Theory of surface morphology of wurtzite GaN (0001) surfaces

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The influence of growth conditions and surface polarity upon the morphology of (0001) GaN surfaces is studied from first principles. The charge transfer between the Ga and N atoms in GaN and the very large electronegativity of nitrogen are found to play decisive roles in determining the stable reconstructions. Further, hydrogen stabilizes the ideally cleaved surface irrespective of polarity. For both polarities, adsorption of 3/4 of a monolayer of hydrogen results in a very stable surface with a 2×2 symmetry.

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The commercial production of high-brightness blue LED's and the recent demonstration of laser diodes¹ have realized the expectations that have been held out for the III-V nitrides as optoelectronic materials. Advances in the application of this material to devices have been very closely tied to progress in the growth of epitaxial layers and heterostructures. Thus, a refined understanding of its growth is necessary for a further improvement of the quality of the material. In spite of the great effort that has been expended on the study of growth, even the polarity of the surface, i.e., whether the surface is Ga or N terminated, remains to be fully determined.² The surface morphology depends critically upon polarity,³ and the uncertainty about the surface polarity will hinder progress in growth technology.

The two chief methods employed for epitaxial growth of GaN are metalorganic chemical vapor deposition (MOCVD) and molecular-beam epitaxy (MBE). Further, a variety of substrates and a spectrum of buffer layers have been used to grow GaN, making interpretation of the experimental data difficult. This is reflected in the fact that MBE-grown samples of unknown polarity exhibit a 2×2 reconstruction,⁴ while samples grown by MOCVD on sapphire have been shown to have different terminations depending upon the preparation of the buffer layer or growth parameters.^{3,5,6} It is generally agreed that the Ga-terminated MOCVD-grown samples are smooth, which is consistent with the observed two-dimensional growth in MBE of a presumed Ga-terminated surface. However, conflicting conclusions have been made about the N-terminated surface; it has been shown to have inversion domains,³ to be faceted,⁵ and to have a 1×1 reconstruction with a 3/4 monolayer of hydrogen coverage.⁶

In this situation, a theoretical characterization of the surface morphology can provide a framework for the interpretation of the experimental results. Thus, we have studied the dependence upon growth conditions of the 2×2 reconstructions of clean GaN (0001) surfaces with both polarities. We find that the ionic nature of GaN and the very large electronegativity of nitrogen determine the adsorption sites for the lowest-energy adatom reconstructions and their subsequent behavior. Because the presence of hydrogen in MOCVD constitutes a major difference between the growth parameters of MBE and MOCVD, we have also studied the influence of adsorbed hydrogen on the surface morphology of GaN.

All calculations were carried out within the framework of a multigrid-based total-energy method that uses a real-space grid as the basis. Multigrid methods provide effective convergence acceleration and preconditioning on all length scales.⁷ The Perdew-Zunger parametrization⁸ of the Ceperley-Alder form⁹ of the exchange-correlation energy was used. Nonlocal, norm-conserving pseudopotentials¹⁰⁻¹² were included using the Kleinman-Bylander approach.¹³ The slabs contained four bilayers of GaN, three of which were relaxed. Relaxations in the third bilayer were negligible, indicating that a sufficiently large slab was employed. For calculations of the reconstructions of the Ga-terminated surface, pseudo-hydrogens of charge 0.75 passivated the N-terminated face, while for the study of the N-terminated face, pseudo-hydrogens of charge 1.25 passivated the Ga-terminated surface.¹⁴ A vacuum region of 10 Å was used. An orthorhombic supercell with grid spacing of 0.27, 0.26, and 0.27 a.u. in the x , y , and z directions, respectively, was employed after a careful convergence study, thereby ensuring that the real-space description of the pseudopotentials is accurate.¹⁵ Due to the well-known failure of the local-density approximation to describe the band gap, we obtain a bulk LDA gap of 2.26 eV for GaN, as compared to the experimental value of 3.4 eV. However, the relative positions of the bulk and surface states are determined far more accurately. Further discussion of the calculations is given elsewhere.^{16,17}

For the clean gallium- and nitrogen-terminated surfaces, we studied the 1×1 ideal, relaxed structure and seven different 2×2 reconstructions, namely the 2×2 vacancy structure, and 2×2 nitrogen adatom, gallium adatom and nitrogen-trimer structures, each on the T_3 and H_3 sites (see Fig. 1). The lowest-energy reconstructions are all semiconducting and have surface states in the gap. We also investigated 1/4 and 3/4 monolayers of hydrogen adsorbed on the ideally cleaved surfaces of both polarities.

Figure 2 displays the relative surface energies for the five lowest energy reconstructions of each type on the Ga-terminated (0001) surface. For gallium-rich conditions, the gallium adatom sits on the T_3 site above the subsurface nitrogen atom. Because bonding in GaN has a strongly ionic component, charge is transferred from the Ga to the N atom. Consequently, the proximity of the gallium adatom to the nitrogen subsurface atom lowers the electrostatic energy and

FIG. 1. Schematic top view of the (0001) GaN surface. On the Ga-terminated (0001) surface, the black atoms are gallium atoms; while the white atoms are nitrogen atoms; the situation is reversed on the N-terminated (000 $\bar{1}$) surface. An atom in the T_3 site (represented by a square inside of a white circle) sits above a subsurface atom (a white circle), while an atom in the H_3 site (represented by a square) sits in the hollow site as shown. The circled atoms are in the 2×2 cell.

makes this particular configuration more favorable energetically than the gallium adatom reconstruction with the adatom on the hollow site. Due to the stoichiometry of the gallium-adatom reconstruction on the (0001) surface, the dangling bond on the nonbonded gallium surface atom is empty. A surface state is nonetheless present at about 1.1 eV. This state corresponds to a bonding state between the gallium adatom and a gallium surface atom. The character of this bond is similar to the covalent bond seen in α -Ga.

Under nitrogen-rich conditions, the nitrogen adatom sits on the hollow (H_3) site. This configuration is stabilized because it separates the nitrogen adatom from the subsurface

FIG. 2. Relative surface energy vs gallium chemical potential for the (0001) Ga-terminated surface. The energies are calculated with respect to the 2×2 vacancy reconstruction. The maximum chemical potential for N (Ga) is equal to the energy per atom calculated for N_2 (bulk Ga).

FIG. 3. Formation energy vs gallium chemical potential for the nitrogen-terminated (000 $\bar{1}$) surface. The energies are quoted with respect to the vacancy reconstruction. The maximum chemical potential for N (Ga) is equal to the energy per atom calculated for N_2 (bulk Ga).

nitrogen atom and thereby lowers the electrostatic energy. The presence of dangling bonds in the nitrogen-adatom reconstruction leads us to expect surface states in the gap. This is confirmed by the calculation, which shows surface states localized on the nitrogen adatom. There is a flat surface band of p_x - p_y character that lies just below the valence-band maximum (VBM) throughout the whole Brillouin zone and decays into a resonance at Γ . We find that the true dangling-bond state of the nitrogen adatom lies about 1.0 eV above the VBM.

Figure 3 shows the relative surface energies for the five lowest energy reconstructions of each type on the N-terminated (000 $\bar{1}$) surface. Under gallium-rich conditions and for most of the range of the chemical potential, the reconstruction with the gallium-adatom on the H_3 site is the most energetically favorable. The adatom sits on the H_3 site. The same electrostatic argument applied to the Ga-terminated reconstructions is valid here: the gallium adatom on the hollow site optimizes the electrostatic energy by maximizing the separation between the gallium adatom and the gallium subsurface atoms. As a result of the stoichiometry of the gallium-adatom reconstruction, there is an occupied dangling-bond state on the nonbonded surface nitrogen atom. This gives rise to a surface state at about 0.3 eV above the VBM that has a p_z character.

Under nitrogen-rich conditions, a unique scenario occurs: the nitrogen adatom reconstructs to form an N_2 molecule that is bonded to a substrate that has a reconstruction very similar to the nitrogen-vacancy reconstruction (see Fig. 4), which, by itself, is unstable over the whole range of chemical potential (cf. Fig. 3). The strength of the N-N bond in the N_2 molecule is the driving force behind this reconstruction. Indeed, the dimerization of the nitrogen adatom is found to occur irrespective of our trial initial position of the extra nitrogen atom. This suggests that free nitrogen atoms in the vicinity of the nitrogen surface will prefer to bond to one of the surface atoms and form N_2 molecules. The binding energy of the N_2 molecule to the substrate is 0.3 eV, while the

FIG. 4. Schematic side (a) and top (b) views of the 2×2 nitrogen dimer/nitrogen vacancy reconstruction on the (0001) N-terminated surface of GaN. The reconstruction consists of a nitrogen dimer bound to a 2×2 nitrogen vacancy structure. The white circles denote the nitrogen atoms on the surface, while the dark circles denote gallium atoms in the first subsurface layer. The shaded atoms comprise the N_2 dimer.

theoretical binding energy per nitrogen atom of N_2 is 5.9 eV. Consequently, the evaporation of N_2 from the surface is much more likely to occur than the dissociation of the molecule itself. As the vacancy reconstruction is unstable over the entire range of chemical potential, evaporation of the N_2 molecule will lead to a cascade of reconstructions. Correcting for the 1.1 eV/atom overestimate of the binding energy of the molecule by density functional theory will not alter this conclusion. A filled dangling-bond state with p_z symmetry is found just above the VBM in the case of the nitrogen-dimer/nitrogen-vacancy reconstruction. The molecular levels of the triple bond of the nitrogen dimer lie deep in the valence band, with a spectrum that resembles very closely the spectrum of the isolated molecule.

Characteristic of MOCVD growth is the presence of hydrogen. We have therefore studied how adsorbed hydrogen affects the surface morphology and find that its impact is significant. For both polarities, a surface with a $3/4$ monolayer of hydrogen adsorbed on the ideally cleaved structure is more stable than any of the previously considered 2×2 reconstructions over the entire spectrum of the chemical potentials, where the ranges of the chemical potentials for gallium and nitrogen are bounded by the chemical potential for gallium metal and N_2 and the chemical potential of hydrogen is the binding energy per atom in the H_2 molecule.

For a $3/4$ monolayer coverage on the Ga-terminated surface, the hydrogen atoms sit above the gallium atoms. As a

FIG. 5. Surface-projected band-structure for a $3/4$ monolayer of hydrogen adsorbed on the nitrogen-terminated surface of GaN. The circles represent the experimental results of Ref. 18.

result of the relaxation of the gallium atom not bonded to a hydrogen atom, the surface has a 2×2 symmetry. No surface states are found in the gap; however, there is a flat surface band at -0.9 eV, which decays into the bulk at Γ .

For a $3/4$ monolayer of hydrogen adsorbed on the N-terminated surface, the hydrogen atoms sit above the nitrogen atoms. The H-N bond length is the very close to H-N bond length in NH_3 . The nitrogen atoms bonded to the hydrogen atoms undergo a small inward relaxation, while the nonbonded nitrogen relaxes very slightly outwards, so that the surface, in fact, has a 2×2 symmetry. As shown in Fig. 5, this reconstruction has a surface band just below the valence band maximum. The band arises from the filled dangling-bond state on surface nitrogen atom that is not bonded to an adsorbed hydrogen atom and has p_z symmetry.

LEED measurements on the N-terminated surface concluded that a surface with a $3/4$ monolayer of hydrogen adsorbed has a 1×1 symmetry. The relaxation of the surface nitrogen atoms was found to be below the resolution of LEED,⁶ which is in agreement with the small relaxations found here. Further a recent experiment on a sample grown by MBE on a sapphire substrate revealed a semiconducting surface with a 1×1 symmetry, which has a flat surface band just below the valence-band maximum.¹⁸ We have compared these data to all of the stable surface structures described above. The only structure that reproduces the experimental results is the $3/4$ monolayer H structure, in a 2×2 reconstruction on the N-terminated surface. In all other cases, the agreement is poor. In Fig. 4, the experimentally observed surface band is shown superimposed on the theoretically determined projected-band structure for $3/4$ H-adatom structure on the N-terminated surface. The good agreement between our results and the data suggests that this sample is N terminated with adsorbed hydrogen. However, it should be noted that the samples were grown by MBE and that hydrogen was

not intentionally introduced into the system.¹⁸

In summary, we have investigated the dependence of the equilibrium surface morphology of GaN upon the growth conditions. The decisive factors favoring the lowest-energy reconstructions are the ionic character of the Ga-N bond and the strength of the N-N bond. Under gallium-rich conditions, gallium-adatom reconstructions are the most energetically favorable of the 2×2 reconstructions studied, irrespective of the polarity of the surface. Under nitrogen-rich conditions, a nitrogen-adatom reconstruction is most stable on the Ga-terminated surface. On the N-terminated surface, a nitrogen atom spontaneously bonds to a surface nitrogen atom creating a nitrogen molecule and a vacancy substrate. The molecule is weakly bound and is expected to evaporate at the

high temperatures of growth. Since the vacancy reconstruction is unstable over the whole range of chemical potential, the evaporation of the N_2 molecules should lead to a cascade of reconstructions of the substrate. For both polarities, a $3/4$ monolayer of hydrogen stabilizes the relaxed, ideally cleaved surfaces; these reconstructions have a 2×2 symmetry and a flat surface band below the VBM. The very small relaxation of the surface atoms on the N-terminated surface, which is below the resolution of LEED,⁶ means that this surface will appear as 1×1 .

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- ¹S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, and Y. Sugimoto, *Jpn. J. Appl. Phys.* **35**, L74 (1996).
- ²G. Nowak, S. Krukowski, I. Grzegory, S. Porowski, J. M. Baranowski, K. Pakula, and J. Zak, *MRS Internet J. Nitride Semicond. Res.* **1**, 5 (1996); E. S. Hellman, D. N. E. Buchanan, D. Wiesmann, and I. Brener, *ibid.* **1**, 16 (1996); W. E. Packard, J. D. Dow, R. Nicolaides, K. Doverspike, and R. Kaplan, *Superlattices Microstruct.* **20**, 145 (1996).
- ³B. Daudin, J. L. Rouvière, and M. Arlery, *Appl. Phys. Lett.* **69**, 2480 (1996); J. L. Rouvière, M. Arley, R. Niebuhr, K. H. Bachem, and O. Briot, *MRS Internet J. Nitride Semicond. Res.* **1**, 33 (1996).
- ⁴W. C. Hughes, W. H. Rowland, Jr., M. A. L. Johnson, S. Fujita, J. W. Cook, Jr., J. F. Schetzina, J. Ren, and J. A. Edmond, *J. Vac. Sci. Technol. B* **13**, 1571 (1995); M. A. L. Johnson, Z. Yu, C. Boney, W. H. Rowland, Jr., W. C. Hughes, J. W. Cook, Jr., J. F. Schetzina, N. A. El-Masry, M. T. Leonard, H. S. Kong, and J. A. Edmond, in *III-V Nitrides*, edited by F. A. Ponce, T. D. Moustakas, I. Akasak, and B. A. Monemar, *MRS Symposia Proceedings No. 449* (Materials Research Society, Pittsburgh, 1997), p. 271; T. D. Moustakas, in *Gallium Nitride and Related Materials*, edited by R. D. Dupuis, J. A. Edmond, F. A. Ponce, and S. Nakamura, *MRS Symposia Proceedings No. 395* (Materials Research Society, Pittsburgh, 1996), p. 111.
- ⁵F. A. Ponce, D. P. Bour, W. T. Young, M. Saunders, and J. W. Steeds, *Appl. Phys. Lett.* **69**, 337 (1996).
- ⁶M. M. Sung, J. Ahn, V. Bykov, J. W. Rabalais, D. D. Koleske, and A. E. Wickenden, *Phys. Rev. B* **54**, 14 652 (1996).
- ⁷E. L. Briggs, D. J. Sullivan, and J. Bernholc, *Phys. Rev. B* **52**, R5471 (1995); **54**, 14 362 (1996).
- ⁸J. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ⁹D. Ceperley and B. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- ¹⁰G. Bachelet, D. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 4199 (1982).
- ¹¹D. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).
- ¹²D. Hamann, *Phys. Rev. B* **40**, 2980 (1989).
- ¹³L. Kleinman and D. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).
- ¹⁴K. Shiraishi, *J. Phys. Soc. Jpn.* **59**, 3455 (1990).
- ¹⁵C. Bungaro (private communication).
- ¹⁶M. Buongiorno Nardelli, K. Rapcewicz, and J. Bernholc, *Phys. Rev. B* **55**, R7323 (1997).
- ¹⁷K. Rapcewicz, M. Buongiorno Nardelli, and J. Bernholc (unpublished).
- ¹⁸S. S. Dhesi, C. B. Stagarescu, K. E. Smith, R. Singh, and T. D. Moustakas (unpublished).