

Electronic structure of 1×1 GaN(0001) and GaN(000 $\bar{1}$) surfaces

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The electronic structure of clean and Ga- or N-covered 1×1 GaN(0001) and GaN(000 $\bar{1}$) surfaces is studied using the local-density approximation of density-functional theory employing *ab initio* pseudopotentials together with Gaussian orbital basis sets. We use both standard and self-interaction- and relaxation-corrected pseudopotentials. The latter allow for a most accurate description of the electronic structure of these surfaces. Comparing the formation energies for the clean and adatom-covered 1×1 configurations, we determine optimal surface structures for various growth conditions. For the GaN(0001) surface in the Ga-rich case, we find a structural model consisting of Ga adatoms adsorbed in T_4 positions above the substrate surface to be most favorable. In the N-rich case, the clean GaN(0001) surface is the most stable 1×1 configuration. For the GaN(000 $\bar{1}$) surface, our results for both Ga- and N-rich growth conditions indicate that a full monolayer of Ga adatoms adsorbed in on top positions is the most stable configuration. Our theoretical results allow for a comparison of full calculations of the surface electronic structure for a number of optimized structural models with most recent angle-resolved photoemission spectroscopy data.

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I. INTRODUCTION

Group-III nitrides have very promising potential for short-wavelength light-emitting diodes,¹ semiconductor lasers,^{2,3} and optical detectors.⁴ In view of these exciting challenges they are currently under intensive theoretical and experimental investigations.⁵⁻¹⁶ A fundamental understanding of the electronic structure of group-III nitrides is required if they are to achieve their full technological potential. To this end, understanding the electronic properties of clean and adsorbate-covered surfaces is of particular importance, since it is the first step in understanding fundamental issues of contact formation, chemical reactivity, growth processes, and structural stability. GaN is a highly ionic wide-band-gap semiconductor due to the cationic and anionic characters of Ga and N, respectively, on the one hand, and to the strong disparity of the covalent radii of Ga ($r_c^{Ga} = 1.25 \text{ \AA}$) and N ($r_c^N = 0.70 \text{ \AA}$), on the other hand. The usual growth direction of hexagonal GaN crystals is along the [0001] or [000 $\bar{1}$] axes, where cation and anion layers alternate. The respective polar surfaces show a variety of reconstructions. For GaN(0001), 1×1 , 2×2 , 4×4 , 5×5 , and 6×4 surface unit cells have been reported, while for GaN(000 $\bar{1}$) 1×1 , 3×3 , and 6×6 reconstruction patterns have been observed.^{5,6,16} The structure of some of the more complex reconstructions was previously addressed by first-principles calculations, concentrating, in particular, on GaN(0001)-(2 \times 2) structures.^{12,13} Interestingly enough, the apparently most simple 1×1 surface turns out to be particularly intriguing, since it is not fully understood as yet.

The *atomic structure* of hexagonal 1×1 GaN surfaces was addressed in a number of investigations. Sharp 1×1 patterns were observed in various low-energy electron-diffraction (LEED) and reflection high-energy electron-diffraction (RHEED) studies.^{8,11} However, the surface polarity, as well as its correlation to the surface structure, were not well established in some of these investigations.^{11,14} Sung

*et al.*⁸ and Ahn *et al.*⁹ concluded from their time-of-flight scattering and recoiling spectrometry and LEED studies that both GaN(0001) and GaN(000 $\bar{1}$) surfaces are neither reconstructed nor relaxed. Nevertheless, a small amount of residual C and O atoms seems to be responsible for the stabilization of the ideal (0001) surfaces in these experiments, while the observed (1×1)-(000 $\bar{1}$) structure turns out to be induced by adsorbed H atoms. Smith and co-workers studied the reconstruction of GaN(0001) and GaN(000 $\bar{1}$) surfaces by scanning tunneling microscopy (STM) and first-principles theory.^{5,6} They found that on the GaN(000 $\bar{1}$) surface a monolayer of Ga bonded to the topmost N-terminated GaN bilayer is the most stable 1×1 structure. On GaN(0001), two or three additional monolayers of Ga bonded to the topmost Ga-terminated bilayer form a pseudo-(1×1) structure. Both of these surfaces were found to be metallic.⁶

The *electronic structure* of hexagonal 1×1 GaN surfaces was addressed more recently in experiment by angle-resolved photoemission spectroscopy (ARPES). Dhesi *et al.*¹⁰ investigated the bulk electronic structure of thin-film wurtzite GaN grown by molecular beam epitaxy. In addition to the bulk bands, the authors observed a dispersionless surface-state band near the valence-band maximum (VBM), as well. More recently, Chao *et al.*¹¹ reported a more complete account on the electronic structure of hexagonal GaN 1×1 surfaces using synchrotron-radiation-excited ARPES. In the latter case, the samples were grown by metal-organic chemical-vapor deposition (MOCVD). ARPES does not provide unambiguous direct information on the termination or polarity of thin-film sample surfaces. The authors of Ref. 11 thus used the label GaN(0001), synonymous for both the (0001) and (000 $\bar{1}$) surfaces, since they could not differentiate between the two. Chao *et al.*¹¹ observed two distinct surface-state bands. The identification of the respective surface states was confirmed by the photon-energy independence of their dispersion, as well as their sensitivity to hy-

drogen adsorption. One band, near the VBM, was found to be weakly dispersive and very sensitive to hydrogen adsorption, suggesting it is a dangling-bond band.¹¹ The other observed band displays a strong dispersion throughout the two-dimensional surface Brillouin zone (SBZ), and was found to depend strongly on the quality of the structure of the 1×1 surface, as monitored by LEED. For an analysis of the origins of these surface states, respective electronic structure calculations are needed. Since these were not available at the time, Chao *et al.* used the linearly polarized nature of the synchrotron radiation to obtain at least some information on the symmetry and the wave-function character of the surface states involved. They found that both surface-state bands are comprised of states of even symmetry with respect to the surface-perpendicular mirror plane containing the $[\bar{1}2\bar{1}0]$ direction, and which have strong p_z character. In view of this intriguing situation, as far as experimental data on the hexagonal 1×1 GaN surfaces is concerned, it seems particularly interesting and useful to find out which surface electronic structure of which surface atomic structure compares best with experiment and allows for a convincing interpretation of the data. If this goal can be achieved, at the same time it would allow for some conjectures concerning the actual surface structure under investigation in experiment.¹¹

Trying to resolve the issues raised above, at least to contribute to a better understanding of the origins of the electronic surface states seen in experiment,^{10,11} we present and discuss the results of our *ab initio* calculations of the atomic and electronic structures of various conceivable 1×1 structural models for hexagonal GaN surfaces. In these calculations, we have employed both standard pseudopotentials, as well as our self-interaction- and relaxation-corrected pseudopotentials.¹⁷ The latter overcome the well known local-density-approximation (LDA) gap problem to a large extent.

In Sec. II, the calculational method is briefly outlined. In Sec. III, we discuss our results for clean as well as Ga- or N-covered surfaces, as obtained by standard pseudopotential calculations. The grandcanonical potential or formation energy for the different models is compared in this section, and an assessment of the most stable configurations is made. In Sec. IV, we address the improvements introduced in the calculated band structures by employing self-interaction- and relaxation-corrected pseudopotentials (SIRC-PP's). In Sec. V, we compare our results with experimental ARPES data. A short summary concludes the paper in Sec. VI.

II. THEORY

Our calculations are carried out within the LDA of density-functional theory (DFT) using the Ceperley-Alder exchange-correlation potential.¹⁸ In our standard pseudopotential calculations, we apply soft pseudopotentials of Troullier-Martins type,¹⁹ and expand the wave functions in terms of Gaussian orbitals with s, p, d , and s^* symmetry. The d electrons of Ga are fully retained in the valence electron shell. In our basis set we have used 40 Gaussian orbitals per Ga atom and 30 orbitals per N atom. The decay constants for Ga atoms are 0.21, 0.72, 2.27, and 8.02, while decay

constants of 0.21, 0.84, and 3.60 have been used for the N atoms. All constants are given in atomic units. Supercells including eight atomic layers, i.e., four GaN bilayers, and about 10 Å of vacuum region are employed. The lowest two bilayers are fixed in the bulk configuration with experimental lattice constants $a = 3.19$ Å and $c = 1.63$ Å. For calculations of the GaN(0001) surfaces, pseudohydrogen atoms with a charge of $0.75 e$ passivate the N-terminated face at the bottom of the slabs, while for the study of GaN(000 $\bar{1}$) surfaces, pseudo hydrogen atoms with a charge of $1.25e$ passivate the Ga-terminated bottom faces.²⁰ For each of the saturating H atoms we have used ten Gaussian orbitals with a decay constant of 0.35 in the expansion of the wave function. All computations are performed with a well converged set of 12 \mathbf{k}_{\parallel} points in the 1×1 SBZ. The optimal surface relaxation is determined by calculating the forces.

In order to compare the energies of different systems having a varying number of atoms, we use the formation energy of the surface defined as

$$E_{form} = E_{ad} - E_{clean} - \Delta n_{Ga} \mu_{Ga} - \Delta n_N \mu_N \quad (1)$$

where E_{ad} and E_{clean} are the total energies of the adsorbate-covered and clean surfaces, respectively. μ_{Ga} (Δn_{Ga}) and μ_N (Δn_N) are the chemical potentials (differences in the number of atoms per unit cell) of Ga and N. If a system consisting of a GaN crystal and Ga and N atoms in the gas phase is in thermodynamic equilibrium, the following relation holds:

$$\mu_{Ga} + \mu_N = \mu_{GaN}^{bulk} \quad (2)$$

Here μ_{GaN}^{bulk} is the chemical potential of bulk GaN. Introducing the heat of formation ΔH_f of bulk GaN, the chemical potential of Ga in its bulk phase μ_{Ga}^{bulk} and the chemical potential of an N_2 molecule μ_{N_2} , we obtain

$$\mu_{GaN}^{bulk} = \mu_{Ga}^{bulk} + \mu_{N_2} - \Delta H_f \quad (3)$$

The relative stabilities of possible 1×1 structures for both the (0001) and (000 $\bar{1}$) polarities are determined within the thermodynamically allowed range of the Ga chemical potential: $\mu_{Ga}^{bulk} - \Delta H_f < \mu_{Ga} < \mu_{Ga}^{bulk}$. Our calculation of the heat of formation ΔH_f of GaN yields a value of $\Delta H_f = 1.15$ eV in agreement with the experimental value of 1.15 eV.²¹

III. RESULTS

A. Clean and Ga- or N-covered GaN(0001) surfaces

According to conventional notation, the clean GaN(0001) surface ends with a GaN bilayer which is Ga terminated. Side and top views of this surface are shown in Figs. 1(a) and 1(c). The structure parameters d_{12} and d_{23} characterizing the clean relaxed 1×1 surface are introduced in the figure as well. In addition, most likely adsorption sites for Ga or N adatoms in a single adlayer are indicated in the top view of Fig. 1(c). We have considered single adlayers of Ga or N atoms adsorbed in on top, T_4 , or H_3 positions. Adatoms in on top positions reside directly above the Ga atoms of the first GaN(0001) substrate layer. Adatoms in T_4 positions re-

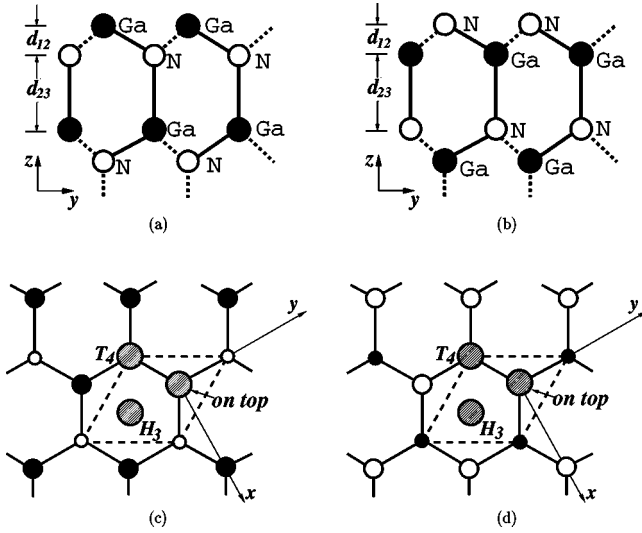


FIG. 1. Side view of (a) the ideal GaN(0001) surface and (b) the ideal GaN(000 $\bar{1}$) surface. Bonds lying in the drawing plane or parallel to it are shown as full lines while those forming an angle with the drawing plane are shown by dashed lines. Top view (c) of the GaN(0001) and (d) of the GaN(000 $\bar{1}$) surface in which the 1×1 unit cell is indicated by heavy dotted lines. The shaded circles indicate the three different adsorption positions on top, T_4 , and H_3 in each case. In the top views, the adatoms are shown by the largest and the second layer atoms by the smallest circles.

side above the N atoms of the second substrate layer. Finally, adatoms in H_3 positions are located in hollow sites above the substrate surface.

The calculated formation energies for seven configurations, i.e., for the clean, Ga-covered or N-covered GaN(0001) surfaces, are shown in Fig. 2. The figure reveals, that for all allowed values of the Ga chemical potential a monolayer of Ga adatoms adsorbed on the surface in on top, H_3 , or T_4 positions, respectively, has very similar formation energies (within 0.03 eV per 1×1 unit cell). In particular, we find that the relaxed clean GaN(0001) surface is favored

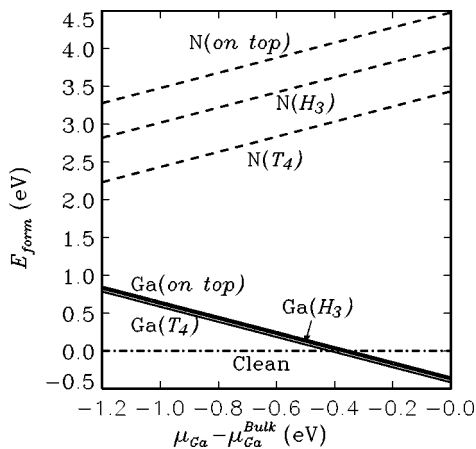


FIG. 2. Comparison of formation energies (relative to that of the relaxed clean surface) for six different structural models (see the text) of the GaN(0001) surface as a function of the chemical potential μ_{Ga} for the allowed range.

TABLE I. Structural parameters of surface relaxations. The distances between adsorbed and top layers, the first and second layers, and the second and third layers are labeled d_{ad} , d_{12} , and d_{23} , respectively, and are given in Å. The normal distances between respective layers in bulk GaN are $d_{12}^b = 0.65$ Å and $d_{23}^b = 1.94$ Å.

System	d_{ad}	d_{12}	d_{23}
clean GaN(0001)		0.72	2.01
Ga(T_4):GaN(0001)	1.97	0.65	1.92
clean GaN(000 $\bar{1}$)		0.37	2.01
Ga(on top):GaN(000 $\bar{1}$)	2.06	0.68	1.95

under N-rich growth conditions, while a Ga adlayer in T_4 positions is most favorable under Ga-rich growth conditions. This result is in good agreement with earlier theoretical results.^{5,22} On the other hand, a monolayer of N adatoms adsorbed on the GaN(0001) surface is very unfavorable in the whole range of the Ga chemical potential and for all three adsorption sites considered. When the comparatively small N adatoms ($r_c^N = 0.70$ Å) are adsorbed in on top positions, e.g., they have three unsaturated and almost noninteracting dangling bonds which are filled by only 3.75 electrons in total. Such a configuration is energetically very unfavorable as compared to N_2 molecules in the gas phase.

The calculated vertical distances between the first layers of the two energetically most favorable structures in the allowed range of μ_{Ga} are given in Table I. At the clean Ga-terminated GaN(0001) surface, the topmost GaN bilayer moves almost rigidly outward by roughly 0.07 Å with respect to its ideal bulk position. In the case of the Ga adlayer adsorbed in T_4 positions above the Ga-terminated substrate, nondirectional metallic bonds are established between atoms in the two topmost Ga layers. The vertical distance between the Ga adlayer and the Ga substrate surface layer is $d_{ad} = 1.97$ Å. This value translates into a bond length of 2.70 Å between the atoms of the two Ga top layers which is very close to the Ga-Ga bond length of 2.71 Å in bulk Ga.

We have calculated the surface electronic structure of the clean GaN(0001) surface and for all adsorption models described above. For the sake of brevity, we restrict ourselves to a discussion of the surface band structure of the two energetically most favorable structures. Figure 3(a) shows the LDA surface band structure of the relaxed clean GaN(0001) surface as calculated using standard *ab initio* pseudopotentials (cf. Sec. II). The vertically shaded areas represent the projected band structure (PBS) of hexagonal bulk GaN. The PBS has a direct gap of 1.43 eV at the Γ point of the SBZ. It is considerably smaller than the experimental gap of 3.5 eV due to well-known shortcomings of DFT-LDA. Most salient, the surface band structure shows a Ga-derived dangling-bond band (D_{Ga}) in the projected fundamental gap. This band is partially occupied by 3/4 of an electron, giving rise to a metallic clean surface and pinning the intrinsic Fermi level. The considerable dispersion of 1.61 eV of this band results from a significant overlap of the dangling-bond wave functions of neighboring Ga atoms in the surface layer. For the Ga monolayer adsorbed in T_4 positions above the

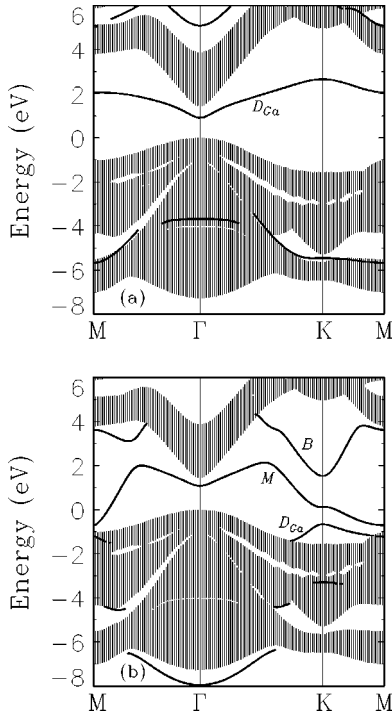


FIG. 3. Surface band structures of (a) the relaxed clean GaN(0001) surface (top panel) and (b) the Ga(T_4):GaN(0001) surface (bottom panel). The projected bulk band structure is shown by vertically dashed lines. The labels of the bands are introduced in the main text.

GaN(0001) surface, which we label in the following as Ga(T_4):GaN(0001), there are three Ga-derived bands in the projected gap [Fig. 3(b)]. The energetically lowest one of them (D_{Ga}) is derived from Ga dangling bonds at the Ga(T_4) adatoms. The character of the surface-state wave functions forming this band is mostly Ga s and p_z like. Contrary to the D_{Ga} band at the clean surface, this band is completely occupied. The additional adatom-induced bands M and B are partially occupied. They originate from states between the two Ga layers (M) or from bridge states (B) within the Ga adlayer, respectively. Their strong dispersion originates from strong Ga-Ga interactions in the Ga double layer on top of this system.²³

B. Clean and Ga- or N-covered GaN(000 $\bar{1}$) surfaces

Since it is not clear which one of the hexagonal GaN surfaces has been studied in the ARPES experiments,^{10,11} we have also investigated several structural models of the GaN(000 $\bar{1}$) surface. Side and top views of this surface are given in Figs. 1(b) and 1(d). Also, in this case we have considered the clean surface as well as Ga or N adlayers in on top, T_4 , or H_3 positions. These adsorption sites are indicated in Fig. 1(d) as well. Reactions of the clean surface with N adatoms lead to an abstraction of N surface atoms by formation of N_2 molecules due to the very strong N-N molecular bond of 9.8 eV.²¹ After N abstraction, the resulting surface structure corresponds to the case of Ga adsorption on

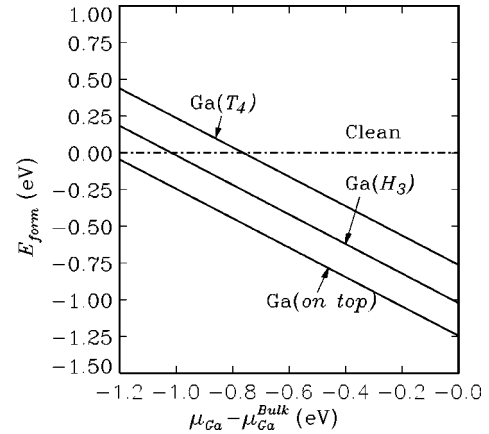


FIG. 4. Comparison of formation energies (relative to that of the relaxed clean surface) for three different structural models (see text) of the GaN(000 $\bar{1}$) surface as a function of the chemical potential μ_{Ga} for the allowed range.

the clean GaN(000 $\bar{1}$) surface (see below). Therefore, we restrict ourselves to a discussion of the clean and Ga-covered GaN(000 $\bar{1}$) surfaces.

The formation energies resulting from our calculations for the remaining four different models are given in Fig. 4. It is found that a monolayer of Ga atoms adsorbed in on top positions is the most stable configuration under both Ga- and N-rich conditions. This result is in good agreement with the findings of other calculations of the surface atomic structure^{5,22} and experimental results.¹⁵

The calculated structural relaxation parameters of this configuration are also given in Table I together with those of the relaxed clean surface. At the clean surface, a considerable nonrigid surface relaxation of the topmost bilayer is obtained. In the case of the Ga-covered GaN(000 $\bar{1}$) surface, strong directional Ga-N bonds are established when the Ga adatoms are adsorbed in on top positions. In this case the resulting interlayer distances d_{12} and d_{23} are very close to the respective bulk distances (see Table I).

To shed some more light on the physical properties of the optimized adsorption system, in Fig. 5 we show the electronic *charge-density difference* distribution induced by Ga(on top) adsorption. Obviously, the electronic charge density increases near the N atoms and decreases near the Ga adatoms, so that they become more anionic or cationic, respectively. In addition, there is a significant increase in the electronic charge density between the Ga adatoms in the surface plane to be noted indicating the formation of metallic bonds between neighboring Ga adatoms. So there is a two-dimensional metallic Ga layer on top of the N-terminated GaN(000 $\bar{1}$) surface. Figure 5 also reveals that the changes in the charge density show a considerable spatial extent into the substrate.

The calculated band structure of the clean GaN(000 $\bar{1}$) surface and of the energetically most favorable Ga(on top) configuration are shown in Fig. 6. At the clean GaN(000 $\bar{1}$) surface [Fig. 6(a)], there is one N-derived dangling-bond band (D_N) in the fundamental gap. This band is partially

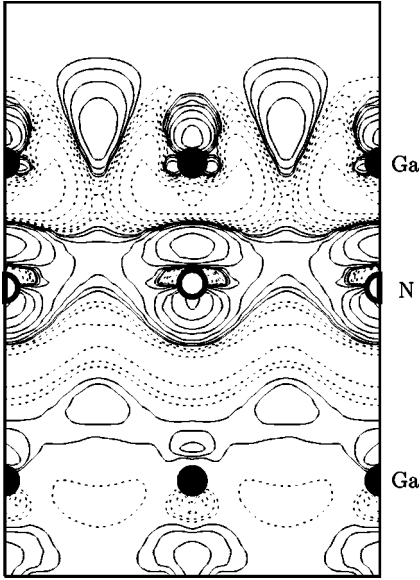


FIG. 5. Contours of the electronic charge density difference of the Ga(on top):GaN(000 $\bar{1}$) surface obtained by subtracting the charge density of free Ga adatoms and of the clean GaN(000 $\bar{1}$) surface from that of the adsorbate system. The contours are presented in the x - z plane [see Fig. 1(d)]. Solid (dashed) lines represent an increase (decrease) of charge density.

occupied by $5/4$ electrons. Therefore, this surface is metallic, and the D_N band pins the Fermi level. The dispersion of the D_N band is very small, since the interaction between the very localized dangling bonds on the second-nearest-neighbor N

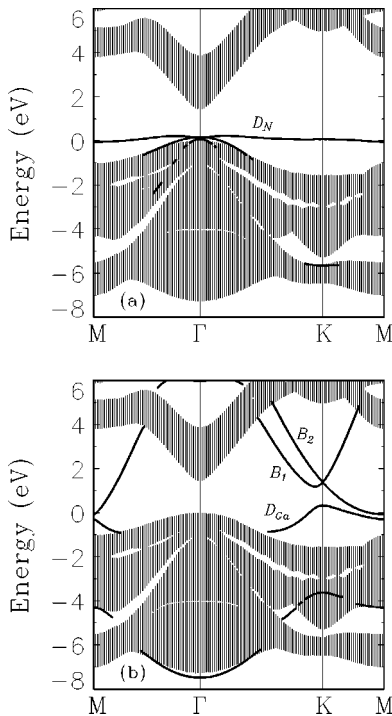


FIG. 6. Surface band structures of (a) the relaxed clean GaN(000 $\bar{1}$) surface (top panel) and (b) the Ga(on top):GaN(000 $\bar{1}$) surface (bottom panel). The projected bulk band structure is shown by vertically dashed lines.

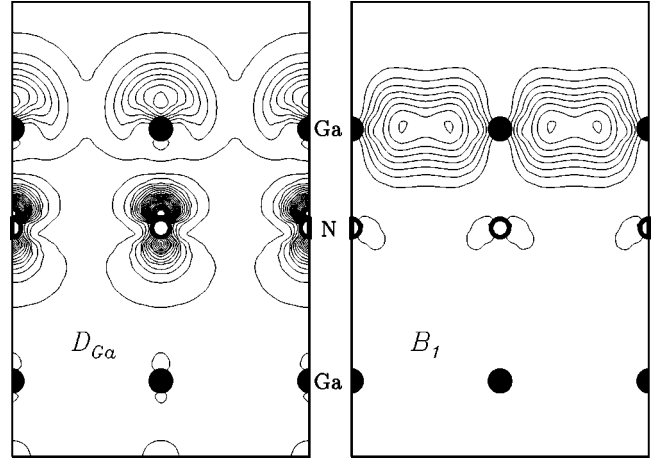


FIG. 7. Electronic charge density contours of the dangling bond D_{Ga} (left panel) and the bridge bond B_1 (right panel) states at the K point of the surface Brillouin zone of the Ga(on top):GaN(000 $\bar{1}$) surface. The contours are presented in the x - z plane [see Fig. 1(d)].

atoms in the surface layer is very weak. In the Ga(on top) configuration, there are three Ga adatom-derived bands within the projected fundamental band gap [Fig. 6(b)]. The D_{Ga} band originates from the dangling bonds at the Ga adatoms and from the N atoms at the substrate surface layer. The dispersion of this band of about 1.19 eV results from a considerable overlap between neighboring dangling-bond wave functions of the relatively large Ga cations. Additional strong interactions between neighboring Ga adatom wave functions give rise to the bands B_1 and B_2 , whose corresponding dispersions are very large. These two latter bands behave very much like backfolded parabolic free-electron bands, underlying their metallic character anew. The band D_{Ga} is fully occupied, while the band B_2 is only occupied to a very small extent. The band B_1 is completely empty. Thus this surface is metallic, as well.

The wave-function character of the states giving rise to these surface bands becomes most obvious in the energy- and \mathbf{k} -vector-resolved charge densities shown in Fig. 7. The left panel shows the D_{Ga} dangling-bond state whose charge density exhibits strong contributions at the Ga adatoms and at the N atoms in the topmost substrate layer. The B_1 state, conversely, is fully localized at the adlayer, and consists of Ga p_x and p_y contributions (see the right panel of Fig. 7).

IV. RESULTS OF SIRC-PP CALCULATIONS

Before comparing our results for the surface electronic structure with experimental data, it seems useful to first briefly address the accuracy of the above LDA calculations. It is well known that standard DFT-LDA calculations fail to correctly describe excited states in general, and band gaps of semiconductors and insulators in particular. This is partially due to unphysical self-interactions contained in any standard LDA calculation, and due to the neglect of electronic relaxation. SIRC-PP's (Refs. 24 and 25) have been shown to overcome these obstacles for group-III nitrides and group-II-VI compounds to a large extent.^{17,25} To overcome these

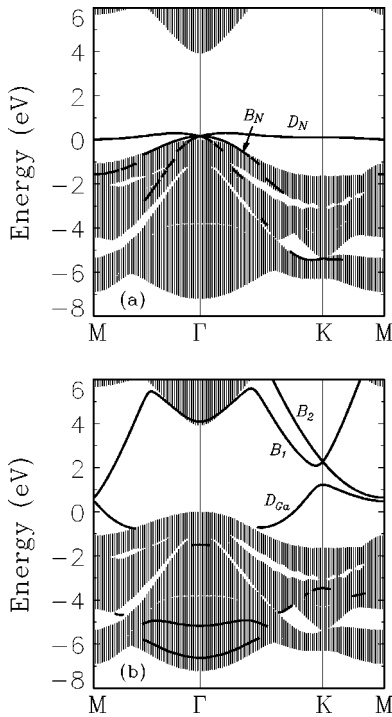


FIG. 8. Surface band structures of (a) the relaxed clean GaN(000 $\bar{1}$) surface (top panel) and (b) the Ga(on top):GaN(000 $\bar{1}$) surface (bottom panel) resulting from our calculations using SIRC pseudopotentials. The projected bulk band structure is shown by vertically dashed lines. Note the significant increase of the projected gap (by 2.39 eV, from 1.43 to 3.82 eV), as compared to Figs. 3 and 6.

problems in the present case, we have used SIRC pseudopotentials to calculate the electronic properties of the GaN surface systems studied in this work. For the sake of brevity, in Fig. 8 we only show results for the clean GaN(000 $\bar{1}$) surface and the Ga(on top):GaN(000 $\bar{1}$) adsorbate system (see Fig. 6, for comparison), respectively. The global topology of the band structures in Figs. 6 and 8, respectively, is similar. However, the bulk band gap opens up from 1.43 to 3.92 eV when SIRC pseudopotentials are used. The position and dispersion of the N-derived dangling-bond band D_N at the clean GaN(000 $\bar{1}$) surface remains largely unchanged [compare Figs. 6(a) and 8(a)]. This is due to the fact that this band is basically derived from N bulk valence states which hardly change when we employ SIRC pseudopotentials. The width of the Ga-derived dangling-bond band D_{Ga} of the Ga(on top):GaN(000 $\bar{1}$) system increased by 0.76 eV in Fig. 8(b), as compared to Fig. 6(b). Interestingly enough, the dispersion of the B_1 band and the B_2 band for energies larger than 1 eV is not changed by the SIRC pseudopotentials. Only their absolute energy position is shifted up by 0.87 eV (cf. the bottom of B_1). This confirms again that these bands are free-electron-like metallic Ga bands. They are basically shifted upward rigidly, since the energy difference between the Ga and N atomic term values increases by going from standard to SIRC pseudopotentials.¹⁷

The occupation of the D_N band at the clean N-terminated surface and of the D_{Ga} band at the Ga(on top):GaN(000 $\bar{1}$) surface, as calculated with standard pseudopotentials, do not change when SIRC pseudopotentials are employed. The band (D_N) at the VBM has a very small dispersion and only 3/4 electrons per 1×1 unit cell are missing to fully occupy the band. There is a large gap of roughly 3.64 eV above this band. For the Ga(on top):GaN(000 $\bar{1}$) surface, the D_{Ga} band is fully occupied and the B_1 band is only partially filled with electrons, so that this system remains metallic as well. In this latter case, the bulk gap is completely closed by Ga adatom-induced surface-state bands. The topology of the upper part of the resulting band structure is close to that of ordinary sp -like metals. Therefore, the screening and transport properties of the Ga adlayer system are drastically different from those of the clean surface. This kind of metallic behavior is in accord with the results of scanning tunneling spectroscopy experiments.⁶ A very strong dependence of the tunneling current on the nature of the STM probe tip in these measurements did not allow for a more detailed experimental investigation of the electronic properties in those studies.⁶

We have also calculated the surface band structures of the clean GaN(0001) surface and the Ga(T_4):GaN(0001) adsorbate system using SIRC pseudopotentials. The resulting changes with respect to the standard LDA band structures given in Fig. 3 show largely the same global behavior as those discussed above for the 1×1 GaN(000 $\bar{1}$) systems. Therefore, we also refrain from showing these band structures.

V. COMPARISON WITH EXPERIMENT

In Sec. I we mentioned that Chao *et al.*¹¹ recently carried out synchrotron radiation excited ARPES measurements of hexagonal MOCVD-grown GaN surfaces which show very sharp 1×1 LEED patterns. Two dominant features have been detected in the recorded spectra throughout the whole surface Brillouin zone, and have been shown by appropriate means to be surface derived. The upper band near the VBM exhibits only a very weak dispersion, while the lower band shows a strong dispersion from E_{VBM} at the zone center toward the bottom of the valence bands at the K point. Since Chao *et al.*¹¹ could not unambiguously identify the termination or polarity of their samples, we have compared the experimental ARPES data of Ref. 11 with all of our results for the electronic structure of the models studied in this work. In Fig. 9 we show the data of Chao *et al.*¹¹ by open squares. The comparison of the data with all of our theoretical results revealed that there is no way to reconcile the ARPES data with the electronic structure of the clean GaN(0001) or the optimal Ga(T_4):GaN(0001) surface (Fig. 3). The same holds for our results of respective SIRC calculations for these two surface structures. Also the SIRC-PP band structure for the optimal Ga(on top):GaN(000 $\bar{1}$) surface [Fig. 8(b)] does not allow for any convincing interpretation of the data. Interestingly enough, only the surface band structure of the clean N-terminated GaN(000 $\bar{1}$)-(1 \times 1) surface [Fig. 8(a)] is in

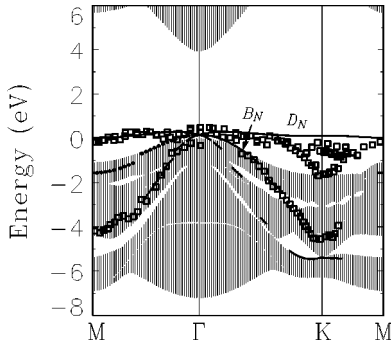


FIG. 9. Comparison between the calculated SIRC band structure of the clean relaxed GaN(000 $\bar{1}$) surface [cf. Fig. 8(a)] with experimental ARPES data (open squares) from Ref. 11. Bands from the M point to the Γ point originating from even (odd) states with respect to the mirror plane of the surface are shown by full (dotted) lines. The bands from Γ over K to M (full lines) do not have a definite symmetry with respect to the mirror plane (see Ref. 27).

reasonable accord with the measured data. We have superimposed the results of our SIRC pseudopotential calculation from Fig. 8(a) onto the measured two-dimensional bands²⁶ in Fig. 9. The dispersion of the N-derived dangling bond band D_N nicely agrees with the flat measured band along M - Γ and from Γ to $\Gamma K/2$. Near the K point, there are larger deviations between theory and experiment. At this point, the measurements show two structures: one with a slightly larger dispersion than in the theoretical results, and a second band with a remarkably stronger dispersion of some 2 eV. There is no *surface-state band* in the theoretical results for the clean GaN(000 $\bar{1}$) surface corresponding to this feature. The calculated N-derived resonance B_N agrees well with the experimental data in the energy region from 0 to -3 eV. For larger binding energies $E \leq -3$ eV, however, the measured dispersion is larger than the calculated one. In the energy region below -3 eV and \mathbf{k} region between M and $\Gamma M/2$, we find only a pronounced supercell band (i.e., bulklike) which does not have a very strong surface character.

In the interpretation of their results, Chao *et al.*¹¹ identified the symmetry of the observed surface states with respect to the mirror plane of the surface system, which contains the $[\bar{1}2\bar{1}0]$ direction.²⁷ In their experimental setup they could only detect even states with respect to the mirror plane. The \mathbf{k} vectors corresponding to the mirror plane are along the M - Γ direction. We can unambiguously resolve our surface bands with respect to even or odd symmetry from M to Γ . Accordingly, we have plotted bands of even symmetry by full lines and bands of odd symmetry by dotted lines from Γ to M in Fig. 9. The figure reveals that the two bands detected in experiment are comprised of even surface states, while bands originating from states with odd symmetry have not been observed. Along the Γ - K and K - M lines, the states are superpositions of contributions with even and odd symmetries.²⁷

From our comparison we conclude that a clear signature of N-derived dangling-bond states was observed in

experiment.¹¹ There is encouraging agreement between a considerable part of the calculated surface band structure of the clean GaN(000 $\bar{1}$) surface and experiment. Even the experimentally detected symmetry of the observed surface states is confirmed by the calculations. Obviously, the investigated sample surface was not a Ga(on top):GaN(000 $\bar{1}$) structure, which is favored by our structure optimization calculations. The deviations between theory and experiment might be related to the existence of domains, facets, or defects near the surface,^{28,29} or to order-disorder transitions.³⁰ Additional experimental investigations on well-defined, well-ordered, and defect-free single-crystal surfaces would be most useful to clarify these points.

VI. SUMMARY

We have calculated formation energies and band structures of conceivable clean and Ga or N covered 1×1 GaN(0001) and GaN(000 $\bar{1}$) surface configurations. In the case of the GaN(0001)-(1×1) surface, a monolayer of Ga adsorbed in T_4 sites is the most stable structure under Ga-rich conditions, while the relaxed clean Ga-terminated surface is the most stable structure under N-rich conditions. In the case of the GaN(000 $\bar{1}$)-(1×1) surface, a full monolayer of Ga adsorbed in on top positions is the most stable configuration throughout the allowed range of the Ga chemical potential. The surface band structures of the clean GaN(0001) and GaN(000 $\bar{1}$) surfaces show one salient Ga- or N-derived dangling bond band in the gap energy region, respectively. The surface band structures for the adlayer configurations are dominated by metallic, highly dispersive Ga induced bands in the projected fundamental bulk band gap. This holds for the results of our calculations using standard LDA pseudopotentials, as well as, for the results of our calculations employing SIRC pseudopotentials. Scanning tunneling spectroscopy experiments support metallic surfaces. Our results for the clean GaN(0001), the clean GaN(000 $\bar{1}$), as well as, the Ga(T_4):GaN(0001) and Ga(on top):GaN(000 $\bar{1}$) surfaces are in general agreement with this finding. They are all metallic. The results of recent angle-resolved photoemission measurements cannot be interpreted in terms of the surface band structures of the discussed Ga adsorbate systems. Instead, only the surface band structure of the clean N-terminated GaN(000 $\bar{1}$) surface is in favorable agreement with experiment.

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