Surface and bulk electronic structure of thin-film wurtzite GaN

Sarnjeet S. Dhesi,* Cristian B. Stagarescu,† and Kevin E. Smith‡
Department of Physics, Boston University, Boston, Massachusetts 02215

Dharanipal Doppalapudi, Raj Singh, and Theodore D. Moustakas
Department of Electrical and Computer Engineering, Boston University, Boston, Massachusetts 02215

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The bulk and surface valence-band electronic structure of thin-wurtzite GaN has been studied using angle-resolved photoemission spectroscopy. The bulk band dispersion along the $\Gamma\Delta A$, $\Gamma\Sigma M$, and ΓTK directions of the bulk Brillouin zone was measured. Our results indicate the local-density approximation band-structure calculations using partial-core corrections for the Ga $3d$ states predict the relative dispersion of many of the observed bands with a high degree of accuracy. Furthermore, a nondispersive feature was identified near the valence-band maximum in a region of k space devoid of bulk states. This feature is identified as emission from a surface state on GaN(0001)-(1×1). The symmetry of this surface state is even with respect to the mirror planes of the surface and polarization measurements indicate that it is of sp_z character, consistent with a dangling-bond state. [S0163-1829(97)03640-0]

Gallium nitride and related nitride wide-band-gap semiconductors are an important class of electronic material due to potential use in optoelectronic devices operating in the blue to ultraviolet spectral range.[1–3] Consequently, a thorough understanding of the electronic structure of such nitrides is of fundamental importance. While there have been numerous theoretical studies of the electronic structure of GaN, there have been far fewer spectroscopic measurements against which these calculations can be tested.[1–3] Recently, a measurement of the occupied and the unoccupied partial density of states of GaN obtained using high-resolution soft-x-ray emission and absorption spectroscopies was reported.[4] However, these spectroscopies do not directly provide information on the *dispersion* of the bands, nor are they surface sensitive. To obtain a direct measurement of the band dispersion of surface and bulk states, angle-resolved photoemission (ARP) spectroscopy must be employed.[5] Photoemission spectroscopy has been used previously to study wurtzite GaN, and substantial band-bending due to Fermi-level pinning at the sample surface has been reported.[6] Among the possible origins of this pinning are extrinsic defect states or intrinsic localized surface states. Direct measurements of the existence and properties of GaN surface states is important since there is a wealth of indirect evidence that if such states do exist (and are similar to states associated with dislocations) then they cannot lie in the bulk band gap,[7] they must be occupied,[8] and they are not recombination centers.[9]

We present here results of a high-resolution ARP study of the surface and bulk electronic structure of n-type wurtzite GaN(0001). The dispersion of states along selected high-symmetry directions of the bulk Brillouin zone has been measured. A comparison of the results with the local-density approximation (LDA) band-structure calculation of Rubio *et al.* indicates good relative agreement between theory and experiment over wide regions of the Brillouin zone.[10] However, we also observe a nondispersive emission feature near the valence-band maximum (VBM) that does not correspond to any calculated bulk state. We identify this feature as a surface state with sp_z character, consistent with a dangling-bond state. The ARP spectra indicate that this state is destroyed by adsorption of O_2 or activated H_2 or by ion bombardment of the surface.

The experiments were performed at the National Synchrotron Light Source (NSLS), on the Boston University/North Carolina State University/NSLS bending magnet beamline U4A, which is equipped with a 6-m torroidal grating monochromator and a custom designed hemispherical electron analyzer.[11] Typical energy and full angular resolution were 100 meV and 1°, respectively. The wurtzite GaN films studies were grown using electron cyclotron resonance-assisted molecular-beam epitaxy on sapphire substrates as described elsewhere[12] and were Si-doped n type with carrier concentrations of 5×10^{17} cm^{-3}. The films were of high quality as determined from resistivity, mobility, carrier concentration, and photoluminescence measurements. Samples were transported in air, rinsed in a 1:10 solution of concentrated HCl and deionized water, mounted in the analyzer chamber (base pressure less than 2×10^{-10} Torr), and outgassed for several hours at 900 °C. The sample surfaces were cleaned using a procedure similar to that of Bermudez *et al.*[13] First a Ga layer is evaporated onto the surface, which is then partially removed by repeated annealing to 900 °C, resulting in the simultaneous removal of much of the surface O. The sample is next subjected to repeated cycles of sputtering with 1.5-keV N_2^+ ions and annealing in ultrahigh vacuum at 900 °C. Auger electron spectroscopy indicated that this procedure reduced the surface O concentration levels to less than 2%, with no indication of any other surface contamination. Such surfaces exhibited a sharp 1×1 low-energy electron diffraction (LEED) pattern on a low background with no evidence of a surface reconstruction or faceting. All measurements reported here were performed with the sample held at room temperature. Binding energies are referenced either to the VBM or to the Fermi level E_F. The VBM was determined by extrapolating the leading edge of the valence-band spectra. However, the determination of the bulk VBM from off-

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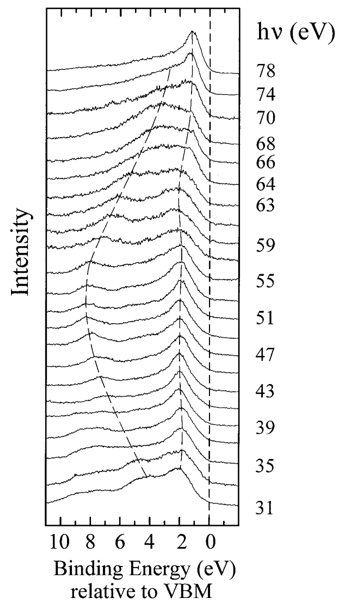

FIG. 1. Series of normal emission ARP spectra from GaN(0001). The photon energy was varied from 31 to 78 eV. The light was incident at 45° to the sample normal. Spectra are aligned with the valence-band maximum (VBM). Lines are guides to the eye. These spectra reflect emission from states along the $\Gamma\Delta A$ direction of the bulk Brillouin zone. See the inset to Fig. 2 for the zone labels.

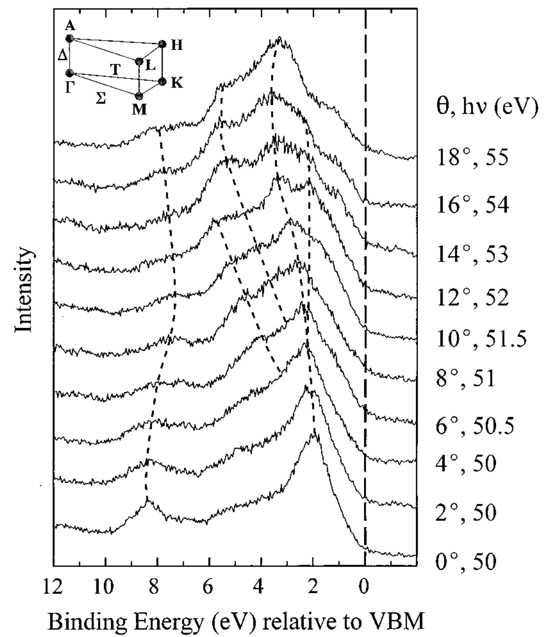

FIG. 2. Series of ARP spectra from GaN(0001) where the photon energy and angle of detection are varied to probe emission from states along the $\Gamma\Sigma M$ direction in the bulk Brillouin zone. See the text for details. The irreducible portion of the zone is illustrated in the inset. Lines are guides to the eye.

normal spectra is complicated by the existence of a surface state visible in the spectra (see below). E_F was determined from a sputtered metal target in electrical contact with the sample. Samples were aligned relative to the polarization vector of the synchrotron radiation using LEED and unless noted the light was incident at 45° to the surface normal. Contamination from residual gases (as monitored by the quality of ARP spectral features) required that a fresh surface be prepared by sputtering and annealing every 2 h.

Figure 1 shows a representative series of normal-emission valence-band ARP spectra taken with photon energies between 31 and 78 eV; the full data set includes spectra recorded from $h\nu=21$ to 104 eV. For the wurtzite (0001) surface,[14] normal-emission ARP probes states with momenta along the $\Gamma\Delta A$ direction in the bulk Brillouin zone.[15] The extremal binding energies of dispersive features in such a set of spectra indicate the positions of **k** space of high-symmetry points within the zone. A comparison of the binding energies of these features with band-structure calculations (for example, Ref. 10) indicates that emission from the Γ point occurs using a photon energy of approximately 51 eV. Using the same symmetry notation employed in Ref. 10, we assign the two dominant features of the $h\nu=51$ eV spectrum located at 2.0 and 8.0 eV to emission from the Γ_{5v} and Γ_{3v} critical points, respectively. (Note that at low photon energies, where states far from Γ are being measured, a nondispersive feature with a binding energy of approximately 8 eV is also visible; this is most likely due to final-state or density-of-states effects rather than being a deep-lying surface state since the feature shows no marked sensitivity to contamination and corresponds to states in the bulk band structure; a similar feature was observed in a study of cubic GaN.[16])

Figures 2 and 3 show ARP spectra corresponding to emission from states in the ΓTK and $\Gamma\Sigma M$ directions in the bulk zone, respectively. This was accomplished in the standard manner by changing the photon energy and angle of emis-

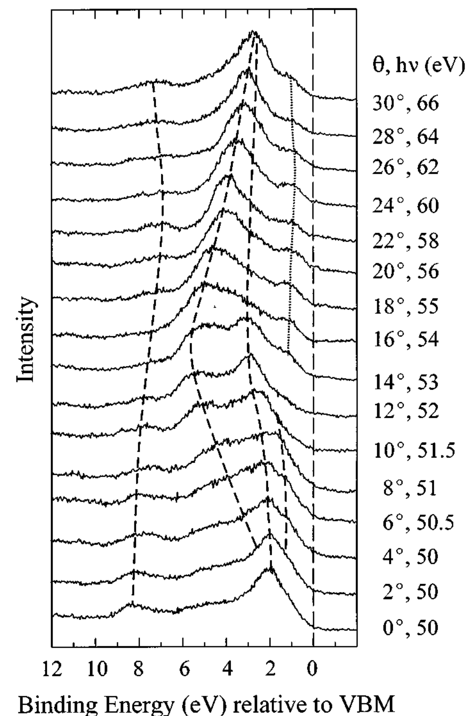

FIG. 3. Series of ARP spectra from GaN(0001) where the photon energy and angle of detection are varied to probe emission from states along the ΓTK direction in the bulk Brillouin zone. See the text for details. Lines are guides to the eye.

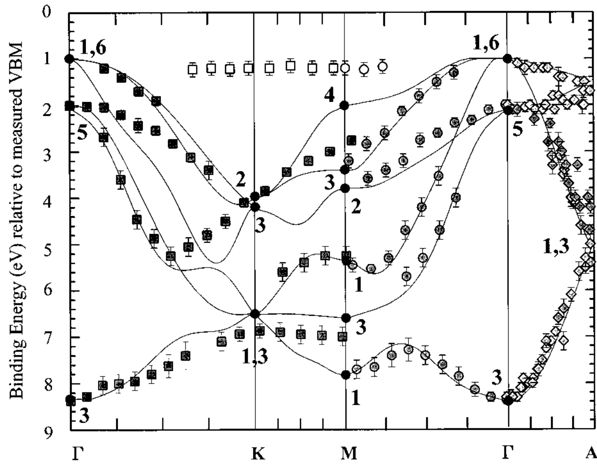

FIG. 4. Comparison of measured band structure for GaN (data points, this work) and the calculation of Rubio *et al.* (solid lines, Ref. 10). The calculated bands have been shifted rigidly to higher binding energies by 1 eV. See the text for details.

sion in concert in order to keep the momentum along the desired direction.[5,17] The spectra in both Figs. 2 and 3 show a rich set of highly dispersive features that can be directly compared to theory. Fortuitously, the range of photon energies and detector angles available in our apparatus allowed us to measure emission from states up to the M point in the second Brillouin zone by continuing along the ΓTK direction. Note that as emission from states away from the Γ point is measured in both the ΓTK and $\Gamma\Sigma M$ directions, a nondispersive feature with a binding energy of approximately 1.3 eV is observed. The origin of this feature will be discussed below.

Figure 4 presents the experimental band structure of wurtzite GaN as determined from the ARP spectra. Here we have assumed a free-electron final state and an inner potential of 10 eV (referenced to E_F). Also shown in Fig. 4 is the calculated band structure from Ref. 10. The calculated bands have been rigidly shifted to higher binding energy by 1 eV. Aside from this rigid shift, the agreement between the experimental data and the calculated band structure is striking over much of the Brillouin zone. (The experimental bands could just have easily been shifted with respect to the calculation; however, by shifting the calculated bands a direct comparison to the spectra is made possible.) The relative binding energies of the LDA band-structure calculation critical points match those of the experimental data and the dispersion of the states closely follows the experimental data within the error bars. Note, however, that some discrepancies are apparent, most notably in the ΓKM direction. We find that in general most calculations predict the binding energies of the upper-valence-band critical points accurately, but that there are significant differences concerning the energy of the Γ_3 critical point in the lower valence band. Using this discrepancy as a general guideline, the LDA band-structure calculations of Rubio *et al.*[10] and Min, Chan, and Ho[18] agree most closely with our experimental data. It is noteworthy that both calculations employ partial-core corrections to describe the core and valence-electron overlap.

One of the most striking aspects of Fig. 4 is the existence of a state near the VBM that becomes visible as the bulk

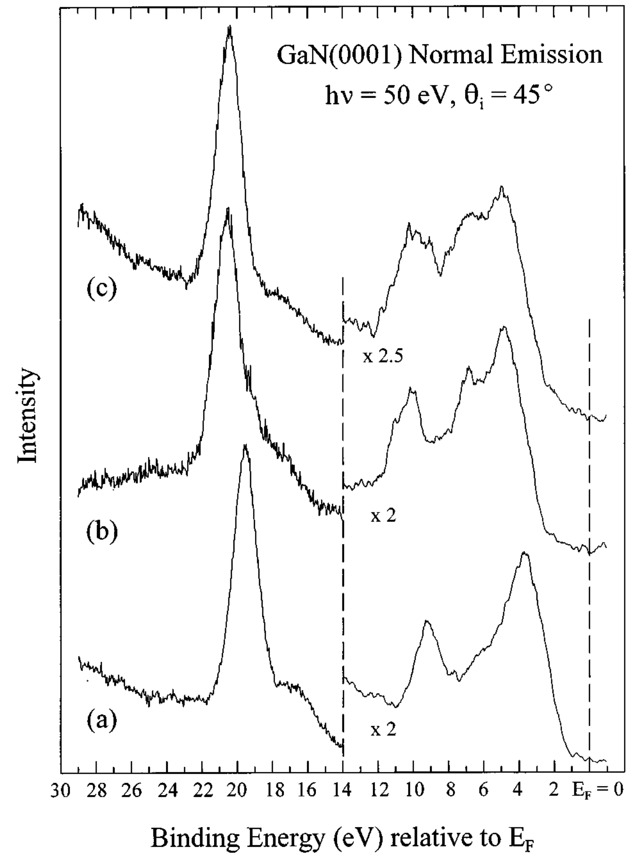

FIG. 5. Series of normal-emission ARP spectra from GaN(0001). The photon energy was 50 eV and the light was incident at 45°. (a) Clean GaN(0001) (1×1), (b) after exposure to 1000 L of activated H_2, and (c) after 2-keV N_2^+ ion sputtering for 30 min.

bands disperse away towards higher binding energy. This state is most easily observed near the $\bar{M}$ point of the surface Brillouin zone; see Fig. 3. The existence of this state is not predicted by published band-structure calculations. This state is only observed from clean, well-ordered surfaces and the data in Fig. 4 show that this state is flat across much of the zone and thus has a very large density of states. Figure 5 shows normal-emission ARP spectra recorded from a clean GaN(0001) surface, a clean surface exposed to 1000 L of activated H_2 (1 L=1 Langmuir= 1×10^{-6} Torr sec), and a clean surface sputtered with 2-keV N_2^+ ions for 30 min. The H_2 was activated with hot W filaments in the sample chamber. The binding energies are relative to E_F. The dominant feature in each spectrum (at approximately 19.5 eV with respect to E_F) is due to emission from the Ga 3d states with a shoulder at lower binding energy due to N 2s states. For the clean surface, the VBM is 1.3±0.1 eV below E_F, indicating an upward band bending of 2.1±0.1 eV, assuming a bulk band-gap energy E_g=3.4 eV for GaN at room temperature.[1] From the shift of the spectra away from E_F (1.0±0.1 eV) following H_2 adsorption or N_2^+ ion sputtering it is apparent that band bending at the GaN surface is sensitive to contamination, disorder, and defects at the surface. However, the band bending is not completely removed by these surface modifications, indicating that either the surface states have not been completely destroyed or defect states are also re-

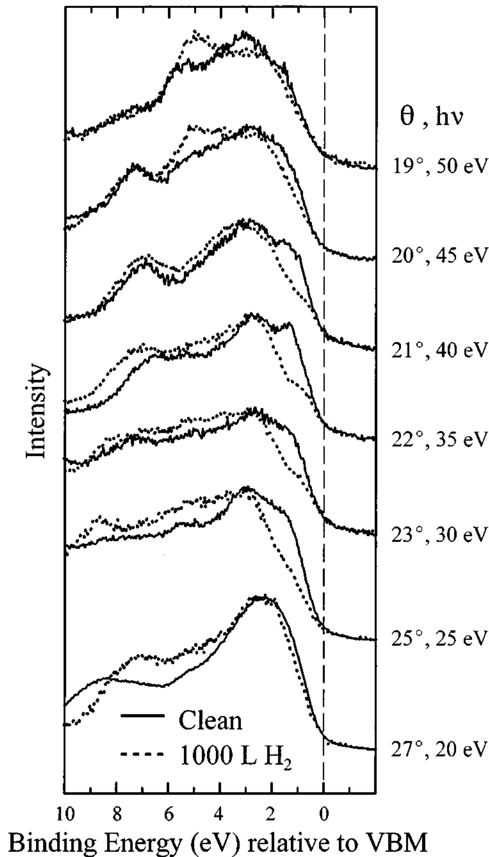

FIG. 6. Series of ARP spectra from clean GaN(0001) and after exposure to 1000 L of activated H_2. The photon energy and angle of emission are varied to maintain a value of $k_{\|}$ corresponding to emission from the $\bar{M}$ point. See the text for details.

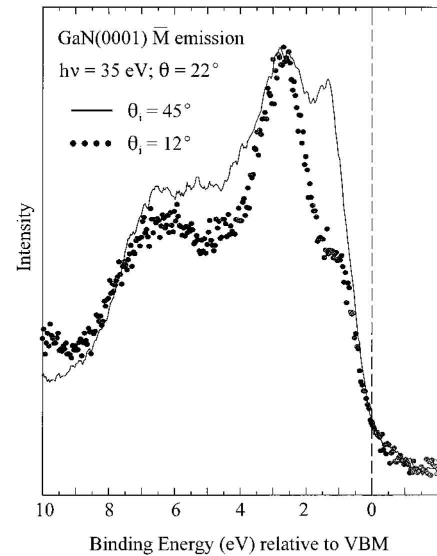

FIG. 7. ARP spectra from GaN(0001) as a function of angle of incidence of the radiation. $h\nu = 35$ eV and $\theta_{\mathrm{emission}} = 22°$, corresponding to emission from the $\bar{M}$ point in the surface Brillouin zone.

sponsible for the observed Fermi-level pinning.

Figure 6 shows a series of off-normal valence-band ARP spectra along the $[10\bar{1}]$ direction from a clean GaN(0001)-(1×1) surface and the corresponding spectra recorded from a surface exposed to 1000 L of activated H_2. In this experiment the photon energy was varied between 20 and 50 eV and the angle of the detector is varied to keep the component of the electron momentum parallel to the surface constant at the $\bar{M}$ point; i.e., each of these spectra reflects emission from states at $\bar{M}$, but excited with different photon energies.[5] Binding energies for these spectra are referenced to the VBM. H_2 adsorption changes the band bending and hence the kinetic energy of photoemitted electrons, so for the purpose of this figure the H_2 spectra are rigidly shifted towards E_F, i.e., placed on a common binding-energy scale. It is clear from the spectra in Fig. 6 that there is a state at the top of the valence band with a binding energy of 1.3 ± 0.1 eV that is highly sensitive to H_2 absorption. It is also clear that this state does not disperse with photon energy and thus has no component of momentum *perpendicular* to the surface. The adsorption of O_2, or bombardment of the surface with N_2^+, have essentially the same effect on the emission at 1.3 eV as reported here for activated H_2 adsorption.

That this state exists in a region of the Brillouin zone devoid of bulk states, is highly sensitive to surface contamination and disorder, and shows no dispersion perpendicular to the surface proves conclusively that this is indeed a surface state. This state exists across the surface Brillouin zone, probably becoming a surface resonance at zone center ($\bar{\Gamma}$). Brief (2–3 min) annealing of the surface to 900 °C following activated H_2 adsorption or N_2^+ ion sputtering resulted in the spectra shifting back towards E_F with the re-emergence of the surface state feature, although with reduced intensity. After one cleaning cycle of N_2^+ ion sputtering followed by annealing to 900 °C the ARP spectra indicated that the clean, ordered surface was completely restored. This in turn indicates that the adsorbed H is easily removed and that this surface state feature is not due to N defects at the surface. Note also that in an angle-integrated photoemission study of O_2 chemisorption on wurtzite GaN, Bermudez alluded to the existence of these surface states.[19] However, in contrast to these results of the present study, Bermudez concluded that these states are not involved in Fermi-level pinning since O_2 chemisorption did not affect the binding energy of the Ga $3d$ state.

Figure 7 shows off-normal ARP spectra recorded at the $\bar{M}$ point of the surface Brillouin zone for near normal incidence of the synchrotron radiation and for radiation incident at 45°. It is clear that the intensity of the surface state emission increases dramatically as the component of the electric light vector perpendicular to the surface increases. This observation allows us to conclude that the surface state has sp_z character.[5] Furthermore, when spectra are recorded from the $\bar{M}$ point of the second zone with the light at normal incidence to the surface then the surface state emission is completely suppressed. For the spectra in Fig. 7 the incident radiation is along the $[10\bar{1}]$ direction and is therefore in the $(11\bar{2})$ mirror plane of the surface. Since this is also the plane of collection, the dipole operator $\mathbf{A}\cdot\mathbf{p}$ is even with respect to this mirror plane and therefore the surface state is also of even symmetry with respect to this mirror plane. Similar behavior for this feature was observed at the $\bar{K}$ point for

spectra along the $[11\bar{2}]$ direction in the $(10\bar{1})$ mirror plane of the surface. Finally, it should be noted that most calculations predict that the clean surface should be reconstructed into a 2×2 pattern since this surface is energetically more stable than the 1×1 surface and electron counting rules also predict a reconstruction of the 1×1 surface.[20–22] However, no such reconstruction has yet been reported by any study of a wurtzite GaN surface.

In summary, ARP spectra were recorded along the $\Gamma\Delta A$, $\Gamma\Sigma M$, and ΓTK directions of the bulk Brillouin zone for wurtzite GaN and the electronic structure along these high-symmetry directions was determined. Our data were compared with existing band-structure calculations and indicate that LDA band-structure calculations using partial-core corrections for the Ga $3d$ states predict the relative band structure with a high degree of accuracy. A nondispersive state was identified near the VBM and it was found to be sensitive to surface contamination or disorder. It exists across the surface Brillouin zone in a region devoid of bulk states. Polarization measurements reveal that this feature originates from a state with sp_z character and has even symmetry with respect to the $(11\bar{2})$ and $(10\bar{1})$ mirror planes of the surface. The preponderance of evidence is that the origin of this emission feature is a surface state due to dangling bonds at the GaN surface. This state is occupied and does not lie in the fundamental band gap; thus it does not act as a recombination center. Destruction of this state only partially removes the observed band bending.

Note added in proof. Another, albeit less extensive, photoemission study of wurtzite GaN can be found in the paper by S.A. Ding, S.R. Barman, V.L. Alperovich, and K. Horn, in *Proceedings of the 23rd International Conference on the Physics of Semiconductors*, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), p. 525. We thank K. Horn for bringing this paper to our attention.

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*Present address: Department of Physics, University of York, York, Y01 5DD, United Kingdom.

†On leave from the Institute of Microtechnology, Bucharest, Romania.

‡Author to whom correspondence should be addressed. Electronic address: ksmith@bu.edu

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