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Dissociative chemisorption of NH_3 molecules on GaN(0001) surfaces

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We performed *ab initio* calculations to study the structure and the relative stability of hydrogenated GaN(0001) surfaces which may form during the growth of gallium nitride using an NH_3 nitrogen source. The surfaces that we have studied contain H ad-atoms and NH_2 ad-complexes adsorbed on GaN(0001). We find that adsorption of H, alone or accompanied by other species, stabilizes the surface of GaN and is able to catalyze the formation of an ideal-like geometry. We give an interpretation of this effect in terms of the electron band structure. Our results suggest, on microscopic grounds, that rough surfaces are formed by metal organic chemical vapor deposition under N-rich conditions. Ga-rich and H-rich conditions are suggested for the attainment of high quality films.

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Group-III nitrides are suitable semiconductors for the fabrication of high-performance electronic and optoelectronic devices.[1] In the field of optoelectronics, they are appealing for the successful operation of blue and ultraviolet light emitting diodes and lasers.[2] In fact, engineered alloys based on group-III nitrides are used to grow materials with an electronic band-gap ranging from 1.9 eV to 6.2 eV, that are exploited as emitters. Moreover, the chemical hardness and the favorable electron transport properties of GaN (e.g., the high electron drift velocity), have prompted its use in electronic devices, such as transistors operating at high temperature and high power. Despite these very appealing properties, the difficulty of growing good quality films represents a limitation in the development of GaN-based technology. In order to improve the quality of the epitaxial materials, the understanding of the microscopic growth mechanisms is demanded, and is still incomplete. A powerful tool to pursue such investigation is represented by *ab initio* simulations of atom and molecule chemisorption at the evolving surfaces, which is the subject of this article.

The formation of native defects and the incorporation of impurities are usually undesired by-products of epitaxial growth. They may act as scattering centers, and modify the optical and electronic properties of the epitaxial films with respect to the bulk materials. Here, we do not wish to evaluate these effects, but we take into account the presence of some defects in order to select a representative subset of the possible configurations that GaN(0001) surfaces may sample during their evolution. As far as native defects are concerned, *ab initio* calculations have proved that Ga vacancies have a high probability of formation in GaN under N-rich conditions, both in the bulk and at the (0001) surface.[3,4] Indeed, Ga vacancies were revealed by positron annihilation spectroscopy in undoped GaN, and the highest concentration was obtained under N-rich conditions.[5] Among the impurities, hydrogen is most likely incorporated in non-negligible concentrations in epitaxial films produced in metal organic chemical vapor deposition (MOCVD) chambers. The presence of hydrogen affects the quality of the growing material during the early deposition stages:[6] eventually, H may improve the growth rate of GaN under Ga-rich conditions,[7] and facilitate doping.[8] Hydrogen atoms behave as donors and form complexes with acceptors (e.g., Mg or Ga vacancies) in *p*-type material.[9] The simultaneous presence of native defects and foreign impurities produces other important effects. For instance, hydrogenated Ga-vacancies have been suggested as the origin of the yellow luminescence in GaN.[9,10] The above motivations have restricted our choice of metastable structures to GaN(0001) surfaces containing Ga vacancies and excess H atoms. The experimental use of NH_3 as the nitrogen precursor in MOCVD growth of GaN, and of H_2 as the carrier gas, as well as the strong dependence of the growth efficiency on the temperature and on the interactions between hydrogen and NH_2 groups adsorbed at the surface, suggested us to study viable mechanisms for the chemisorption of NH_3 at the GaN(0001) surfaces as indicative for the growth process. Our approach was also prompted by previous theoretical studies of the adsorption of NH_2 groups and hydrogen on GaN($10\bar{1}0$),[11] and on GaN($000\bar{1}$).[12]

Although restricted to a limited number of metastable surface configurations, our results allow us to identify relevant conditions for the surface evolution when the growing GaN surface is interacting with the external N supply. In particular, we show that rough surfaces are likely to occur in N-rich conditions, for which the Ga-N bulk bilayers are not completed. Instead, we identify the intermediate structure that may stabilize an ordered phase and conduce to a pseudo-(1×1) GaN(0001) surface in Ga-rich conditions.[13] In all cases, isolated H atoms are relevant to saturate the dangling bonds.

We performed *ab initio* calculations of the equilibrium structure for several GaN(0001) surfaces containing NH_2 ad-complexes bonded to surface Ga atoms, and H ad-atoms bonded to subsurface N atoms. The total energy for each surface was calculated in the frame of the density functional theory with the local density approximation (DFT-LDA).[14] The ions were described by Troullier-Martins pseudopotentials[15] and nonlocal core corrections (NLCC) were included for the Ga species.[16] Comparison of our results with previous calculations[4] revealed that NLCC were sufficient for a correct evaluation of the relative stability of our structures.[17] Thus, we did not treat the Ga $3d$ electrons as valence electrons. For each surface, the equilibrium geometry was determined by minimizing the energy functional

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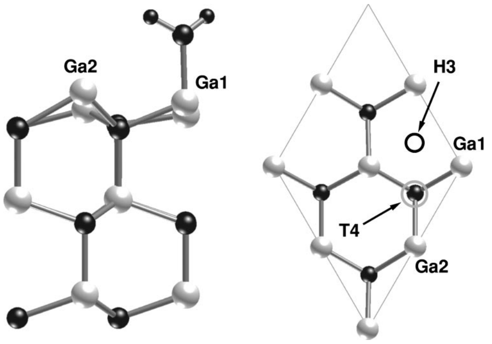

FIG. 1. Left: three-dimensional view of a GaN(0001) surface, covered by one NH_2 ad-complex in a 2×2 cell (this structure is labeled NH2). Large white (black) spheres identify Ga (N) atoms; small black spheres identify H atoms. Right: top view of a 2×2 GaN(0001) surface supercell; Ga1 is the site where the NH_2 group is adsorbed, Ga2 is the site where the Ga vacancy is created; open circles represent Ga (T4) and/or N (H3) ad-atoms.

with respect to the atomic positions and the electronic wave functions,[18] which were expanded in plane waves with kinetic energy up to 60 Ry. The surfaces were simulated by repeated supercells with 2×2 surface periodicity, containing four GaN bilayers, one layer of pseudohydrogen atoms to saturate the N dangling bonds at the $(000\bar{1})$ surface, and 13 Å of vacuum, hosting the adsorbed species. For Brillouin zone (BZ) sums, we used two special **k** points in the irreducible wedge of the 2×2 surface BZ. The pseudohydrogen layer, and the GaN bulk bilayer attached to it, were not allowed to move.

The relative formation energy of a given surface *i*, with respect to an arbitrary structure, is calculated as a function of the chemical potentials of the atomic species involved. For the systems that we studied, it depends on the chemical potentials of H, N, and Ga. However, physical constraints reduce the number of unknowns. We consider the surfaces in equilibrium with the underlying bulk GaN, which fixes the relation between the Ga and N chemical potentials: $\mu_{Ga} + \mu_N = \mu_{GaN}$. With this assumption, the relative formation energy of structure *i* is

$$\Delta_i E_f = \Delta_i E_f^0(\mu_H) - (\Delta_i n_N - \Delta_i n_{Ga})(\mu_N - \tfrac{1}{2}\mu_{N2}), \tag{1}$$

where $\Delta_i E_f^0(\mu_H)$ is the relative formation energy in N-rich conditions and depends on the H vapor pressure. In Eq. (1), n_s and μ_s are the number of atoms and the chemical potential, respectively, of species *s*. $\frac{1}{2}\mu_{N2}$ is the chemical potential of N atoms in their most stable phase, that is a gas of N_2 molecules: this value identifies a N-rich ambient, and fixes the highest allowed μ_N.

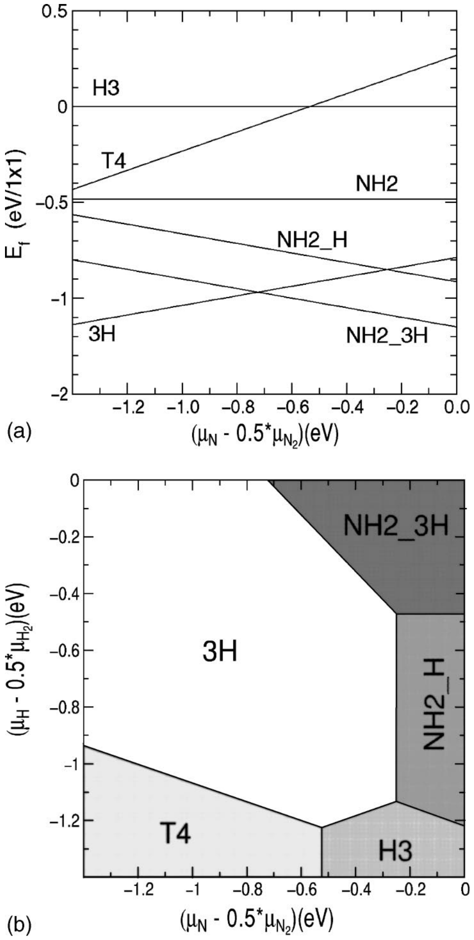

FIG. 2. (a) Relative formation energy of the calculated equilibrium structures as a function of the N chemical potential, with respect to the H3 reference surface; H-rich conditions, $\mu_H = \frac{1}{2}\mu_{H2}$ are assumed. (b) Phase diagram of low-energy GaN(0001) surfaces in presence of NH_3 and H_2 sources. The shaded regions indicate the most favorable structures in the different regions of the allowed phase space.

We studied the energetics of two clean surfaces, one *hydrogenated* surface, and three *nitridated* surfaces. We denote by *hydrogenated* surfaces those containing only H ad-atoms, and by *nitridated* surfaces those containing also NH_2 ad-complexes. The representative clean surfaces were selected on the basis of previous *ab initio* calculations.[4,19] Limiting our selection to 2×2 phases, two surfaces are most likely to occur during surface evolution, depending on the growth conditions. According to the results of Smith and co-workers,[4] in a Ga-rich environment, the most favorable GaN(0001) surface contains one Ga ad-atom per 2×2 cell, situated above a sub-surface N atom, and is labeled T4. In a N-rich environment, the lowest energy structure is a surface containing one N ad-atom per 2×2 cell, situated above a hollow subsurface site (structure labeled H3). The adsorption sites for the N and Ga ad-atoms at the clean surfaces T4 and H3 are indicated with circles in Fig. 1. We considered one *hydrogenated* surface containing $\frac{3}{4}$ monolayers (ML) of H adsorbed on surface Ga (labeled 3H): the Ga-H bonds are perpendicular to the ideal (0001) plane. In the three *nitridated* surfaces, one NH_2 group per 2×2 cell is placed on the Ga1 surface atom (see Fig. 1), forming a Ga-N bond perpendicular to the ideal (0001) plane, e.g., oriented along the [0001] growth direction; zero (label NH2), one (label NH2_H), or three (label NH2_3H) H ad-atoms are adsorbed around the Ga vacancy at site Ga2, forming bonds with the surrounding N atoms.

In Fig. 2, we report our results for the energetics. To obtain the plot in Fig. 2(a), we have fixed H-rich conditions, which corresponds to setting $\mu_H = \frac{1}{2}\mu_{H2}$ (Ref. 20) in Eq. (1), so that the relative formation energy is a function of the N chemical potential alone. The right (left) end of the horizontal axis fixes N-rich (Ga-rich) conditions. Figure 2(b) is obtained by relaxing the condition of fixed μ_H in Eq. (1) and represents the phase diagram of the system: the different shaded areas indicate the most stable structures when both μ_N and μ_H are allowed to vary. μ_N is limited to the left by the formation enthalpy of GaN ($\mu_N = \frac{1}{2}\mu_{N2} - \Delta H_{GaN}$). We have not investigated the physical lower limit of μ_H in terms of possible H-based precipitates, and we have assumed a wide interval, equal to that for μ_N.

Figure 2(a) reveals that both *hydrogenated* and *nitridated* surfaces have lower formation energies than the clean surfaces H3 and T4 under the assumption of H abundance ($\mu_H = \frac{1}{2}\mu_{H2}$). In fact, the lowest energy structure is the NH2_3H *nitridated* surface in N-rich conditions and the 3H *hydrogenated* surface in N-poor conditions. The clean surfaces may turn stable only in a limited region of the phase space corresponding to very H-poor ambient, for $\mu_H \leqslant \frac{1}{2}\mu_{H2}$-1 eV, as shown in the bottom part of Fig. 2(b). This is not likely, e.g., in MOCVD chambers, especially if a H_2 carrier gas is employed. The above results are a signature of the relevant role played by H and by the amino groups for the formation of GaN. Even though the final surfaces may be cleaned by annealing or etching processes that remove the adsorbed atoms, the intermediate stages in thermodynamic equilibrium are strongly marked by the presence of foreign species. In fact, our results prove that they mediate the stable surface reconstructions.

Two different scenarios for the chemisorption of dissociated NH_3 molecules on GaN(0001) are identified through the study of the energetics. The *nitridated* NH2_3H surface, favorable in an extremely N-rich ambient, is characterized by the formation of [0001] bonds between the surface Ga atoms and the N atoms of the chemisorbed NH_2 ad-complexes. These bonds are conducive to the thickening of the GaN(0001) epitaxial overlayer. However, in the NH2_3H surface that we have considered, the formation of these bonds is accompanied by a huge incorporation of H, which is not observed experimentally. The excess H atoms form equal bonds with the three subsurface N atoms that surround the Ga vacancy, in a hexagonal geometry and almost coplanar with the N atoms: the N-H distance is 1.01 Å, and the H-H distance is 1.69 Å. The small H-H distance suggests the presence of residual electrostatic repulsion that contributes with a positive term to the formation energy of this configuration. While the H atoms of the NH_2 groups are likely removed upon further addition of N and Ga species, those around the Ga vacancies would be quenched. Therefore, other mechanisms must be active: for instance, long range reconstruction may accommodate larger concentrations of ammino groups and smaller concentrations of H, minimizing the residual electrostatic repulsion at the Ga-vacancy sites. Our choice for the *nitridated* surfaces was constrained by the selected 2×2 periodicity. Within such a supercell, the inclusion of multiple NH_2 ad-complexes in the cell would induce H-H interactions that may form a H top layer and inhibit continued growth. Instead, in our small concentration of amino groups, many H ad-atoms are necessary to form a stable site. On the basis of the above results and discussion, we suggest that deposition in the N-rich regime would be governed by the formation of the isolated Ga-N [0001] bonds that we have identified, but the establishment of a long range reconstruction should be taken into account to allow for different combinations of ad-atoms and ad-complexes. The formation of steps and defects in such conditions is suggested by our results.

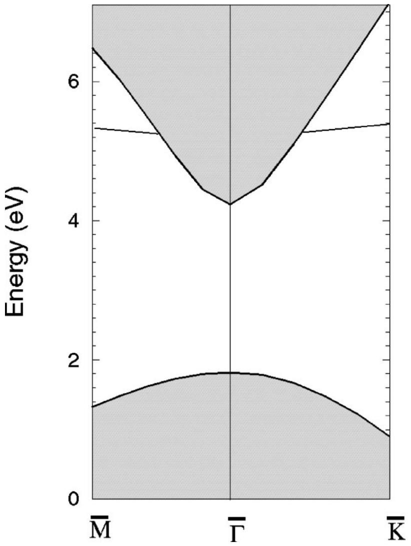

FIG. 3. Surface band structure of the *hydrogenated* stable GaN(0001) surface, along the $\overline{\Gamma M}$ and $\overline{\Gamma X}$ directions: the solid line represents the empty surface band derived from the dangling bond on the Ga rest-atom. Note the absence of surface states in the band gap.

In the opposite regime, under Ga-rich conditions, the lowest energy *hydrogenated* 3H surface is characterized by a flat, almost 1×1 geometry. A mechanism for which H is removed at each step, leaving behind the ideal-like Ga-terminated GaN(0001) surface, may by hypothesized in this case. This picture is consistent with recent observations[13] of stable 1×1 and pseudo-(1×1) reconstructions in Ga-rich conditions. The observed steady state reconstructions contain 1–2 ML of Ga above the ideal-like surface, formed by using a terminating Ga flux. We suggest that a possible evolving mechanism for these pseudo-(1×1) structures is the 3H flat surface identified in our calculations, whose high stability guarantees ordered intermediate deposition stages.

We calculated the band structure for all the optimized surfaces.[21] While the clean surfaces and the *nitridated* surfaces that we have studied exhibit surface electron states in the bulk gap, for the *hydrogenated* 3H structure the gap is free of surface states. The band structure of the 3H surface is shown in Fig. 3. The occupied surface states localized on the Ga-H bonds are completely resonating with the valence bulk continuum. The empty surface state, localized on the Ga rest-atom not bonded to the chemisorbed H atoms, splits off the continuum of bulk conduction states only at the border of the surface BZ, leaving the direct gap at Γ unmodified. Therefore, the optical properties are not altered with respect to crystalline bulk GaN.

To complete our investigation, we performed several finite temperature Car-Parrinello molecular dynamics simulations of an NH_3 molecule hitting the GaN(0001) surface.[22] The vacuum thickness in the 2×2 supercell was increased from 13 Å to 16 Å, and the NH_3 molecule was placed at a starting distance of 3 Å from the surface. In this condition, the impinging molecule is not initially interacting with the substrate,[23] and at the same time spurious interactions with its periodic images are avoided. Before the molecule impact, the substrate was prepared at a temperature of (1000 ± 100) K, controlled through a Nosé thermostat.[22] We considered several initial conditions for the NH_3 molecule, by varying its impact speed and its lateral position with respect to the substrate surface. For the substrate, we considered both the ideal-like surface and the surface with a Ga vacancy at site Ga2 (Fig. 1). When we fixed an initial velocity less than 0.04 Å fs^{-1} (kinetic energy of 0.6 eV), the molecule did not dissociate. Instead, at least within the short simulation time of 1 ps, the molecule bounced several times between different surface sites, with well excited rotational and vibrational degrees of freedom.

With an impact velocity of 0.05 Å fs^{-1} (perpendicular to the surface), independently of the initial orientation and lateral position of the molecule with respect to the (2×2)-GaN(0001) surface with 1/4 ML of Ga vacancies, we observed dissociation of NH_3 into NH_2 and H. By means of the excited molecular rotational degrees of freedom, one of the molecular N-H bonds became oriented towards one of the N atoms around the vacancy site in our 2×2 unit cell, and the resulting GaN-NH_3 interaction activated NH_3 dissociation. One H atom separated from the molecule and formed a bond with a substrate N atom, about 1 Å long. Simultaneously, the NH_2 complex bonded to a substrate Ga atom, with a bond orientation of approximately 45° relative to the (0001) plane, and length of 1.7 Å. This Ga-NH_2 bond was not stable during the short simulation time (1 ps): The NH_2 complex migrated, alternatively forming bonds with the $\frac{3}{4}$ ML of available outermost Ga atoms on the (0001) surface. Each of these "jumps" involved partial molecule-to-surface energy transfer: the jumping path should stop with the accomplishment of a stable Ga-NH_2 bond when the residual kinetic energy of the molecule is no longer sufficient to allow bond-breaking and consequent jumping. The quantitative evaluation of such effects are beyond the scope and possibilities of our short dynamical simulation, which was aimed at demonstrating the viability of NH_3 dissociation during GaN surface/molecule interaction, thus supporting the energetical results obtained for the static configurations.

Summarizing our arguments, we have presented the energetics of metastable structures obtained upon H and NH_2 chemisorption on GaN(0001), and have discussed our results in terms of the role played by the equilibrium surface reconstructions in GaN growth. We have shown that Ga-rich conditions, in presence of ambient H, favor the formation of ordered pseudo-(1×1) surfaces, whose viable precursor during deposition is identified as the *hydrogenated* 3H surface. Instead, in N-rich conditions, a large concentration of defects accompanies the attachment of nitrogen to the basal surface through the NH_2 ad-complexes. Finally, high temperature molecular dynamics simulations have shown that an ammonia molecule in the vicinity of a GaN(0001) surface may indeed dissociate. After dissociation, the residues explore different surface sites, forming structures that resemble dynamically excited versions of the quenched optimized surfaces that we have chosen for the description of NH_3 chemisorption.

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