PHYSICAL REVIEW B VOLUME 59, NUMBER 3 15 JANUARY 1999-I

Surface states and Fermi-level pinning at clean and Al covered GaN surfaces

S. Picozzi and A. Continenza
Istituto Nazionale di Fisica della Materia (INFM), Dipartimento di Fisica, Università L'Aquila, 67010 Coppito (L'Aquila), Italy

A. J. Freeman
Department of Physics and Astronomy and Materials Research Center, Northwestern University, Evanston, Illinois 60208

(Received 14 July 1998)

Ab initio electronic structure calculations have been performed for the clean GaN surface (both N- and Ga-terminated) and for the GaN/Al 1-ML system, obtained from the clean surface by addition of an Al monolayer. In the most stable configuration, Al is found to occupy the bridge site at the clean unreconstructed N-terminated surface. All the systems studied show an appreciable surface charge density due to midgap states strongly localized in the surface region; this localization is particularly enhanced for the N-terminated case, showing the high instability of the unreconstructed clean surface. On the other hand, the Ga-terminated surface is found to be more stable and to behave very similarly to the Al-covered system. The Fermi level E_F is shifted toward the conduction band with respect to the clean N-terminated surface. Additional coverage of Al layers does not significantly affect the initial position of E_F within the GaN band gap, showing that the Schottky barrier height is well established after the first Al layer. [S0163-1829(98)02643-5]

Technological and scientific interest in nitrides has been growing constantly in the last few years. In particular, its important applications, such as blue lasers and light-emitting diodes have made GaN one of the most studied materials. Great attention was paid to the wurtzite phase, both experimentally[1] and theoretically.[2–4] On the other hand, few theoretical[5,6] and experimental[7] investigations have focused on zinc-blende GaN, which is energetically very close to the wurtzite phase and can also be easily stabilized. Among the many important areas which need to be investigated, one of the most important—due to its technological impact—is the metallization on GaN and the search for good Ohmic contacts. Again, many experiments focused on wurtzite GaN,[8] but, at least to our knowledge, there are no experimental characterizations regarding metals deposited on zinc-blende GaN. Recently,[9,10] the problem was investigated from the theoretical point of view, by means of *ab initio* calculations performed for [001]-ordered GaN/Al bulk interfaces.

In the present work, we present results obtained from full-potential linearized augmented plane-wave (FLAPW) (Ref. 11) calculations for a clean (both Ga- and N-terminated) GaN surface and the GaN surface with an Al monolayer. We focus mainly on the effects that Al adsorbtion has on the electronic properties of the clean GaN surface, in terms of surface and interfacial midgap states. This GaN/Al 1-ML system simulates the initial stages of the GaN/Al interface formation; therefore, we can have helpful insights into all the mechanisms which finally lead to the formation of the Schottky-barrier height (SBH).

While it is widely recognized[5] that the most stable 1×1 GaN surface is Ga terminated, it has been experimentally shown[12] that deposition of Al on the clean substrate results in an exchange reaction between Ga and Al with the final release of free metallic Ga. Also, theoretical calculations[10] were able to show that such an exchange reaction at the immediate interface is energetically favorable, indicating that the GaN termination is effectively, in all respects, a N one. Therefore, for our purposes, this termination is the most meaningful to consider. However, we also performed FLAPW calculations for a Ga-terminated surface, in order to compare with the other systems studied.

Our calculations are performed within density-functional theory in the local-density approximation,[13] using one of the most accurate *ab initio* methods, namely the FLAPW (Ref. 11) method. All the computational details (such as muffin-tin radii, k-point sampling, maximum k vectors for the expansions of wave functions and charge density, etc.) are the same as those used in Refs. 9,10. In order to simulate the surface, we used the ''repeated slab'' approach, i.e., a supercell with two equivalent surfaces on the two sides of a slab and a vacuum region thick enough to avoid interactions between surfaces in neighboring slabs. In particular, in the clean GaN surface case, we used 11 layers of GaN along the [001] growth direction, with a vacuum region equivalent to six atomic layers (i.e., $\frac{3}{2}a$, where $a=8.47$ a.u. is the bulk GaN lattice constant). Tests performed on the GaN slab thickness have shown that 11 layers are sufficient to recover bulk conditions in the central slab region. For the GaN/Al 1-ML system, we added one Al layer to the clean surface to obtain 13 atoms in each supercell, keeping the same thickness for the vacuum region as for the clean surface case. We used *ab initio* atomic forces,[14] to study the relaxation of the surface atomic positions. Only atoms at the surface and subsurface layers were relaxed (forces on the inner atoms were negligible), and moved along the [001] growth direction to make the forces vanish. This is a good approximation, since we are not interested in the clean GaN surface reconstruction,[5] but rather on the effect of Al deposition on the ideal surface.[12]

We considered different sites for the adsorbed Al on the clean N-terminated GaN surface: namely the bridge, antibridge, hollow, and on-top sites. Our results show that the most stable configuration is obtained if the overlayer Al atom occupies the bridge site, so that the system would resemble

0163-1829/99/59(3)/1609(4)/$15.00

an ideally truncated Ga-terminated GaN surface, in which the last cationic Ga plane has been replaced by a plane of Al atoms [see Fig. 1, panels (a) and (b)].

Structural minimizations for the clean N-terminated surface with respect to the ideal case (i.e., the unrelaxed surface obtained by just truncating the bulk) lead to a negligible outward displacement of the subsurface layer and to an appreciable contraction of the surface layer: the interplanar distance—i.e., the distance along the growth direction between different atomic layers—is found to be about 14% smaller than the bulk interplanar distance $z_{bulk}^{Ga-N}=2.12$ a.u. After the Al deposition, the subsurface Ga-N distance $z_{subsurf}^{Ga-N}$ relaxes to its bulk value z_{bulk}^{Ga-N}, whereas the surface N-Al interplanar distance ($z_{surf}^{N-Al}=2.06$ a.u.) is found to be very close to the tetragonal distance of AlN grown on a GaN substrate ($z_{tetrag}^{Al-N}=2.00$ a.u.).[9] This suggests that the Al monolayer forms a bond with the surface N atom, similar to the Al-N ionic bond in bulk AlN. This is of course different from that found[9] in the GaN/Al bulk interface, where the presence of several Al layers (bulk Al) caused a reduction of the sp^3 hybridization of the interface Al atom, weakening the Al-N bond.

Let us now focus on the electronic properties and compare the charge density of the gap states[9] in the clean GaN surface and in the GaN/Al 1-ML case, considering both space and energy localization. In Figs. 1(a) and 1(b), we report the top view of the N-terminated and Al-covered surfaces, respectively. In Figs. 1(c) and 1(d), we plot the gap states of these same systems, projected onto vertical planes containing the growth direction and the different atomic bonds, cutting the topmost (001) surface planes through the lines shown in Figs. 1(a) and 1(b).

Figure 1(c), top panel, clearly shows the nonbonding p_z character of the surface N atom; this same character is weakened but is still present in the subsurface N atom shown in Fig. 1(d), top panel. Moreover, a typical behavior of a surface metallic atom is shown by the adsorbed Al atom in Fig. 1(d), central panel. The spatial distribution of the gap states charge density seems to be similar in the two cases; the localization is particularly strong on the surface layer, much lower in the subsurface layer and negligible in the inner layers.

Figure 1(e) shows the planar average, of the gap states charge density $\bar{n}_{GS}(z)$, for the clean GaN surface (solid line) and for the GaN/Al 1-ML system (dashed line), respectively. We note that in the GaN/Al 1-ML system, the decay in the vacuum region is slower than in the clean surface case or, equivalently, the spatial extension of the gap states is broader. We also find that the gap states density is appreciable only in the surface layer and is strongly reduced already in the subsurface layer; this is consistent with the metal induced gap states (MIGS) decay length ($\lambda \sim 3.5$ a.u., equivalent to about 1.5 atomic layers along the z direction) estimated in the GaN/Al bulk interface.[9,10]

In Fig. 2 we show the projected density of states (PDOS) of the surface N atoms in (a) the N-terminated surface, (b) the Ga-terminated surface, (c) the GaN/Al 1-ML system, and (d) the bulk GaN, taking the valence-band maximum (VBM) as the zero of the energy scale. The comparison of panels (a), (b) and (c) with the bulk in the forbidden energy region

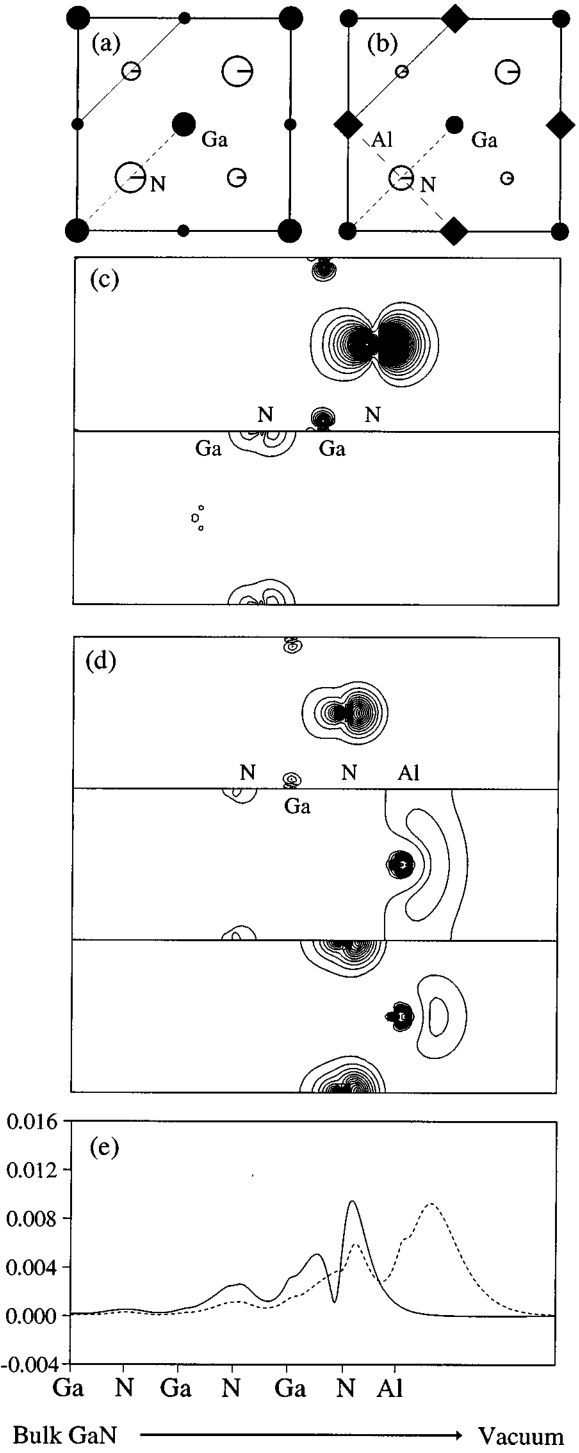

FIG. 1. Panels (a) and (b): top view of the clean N-terminated and Al-covered surfaces. Empty (filled) circles denote the surface (subsurface) N (Ga) atoms; filled diamonds denote the adsorbed Al atoms. Smaller symbols refer to inner atoms. The solid, dashed, and long-dashed lines denote intersections of the vertical planes, used in plotting the charge densities, with the topmost (001) surface plane. Panels (c) and (d): charge density contour plots due to the gap states for the clean GaN surface case and for the GaN/Al 1-ML system, respectively, The plots show planes parallel to the [001] growth direction cutting through all the different bonds in the unit cell. Contours are spaced by 0.002 electrons/cell. Panel (e): Planar average of the charge density due to the gap states. The solid (dashed) line represents the contribution of the clean surface (GaN/Al 1-ML case).

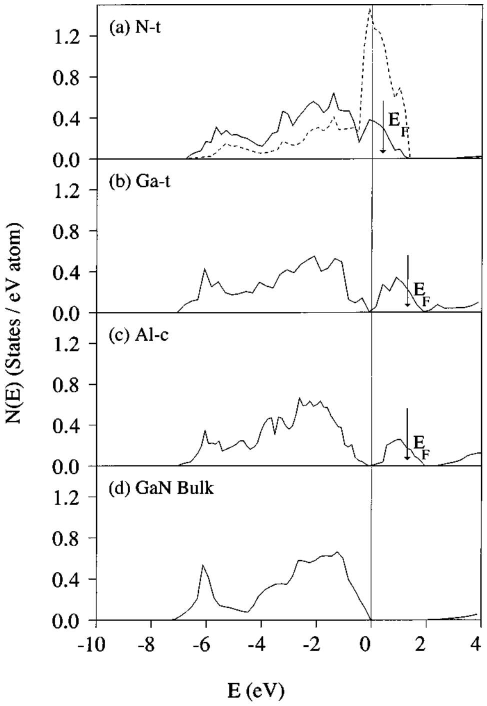

FIG. 2. Panel (a): PDOS of the surface (dashed) and subsurface (solid) N atoms in the N-terminated surface. Panels (b) and (c): PDOS of the subsurface N atoms in the Ga-terminated surface and the GaN/Al 1-ML system. Panel (d): PDOS of the N atom in bulk GaN. Vertical arrows indicate the positions of E_F above the GaN VBM, taken as zero of the energy scale.

shows that all N atoms shown in Fig. 2 have an appreciable density of gap states, which is particularly high in the N-terminated surface [the dashed line in panel (a)]. This indicates an instability that will lead to a reconstruction of the N-terminated clean GaN surface. Already in the subsurface atom [the solid line in panel (a)], the DOS is reduced and becomes comparable with that of subsurface atoms in the cation-terminated surfaces. Moreover, note that, as expected from the similarity of the Ga-terminated surface and the GaN/Al 1-ML system, the shape of the DOS is very similar in panels (b) and (c).

Let us now focus on the Schottky-barrier height problem. In principle, we could not obtain the exact SBH in the GaN/Al 1-ML case following the conventional procedure adopted in all-electron calculations and based on core levels as reference energies. In fact, in the Al side we only have 1 ML, so that Al bulk conditions are obviously not recovered. A rough estimate of the SBH can be obtained using the PDOS and considering the position of the Fermi level (E_F) with respect to the VBM of the inner Ga and N atoms, where bulk GaN conditions are assumed to be recovered. Figure 3 shows the PDOS for the inner Ga atoms in (a) the N-terminated surface, (b) the GaN/Al 1-ML system, and (c) the GaN/Al bulk superlattice, taking the VBM as zero of the energy scale. Vertical arrows indicate the positions of E_F in the different systems. If we compare panels (b) and (c), we note that the position of the Fermi level is similar in the two cases; we could therefore infer that the SBH is already established within only 1 ML of Al coverage. Very similar results for the SBH (within 0.1 eV) are obtained if core levels as reference energies are used, showing good consistency between these two approaches even in the case of ultrathin layers. Our findings seem to be in good agreement with the experimental results obtained by Bermudez *et al.*; in fact, Fig. 11 of Ref. 12 reports the position of E_F above the GaN VBM as a function of Al coverage, and shows that the SBH is very stable (within 0.1 eV) from 1- to 5-ML coverage, thus confirming our theoretical results.

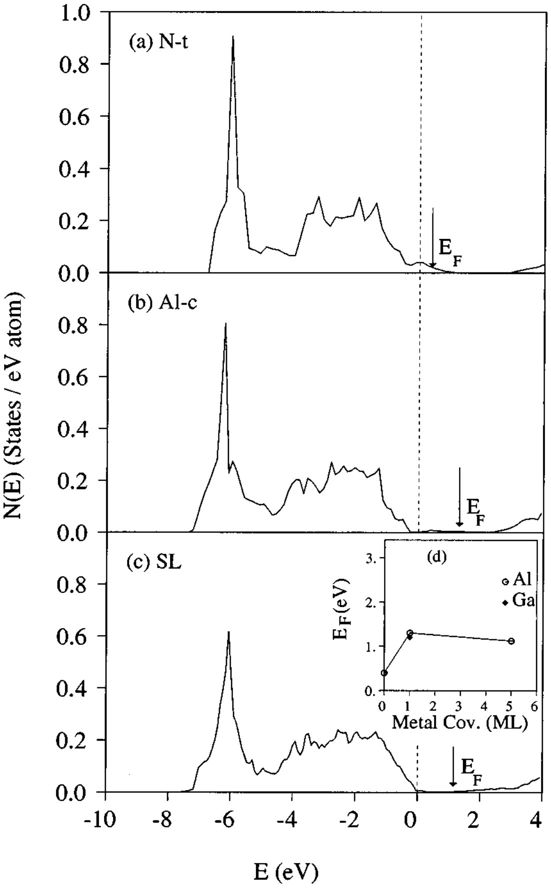

FIG. 3. PDOS of the inner Ga atoms for the (a) clean N-terminated surface, (b) GaN/Al 1-ML system, and (c) GaN/Al superlattice. Vertical arrows indicate the positions of E_F above the GaN VBM, taken as zero of the energy scale. Panel (d): Positions of E_F above the GaN VBM as a function of the metal coverage (circles and filled diamonds denote Al and Ga overlayers, respectively).

An interesting problem is also the ''pinning'' of the Fermi level above the valence-band maximum due to the surface/interface states. The comparison between Figs. 3(a) and 3(b) shows that the position of E_F above the VBM increases by about 1 eV in going from the clean surface to the Al covered one. Moreover, the Fermi-level position is very similar in the Al-covered and Ga-terminated surface [see Figs. 2(b) and 2(c)], and in this last case agrees with other calculations by Neugebauer *et al.*[5] This shows, as expected, that Al and Ga lead to the same Fermi-level pinning [see inset (d) of Fig. 3, which summarizes our results].

Let us now compare our results with the experimental data, keeping in mind that the experimental surface does not have a well-established atomic termination[12] and, moreover, is a 1×1 (0001) wurtzite, while our surface is a 1×1 (001) zinc-blende N-terminated surface. X-ray-photoemission spectroscopy experiments[12] performed on an *n*-doped GaN surface show that E_F moves from its position close to the bulk conduction band minimum down 0.4 ± 0.2 eV toward the VBM as the Al coverage reaches 1 ML and then stays stable (within 0.1–0.2 eV) as the Al coverage is increased. This is consistent with our results, if we note that in undoped bulk GaN (the case we studied) the Fermi level coincides with the VBM. In both cases, the Al overlayer is seen to modify the surface density of states in such a way as to shift the Fermi-level pinning position of less than 1 eV toward midgap.

In conclusion, we presented FLAPW calculations for the clean N-terminated and Al-covered GaN surface.We examined different possible sites for Al adsorption, and find that the bridge site is the most favorable from the energy point of view. We show that the gap states are strongly localized in the surface region. As for the pinning of E_F above the GaN VBM, we find a difference of about 1 eV between the clean and Al- or Ga-covered surfaces. In addition, a comparison of the GaN/Al 1-ML system with the GaN/Al bulk interface[9] shows that the SBH formation is well achieved through deposition of the first metallic layer.

The authors gratefully acknowledge Nate Newman and Sandro Massidda for stimulating discussions and a critical reading of the manuscript. This work was supported by the MRSEC program of the National Science Foundation (Grant No. DMR-9632472) at the Materials Research Center of Northwestern University and by grants of computer time at the CINECA (Bologna, Italy) through the INFM and at the Arctic Region Supercomputing Centers.

---

[1] As a review see for example, Bull. Mater. Res. Soc. **22**, 17 (1997).

[2] M. Buongiorno Nardelli, K. Rapcewicz, and J. Bernholc, Phys. Rev. B **55**, R7323 (1997).

[3] F. Bernardini, V. Fiorentini, and D. Vanderbilt, Phys. Rev. Lett. **79**, 3958 (1997).

[4] S. H. Wei and A. Zunger, Appl. Phys. Lett. **69**, 2719 (1996).

[5] J. Neugebauer *et al.*, Phys. Rev. Lett. **80**, 3097 (1998).

[6] T. Strasser, F. Starrost, C. Solterbeck, and W. Schattke, Phys. Rev. B **56**, 13 326 (1997).

[7] O. Brandt *et al.*, Phys. Rev. B **52**, R2253 (1995); H. Yang *et al.*, Appl. Phys. Lett. **68**, 244 (1996); D. Schikora *et al.*, Phys. Rev. B **54**, R8381 (1996); G. Feuillet *et al.*, Appl. Phys. Lett. **70**, 1025 (1997).

[8] S. C. Binari, H. B. Dietrich, G. Kelner, L. B. Rowland, K. Doverspike, and D. K. Gaskill, Electron. Lett. **30**, 909 (1994); J. D. Guo, C. I. Lin, M. S. Feng, F. M. Pan, G. C. Chi, and C. T. Lee, Appl. Phys. Lett. **68**, 235 (1996).

[9] S. Picozzi, A. Continenza, S. Massidda, and A. J. Freeman, Phys. Rev. B **57**, 4849 (1998).

[10] S. Picozzi, A. Continenza, S. Massidda, N. Newman, and A. J. Freeman, Phys. Rev. B **58**, 7906 (1998).

[11] H. J. F. Jansen and A. J. Freeman, Phys. Rev. B **30**, 561 (1984); E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, *ibid.* **24**, 864 (1981).

[12] V. M. Bermudez *et al.*, J. Appl. Phys. **79**, 110 (1996).

[13] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1984); W. Kohn and L. J. Sham, *ibid.* **145**, 561 (1966).

[14] A. Di Pomponio, A. Continenza, R. Podloucky, and J. Vackár, Phys. Rev. B **53**, 9505 (1996), and references therein.