functional theory calculations are used to explore the geometry and stability of zinc-blende GaN(001). We find that the surface structure changes from a nitrogen adatom structure under nitrogen-rich conditions to a gallium contracted adlayer structure under gallium-rich conditions. Nitrogen adsorbed on this contracted adlayer has the tendency to penetrate the contracted adlayer, thus allowing for epitaxial growth.

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I. INTRODUCTION

In the last decade, GaN has been investigated intensively, both experimentally and theoretically.[1–5] GaN crystallizes in the stable wurtzite and metastable zinc-blende structure. The zinc-blende structure has a smaller band gap (by 0.2 eV) and lacks the built-in polarization-induced electrical fields in contrast to the wurtzite case. This makes the zinc-blende structure attractive for various applications because polarization-induced electrical fields limit the performance of optoelectronic devices. However, it can only be grown in specific conditions because of its metastability. Using GaAs or SiC as a substrate, it is possible to grow zinc-blende GaN epitaxially.[6–8]

Schörmann *et al.*[9,10] used plasma-assisted molecular beam epitaxy with atomic gallium and nitrogen sources at 720 °C to grow cubic GaN. A roughness minimum occurs when the gallium coverage is 1 ML. This indicates that gallium acts as a surfactant on the surface, similar to the hexagonal case. The atomic surface of the gallium adlayer is, to our knowledge, still unknown. Knowledge of this atomic surface would benefit the understanding of growth morphology and dopant incorporation because both are influenced by the surface structure and its effect on adatom diffusion and incorporation kinetics.

We have calculated various adatom models using first-principles methods. Similar to the case of hexagonal GaN (0001), we find that a contracted gallium adlayer is the most favorable surface structure of zinc-blende GaN(001) under gallium-rich conditions. Furthermore, the energetics of nitrogen atoms placed on top of the surface and between the contracted adlayer and the first GaN layer has been studied. We have found that nitrogen prefers to stay under the contracted adlayer at the position, which is required for ordered bulk GaN growth.

II. COMPUTATIONAL METHODS

The calculations are performed using the density functional theory (DFT) within the generalized gradient approach (GGA)[11,12] as implemented in the Vienna *Ab initio* Simulation Package (VASP).[13,14] The electron-ion interaction is described by the projector-augmented wave (PAW) scheme.[15] The electronic wave functions are expanded into plane waves up to a kinetic energy of 30 Ry. In all calculations, the 3d electrons of the Ga atoms have been treated as valence electrons.

To model the surface, a slab model consisting of 8 GaN layers separated by a vacuum of 20 Å has been used. The bottom surface has been saturated by pseudohydrogen (with 5/4 e each). All atoms were allowed to relax freely except for the two bottom layers which were kept fixed to imitate bulk material. Depending on the coverage and the surface structure model, 1×1, 3×1, 4×1, and 5×1 surface unit cells have been studied. Equivalent sets of Monkhorst-Pack[16] special points have been used to sample the surface Brillouin zone.

The PW91 functional[12] has been used to describe the electron exchange and correlation energy within the GGA. The formation enthalpy per GaN pair is calculated as

$$\Delta H_f^{T=0} = E_{\text{tot}}^{\text{GaN bulk}} - \frac{1}{2}E_{\text{tot}}^{\text{N}_2} - \frac{1}{4}E_{\text{tot}}^{\text{Ga bulk}}. \tag{1}$$

The most stable configuration of pure gallium is the α-gallium structure, which is stable at room temperature and low pressure. We have calculated a formation enthalpy of -1.05 eV—about 20% less than the experimental value of -1.25 eV. The grand canonical potential

$$\Omega = U - \sum \mu(A_i) n_{A_i} \tag{2}$$

of the structures has been calculated considering that the chemical potentials are restricted by

$$\mu(A_i) \leq \mu(A_i)_{\text{bulk}}. \tag{3}$$

Using equilibrium conditions with the bulk, namely

$$\begin{aligned}\mu(\text{GaN})_{\text{bulk}} &= \mu(\text{Ga}) + \mu(\text{N}) \\ &= \mu(\text{Ga})_{\text{bulk}} + \mu(\text{N}_2) - \Delta H_f(\text{GaN}),\end{aligned} \tag{4}$$

we obtain the experimentally relevant range for the chemical potential

$$\Delta H_f \leq \Delta\mu(\text{Ga}) = \mu(\text{Ga}) - \mu(\text{Ga})_{\text{bulk}} \leq 0 \tag{5}$$

of Ga. The nitrogen chemical potential is not independent, but determined by Eq. (4).

III. RESULTS AND DISCUSSION

A large variety of adatom positions has been investigated in order to find the energetically most stable structures. There are four different high-symmetry positions on the clean gallium-terminated 1×1 unit cell. The positions can be seen

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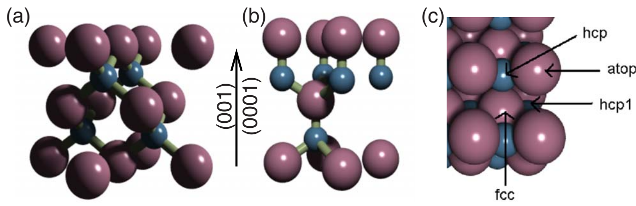

FIG. 1. (Color online) (a) zinc-blende GaN, (b) wurtzite structure, and (c) adsorption sites on the cubic GaN (001) surface. Ga atoms are shown as purple, N atoms as blue spheres.

in Fig. 1(c). Gallium and nitrogen atoms are placed on the fcc, atop hcp and hcp1 positions. Calculations have shown that nitrogen adatoms do not stay on the atop and fcc positions. Gallium adatoms, in contrast, can adsorb also on these positions. Table I sums up the geometric data of the clean and adatom surfaces after relaxation.

The lattice constant of α-Ga bulk is slightly smaller than that of GaN bulk. For hexagonal GaN, this was identified as the main reason for the stability of the contracted adlayer model.[17] Within the contracted adlayer, gallium atoms can form strong Ga–Ga bonds without breaking Ga-N bonds or inducing high strain in the surface Ga-N layer. For the free adlayer, i.e., only the Ga adlayer without the GaN substrate, the energy is minimal for a Ga-Ga spacing of around 2.71 Å for a nearly hexagonal structure (with an angle of 70°) and 2.68 Å for a cubic structure. Figure 2 shows the structures as adsorbed on the GaN substrate, enforcing a 3×1 translational symmetry. The black-filled circles correspond to the atoms in the "free Ga adlayers." If we contract the free adlayers in order to fit the GaN bulk lattice constant, we have to bring up an energy of 27(30) meV/Å^2 for the cubic (hexagonal) adlayer compared to their respective minimum energies. Comparing these results to the atomic spacings in the relaxed adlayer on top of the GaN substrate, we find 2.55 Å (hexagonal structure with 70° angle) and 2.81 Å (cubic structure). The energy difference amounts to 7 meV/Å^2 in this case.[18]

Figure 3 shows the surface energy vs the allowed range of the Ga chemical potential. Nitrogen adatoms are favored for N-rich conditions. Going to gallium-rich conditions, we first find the 1×4 clean surface[19] to become stable and, finally, at even stronger Ga-rich conditions, the surfaces with the contracted Ga adlayers to become the most stable structures. It should be noted here, however, that our models to describe contracted adlayers within (3×1) or (5×1) surface unit cells do only approximate the experimental situation, which

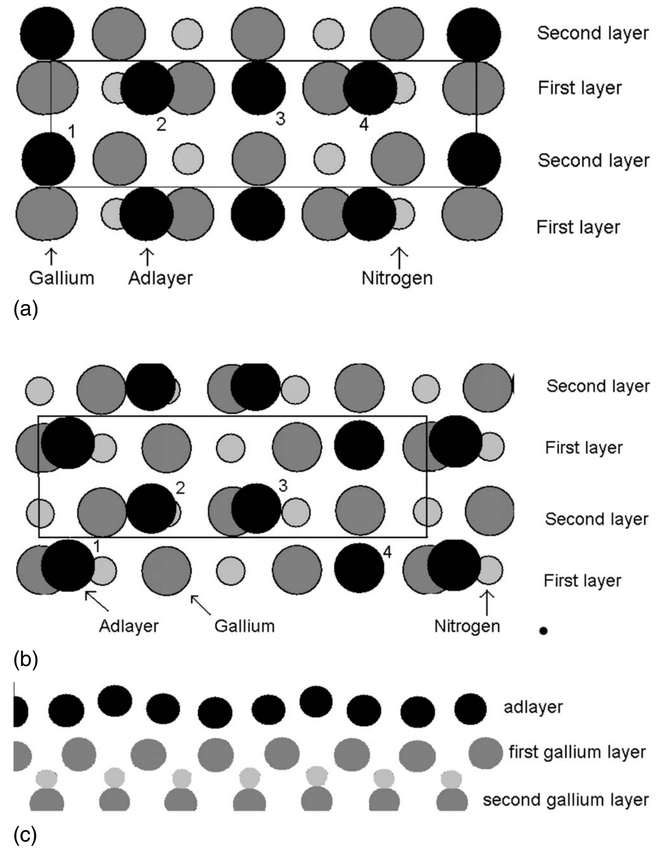

FIG. 2. The contracted gallium adlayer in 3×1 symmetry. Top view of the (a) cubic Ga-adlayer, (b) the structure with the 70° angle, and (c) side view of the structure shown in (a). Black circles denote Ga atoms in the adlayer.

will most likely correspond to an incommensurate and thermally fluctuating overlayer structure.

Experiments were performed at 720 °C.[9,10] At this temperature, the gallium adlayer atoms are mobile and can reorganize to form such a stable adstructure. After formation of the Ga contracted adlayer, nitrogen has to be built in. In order to continue ordered growth of the cubic GaN phase, a two-step mechanism is required: First, N atoms have to be adsorbed on top of the Ga adlayer, and second, a diffusion step through the Ga adlayer has to take place in order to lead the N atom onto the correct crystallographic position to form GaN.

The most favorable adsorption positions have been found by calculating the potential energy surface (PES) of the sur-

TABLE I. Calculated geometry data for the relaxed surface structures. z_0 is the vertical distance between the first and second Ga-N layer, z_1 is the vertical distance between the clean surface and the adatom, and d is the vertical distance between the first and second atom layer. All values are in Å.

	Clean		Ga adatoms				N adatoms	
	Ga term	N term	Fcc	hcp	hcp1	atop	hcp	hcp1
d	2.02	1.87	2.71	2.75	2.73	2.64	1.83	1.83
z_0	1.22	0.94	1.24	1.25	1.20	1.18	1.26	1.03
z_{ad}			1.11	2.25	2.34	2.64	1.33	1.26

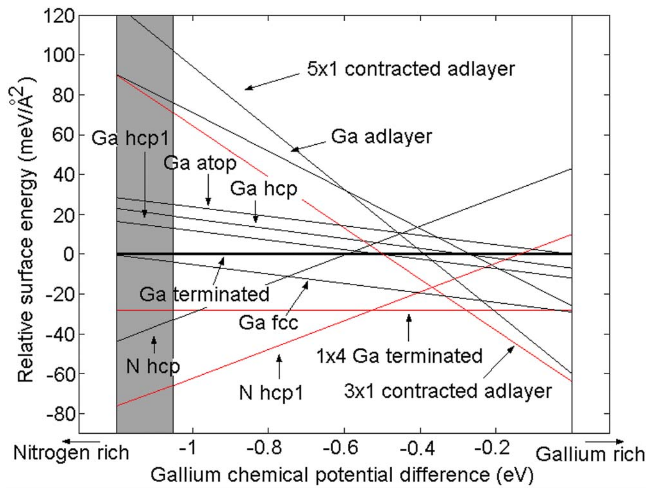

FIG. 3. (Color online) The phase diagram of GaN. The chemical potential of gallium runs from the formation enthalpy to 0. The shaded region is the extrapolation to the experimental value.

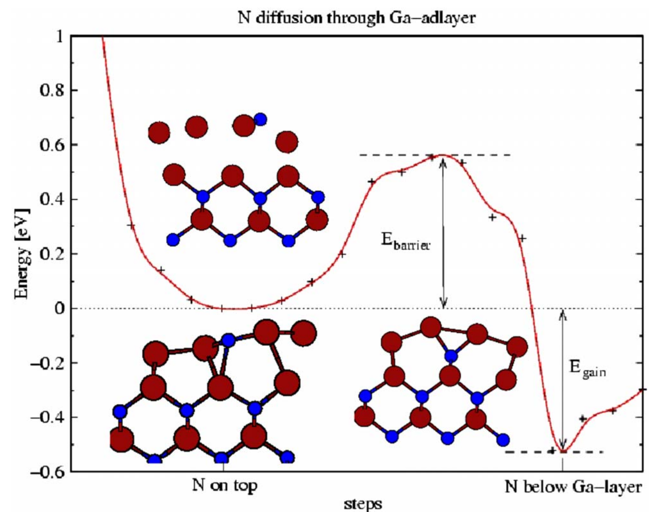

FIG. 5. (Color online) Calculated diffusion path of the first nitrogen atom. The energy reference (0 eV) has been set to the energy value for adsorbed nitrogen. The barrier is 554 meV and the energy gain is 523 meV.

face with the gallium adlayer and a single nitrogen atom. The result is shown in Fig. 4. Nitrogen adsorption is energetically favorable at the contracted adlayer structure due to the bonds the atom can form: while only two bonds can be formed at the clean gallium-terminated surface, the N atom can form four bonds at the contracted adlayer surface. Placing the nitrogen atom subsurface lowers its energy with respect to its minimum adsorption position on top of the contracted adlayer. The reaction paths for a first and second N atom across the contracted adlayer are shown in Figs. 5 and 6, respectively. Relatively high-energy barriers of 554 meV and 340 meV for the first and second nitrogen atom, respectively, have to be overcome in order to get the nitrogen atom to the crystallographic position as it should take in GaN bulk. It should be noted, however, that these calculated barriers correspond to upper limits for the actual penetration energies because lateral movements of the adlayer structures are restricted to preserve the 3×1 symmetry inherent to the model.

In total, the diffusion process leads the nitrogen atom to an energetically more favorable position (1.24 eV lower) and should, therefore, be thermodynamically activated. This energy gain is significant and large compared to the energy barrier, making the proposed model a feasible mechanism for cubic GaN growth under gallium-rich conditions.

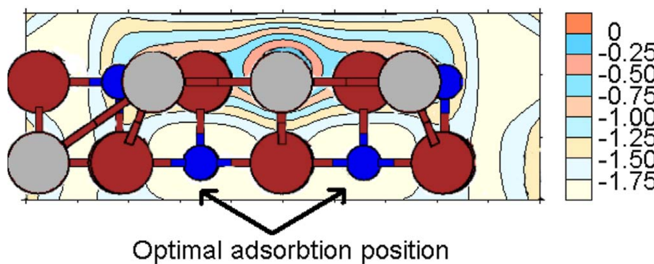

FIG. 4. (Color online) The PES seen by an N atom adsorbed on the contracted adlayer in the (3×1) unit cell. The most likely adsorption site for the N atom is the position with the lowest energy as indicated by the arrows. The legend gives relative adsorption energies in electronvolt.

IV. CONCLUSIONS

We have shown that the contracted adlayer model suggested by Neugebauer *et al.*[19] for surfaces of hexagonal GaN under Ga-rich conditions is favorable in case of cubic GaN (001) surfaces as well. Going from nitrogen-rich conditions to gallium-rich conditions, the N adatom on the hcp1 position, the 1×4 gallium tetramer surface, and finally at extreme gallium-rich conditions, the contracted adlayer becomes most stable. The reason for the stability of this contracted adlayer is the Ga-Ga spacing. The reduction of this length results in an energy gain between 18 meV/Å^2 and 30.4 meV/Å^2 for the calculated structures. The surface energy of GaN is of the order of 100 meV/Å^2. This means

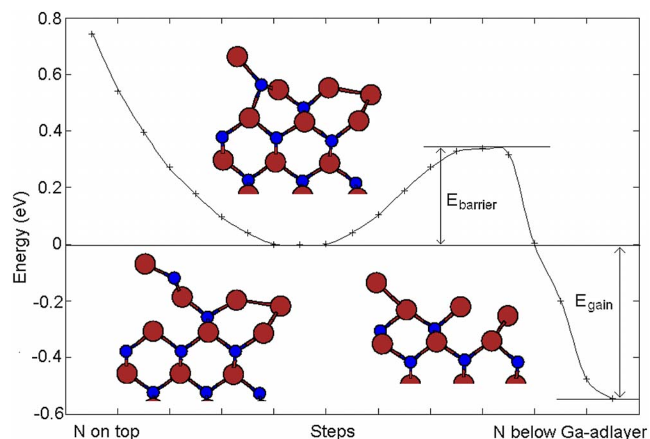

FIG. 6. (Color online) Calculated diffusion path of the second nitrogen atom. The barrier is 340 meV and the energy gain is 545 meV.

that this energy gain is significant. We found that under gallium-rich conditions the 3×1 structures have the lowest surface energies, making them favorable above the other calculated structures. The gallium adlayer atoms are likely to be mobile because of the high temperature (720°) during the MBE process. Our findings indicate that this contracted adlayer may assist the diffusion of nitrogen below the outermost plane to positions that are those pertaining to N atoms in bulk GaN.

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