Published in Appl. Phys. Lett. 89, 171920 (2006).

Electronic States of Oxidized GaN(0001) Surfaces

Y. Dong and R. M. Feenstra
Dept. Physics, Carnegie Mellon University, Pittsburgh, PA 15213
J. E. Northrup
Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, CA 94304

Abstract

The structure and electronic properties of oxidized (0001) surfaces of GaN grown by plasma-assisted molecular beam epitaxy are investigated by scanning tunneling microscopy/spectroscopy, Auger electron spectroscopy, and first-principles theory. For oxygen exposure at room temperature an amorphous gallium oxide layer is found to form, resulting in a distribution of midgap electronic states extending out from the GaN valence band edge. The influence of these states on the electron concentration in buried AlGaN/GaN heterojunctions is discussed.

The electronic properties of oxidized GaN and AlGaN surfaces are relevant for understanding the operation of heterojunction field-effect transistors (HFETs) with channel layers buried ≈50 nm below the surface [1-5]. For structures grown either by plasma-assisted molecular beam epitaxy (PAMBE) [2] or metal organic chemical vapor deposition (MOCVD) [1,3] it has been argued that the air-exposed surface possesses electronic states which act as donors, donating charge to the channel of the HFET. It is observed that the efficacy of this mechanism depends on the depth of the channel below the surface, which for studies of MOCVD-grown material leads to deduced energy level positions of 1.65 eV below the $Al_xGa_{1-x}N$ (x=0.34) conduction band minimum (CBM) for an assumed single donor state [1], or 1.0–1.8 eV below the CBM for a band of such states [3]. For PAMBE-grown material the sensitivity of the transistor characteristics to the GaN surface properties has been employed for fabricating chemical sensors [4,5].

The (0001) surface of GaN grown by PAMBE under Ga-rich conditions is known to be covered by slightly more than 2 monolayers (ML=1.14×10^{15} atoms/cm^2) of excess Ga [6-8]. Exposure of the PAMBE-grown surfaces to oxygen is thus expected to yield an oxide of Ga. A number of prior works have dealt with the structure of oxidized GaN surfaces for which the oxide is found to be generally of the Ga_2O_3 form [9], although, with one notable exception [10], these prior works did *not* start with a well defined Ga-rich PAMBE-grown surface of the type studied here. Our studies reported here deal with surfaces that have been exposed to oxygen while held at room temperature (RT). We find a saturated oxygen coverage of about 2 ML, with a similar value for the excess Ga coverage. STM images reveal the formation of a disordered oxide on the surface. This metal oxide is found to have a band gap of ≈2 eV in size, although with tails of states extending into this gap. We find in particular that the spectrum of states extending in from the GaN valence band, with these states being normally filled i.e. *donor-like*, is

consistent with the spectra indirectly detected in the prior work [1-3]. These states donate electrons to the channel of the HFETs, giving rise to the two-dimensional electron gas.

PAMBE is performed as previously described [6], yielding n-type Ga-polar GaN. The as-grown (0001) surface is exposed in situ to ultra-pure (99.998%) O_2, using various oxygen partial pressures (typically in the range 1.5×10^{-7} to 1.5×10^{-5} Torr, with the ion gauge left on during the exposures). Total exposures of 2×10^4 and 2×10^5 L (1 L = 10^{-6} Torr sec) O_2 have been used; the former is insufficient to produce a saturation coverage but the latter does achieve that. Auger electron spectroscopy (AES) is performed with a double-pass cylindrical mirror analyzer at incident electron energy of 3 keV. Peak-to-peak intensity ratios are converted into surface coverages using a procedure described elsewhere [11]. Commercial Pt–Ir probe tips are used for the scanning tunneling microscopy/spectroscopy (STM/STS) experiments. Topographic imaging is performed at a constant current of 0.1 nA and at sample voltages specified below. For spectroscopic measurements a large dynamic range of currents was achieved by acquiring a sequence of current-voltage curves at varying fixed tip-sample separations. Normalization of the conductance is done by multiplying the measured values of dI/dV by $\exp(2\,?\,?\,s)$ where Δs is the relative change in separation and $\boldsymbol{k}$ is a measured value for the exponential dependence of the current (and conductance) on separation [12].

Figure 1(a) shows an STM image of a GaN(0001) surface that has been exposed to 2×10^5 L O_2 while held at RT. Several steps are visible extending across the image; the height of these is found to be 0.24±0.02 nm, corresponding to a single-bilayer step (0.26 nm) for GaN. For as-grown GaN surface terraces observed in such STM images are nearly featureless, displaying only a weak 1×1 corrugation having typical peak-to-valley amplitude of less than 0.01 nm [6], as shown in Fig. 1(b). In contrast, the terraces seen in Fig. 1(a) are quite corrugated, displaying a disordered structure with corrugation amplitude of about 0.10 nm. Low-energy electron diffraction (LEED) reveals no additional spots beyond the 1×1 of the substrate. AES indicates an O coverages of 2.1±0.5 ML for this surface and a Ga coverage of 2.3±0.5 (i.e. over and above that of the final GaN bilayer). The latter value is consistent with the known excess Ga coverage of 2.3 ML for an as-grown GaN surface, indicating that little or no Ga has left the surface during the RT oxidation.

Additional information on the surface structure comes from the 55 eV AES LMM Ga line which, having an escape depth of about 0.4 nm, is very surface sensitive. Figure 1(c) shows an AES spectrum acquired on the bare GaN surface displaying characteristic features of the Ga^0 oxidation state of metallic gallium [13], arising from the terminating 2 ML of Ga on this surface. In contrast, the spectrum of Fig. 1(d) acquired from the RT-oxidized surface shows broadening and spectral shifts to lower energy, characteristic of the formation of Ga^{3+} oxidation states that form in Ga_2O_3 [13].

In previous work we have studied the structure of oxides formed on MBE-grown GaN when it is held at high temperature (HT) of about 550°C during oxidation. In this case *ordered* structures are found to form on the surface (the same structures can be obtained by annealing of RT-oxidized surfaces). Two different structures are found, one with

$3\sqrt{3}\times3\sqrt{3}-R30^{\circ}$ symmetry as seen by both STM and LEED, and the other displaying a somewhat disordered arrangement of 2×2 features and surface domain boundaries. The surface coverages of the HT-oxidized surface are found to be 2.0±0.5 ML for O and also 2.0±0.5 ML for Ga, i.e. nearly the same as for RT-oxidation (the quoted errors reflect the absolute uncertainty of our coverage estimates, but the *relative* error between the RT- and HT-oxidized surfaces is expected to be significantly less than this, indicating that the stoichiometries of the surface oxides formed in each case are indeed quite close). The AES spectrum from a HT-oxidized surface, Fig. 1(e), and is nearly identical to that from the RT-oxidized surface. First-principles computations were performed for a variety of O-containing structures [11], and minimum energy structures were obtained in which the near surface Ga-atoms were six-fold coordinated to O atoms, as in bulk Ga_2O_3. Importantly, for the lowest energy structure found in the computations the ratio of Ga to O atoms in the oxide is 5:8, close to the 2:3 that occurs for bulk Ga_2O_3. On the basis of these experimental and theoretical results, we conclude that our surfaces consists of an oxide having stoichiometry and structure similar to that of Ga_2O_3, with the structures obtained by RT-oxidation being more disordered (amorphous) than for HT-oxidation.

STS results for as-grown GaN(0001) surfaces and for oxidized surfaces are shown in Fig. 2. Figure 2(a) shows the known result for an as-grown Ga-rich surface, displaying metallic behavior in the conductance. After an exposure of 2×10^4 L at RT, Fig. 2(b), the conductance measurements indicate weakly metallic behavior with reduced conductance values around 0 V but still with nonzero conductance at 0 V. Figure 2(c) shows the result for 2×10^5 L exposure at RT. A gap of width ≈2 eV is apparent in the spectrum, although the conductance edges on either side of the gap are not particularly sharp and it is possible that some small residual conductance (below our detection limit) persists at 0 V.

Prior work by Kocan et al. [10] revealed a Fermi-level position for PAMBE-grown GaN(0001) of 1.65 eV above the surface valence band maximum (VBM); we indicate their result for the GaN band edge locations on our spectrum of Fig. 2(a). In addition, they found a Fermi-level position of 3.14 eV above the surface VBM for an oxidized surface, with the oxidation done in their case by air exposure at RT. This surface is expected to be similar to our surface with saturated oxidation. We may therefore employ their result to indicate GaN band edge positions on the spectrum shown in Fig. 2(c), bearing in mind that some uncertainty occurs in these band edge positions due to possible differences between the oxidized surface of Kocan compared to ours.

The prior work on surface sensitivity of transistors revealed the presence of donor states of unknown nature at the oxidized GaN surface [1-5]. Based on our results the structure of this oxide appears to be an *amorphous thin film phase* of Ga_2O_3. The band gap of bulk Ga_2O_3 is 4.4 eV [14], and the ordered surface oxides we have studied previously have surface gaps as large, or nearly so, as the GaN gap (3.44 eV) [11]. We therefore surmise that the tail of states we observe extending out from the GaN valence band arises mainly from disorder in the oxide. Being derived from the valence band these states are normally filled (i.e. neutral when filled), which gives them donor character. We thus identify these states as being responsible for the surface donors observed indirectly in the prior work [1-3] (i.e. specifically for those works with MBE-grown GaN cap layer

terminating the heterostructure [2]). Following those models, the Fermi-level intersects this tail of midgap states, with the states lying above the Fermi-level donating their charge to the channel of the HFET.

A schematic band diagram for an HFET is shown in Fig. 3, following Ref. [1-3]. The energetic location of the surface donors observed previously was made only for AlGaN surfaces; this energy was reported to be ≈1.65 eV below the CBM [1]. If we assume the same pinned surface Fermi-level position in the GaN-capped heterostructures, then we would expect the relevant donor states to lie at about 1.2 eV below the CBM (i.e. 1.65 eV minus the AlGaN/GaN conduction band offset [15]). Referring to Fig. 2(c), we find the observed onset of the donor band to lie ≈1.5 eV below the CBM, and, as mentioned above, this donor band likely extends up to higher voltages with conductance values below our detection limit. We conclude that the midgap donor states of the amorphous Ga_2O_3 do indeed appear to lie at an energy that would affect the electron concentration of an underlying AlGaN/GaN heterojunction. In this scenario, the sensitivity to adsorbed gases [4,5] arises from the relatively weak pinning of the Fermi-level that occurs for a low density of midgap states. Significant Fermi-level shifts (and concomitant charge transfer to/from the channel) occur depending on the electronegativity of the adsorbed species.

Discussions with A. Rizzi are gratefully acknowledged. This work was supported by the Office of Naval Research, Grant No. N00014-02-1-0933 monitored by C. Wood and N00014-02-C-0433 monitored by C. Baatar.

References:

[1] J. P. Ibbetson, P. T. Fini, K. D. Ness, S. P. DenBaars, J. S. Speck, and U. K. Mishra, Appl. Phys. Lett. **77**, 250 (2000).

[2] B. K. Ridley, O. Ambacher, and L. F. Eastman, Semicond. Sci. and Technol. **15**, 270 (2000).

[3] G. Koley and M. G. Spencer, Appl. Phys. Lett. **86**, 042107 (2005).

[4] J. Schalwig, G. Müller, M. Eickhoff, O. Ambacher, and M. Stutzmann, Sensors and Actuators B **87**, 425 (2002).

[5] G. Steinhoff, M. Hermann, W. J. Schaff, L. F. Eastman, M. Stutzmann and M. Eickhoff, Appl. Phys. Lett. **83**, 177 (2003).

[6] A. R. Smith, R. M. Feenstra, D. W. Greve, M.-S. Shin, M. Skowronski, J. Neugebauer, and J. Northrup, J. Vac. Sci. Technol B **16**, 2242 (1998); J. E. Northrup, J. Neugebauer, R. M. Feenstra, and A. R. Smith, Phys. Rev. B **61**, 9932 (2000).

[7] C. Adelmann, J. Brault, G. Mula, B. Daudin, L. Lymperakis, and J. Neugebauer, Phys. Rev. B **67**, 165419 (2003).

[8] J. S. Brown, G. Koblmüller, F. Wu, R. Averbeck, H. Riechert, and J. S. Speck, J. Appl. Phys. **99**, 074902 (2006).

[9] S. D. Wolter, B. P. Luther, D. L. Waltemyer, C. Önneby, S. E. Mohney, and R. J. Molnar, Appl. Phys. Lett., **70**, 2156 (1997), and references therein.

[10] M. Kocan, A. Rizzi, H. Lüth, S. Keller, and U. K. Mishra, Phys. Stat. Sol. (b) **234**, 773 (2002). The air exposure described here was performed over two months (A Rizzi, private communication).

[11] Y. Dong, R. M. Feenstra, and J. E. Northrup, J. Vac. Sci. Technol. B **24**, 2080 (2006).

[12] R. M. Feenstra and J. A. Stroscio, J. Vac. Sci. Technol. B **5**, 923 (1987); R. M. Feenstra, Phys. Rev. B **50**, 4561 (1994).

[13] Y. Jeliazona and R. Franchy, Surf. Sci. 527, **57** (2003).

[14] M. Passlack, E. F. Schubert, W. S. Hobson, M. Hong, N. Moriya, S. N. G. Shu, K. Konstadinidis, J. P. Mannaerts, M. L. Schnoes, and G. J. Zydzik, J. Appl. Phys. **77**, 686 (1995).

[15] O. Ambacher, B. Foutz, J. Smart, J. R. Shealy, N. G. Weimann, K. Chu, M. Murphy, A. J. Sierakowski, W. J. Schaff, L. F. Eastman, R. Dimitrov, A. Mitchell, and M. Stutzmann, J. Appl. Phys. 87, 334 (2000).

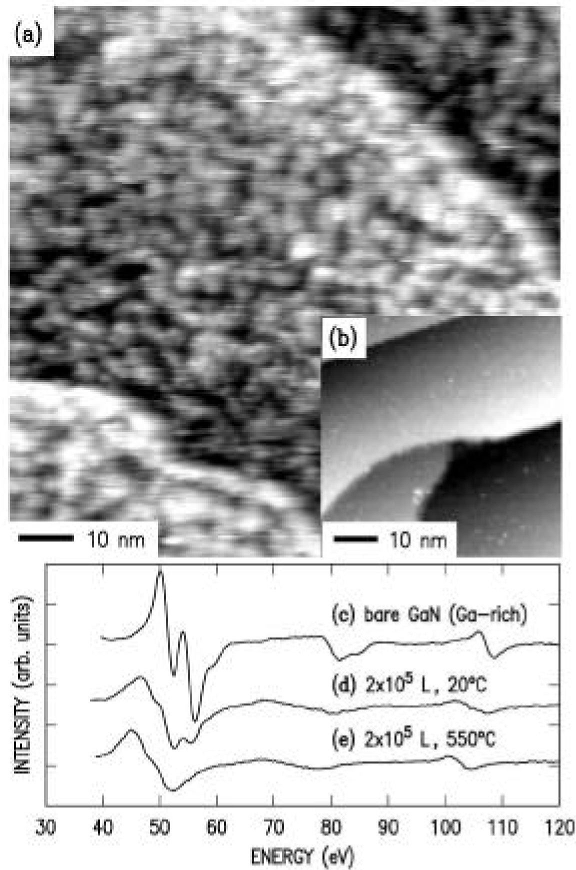

FIG 1. (a) and (b): STM images of GaN(0001) surfaces exposed to (a) $2{\times}10^{5}$ L oxygen at room temperature, or (b) 0 L oxygen. Gray scale range is 0.4 nm for both images. (c)-(e): Auger electron spectra of LMM Ga line for three different GaN(0001) surfaces, indicating oxygen exposure (L) and temperature during exposure. The spectra are displaced vertically from each other for ease of viewing.

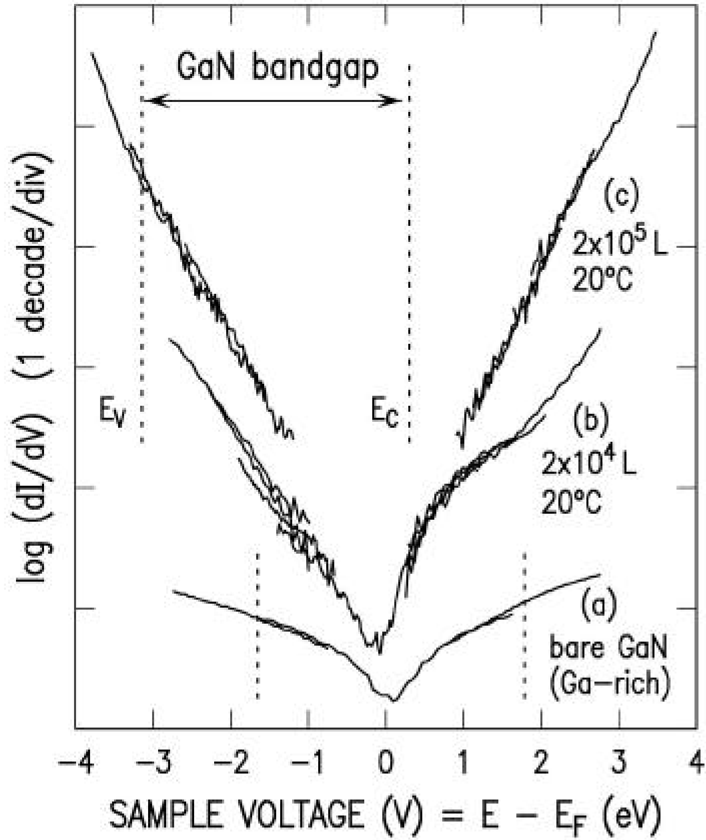

FIG 2. Conductance versus sample voltage for an as-grown GaN(0001) surface and for surfaces oxidized at room temperature, with oxygen exposures (L) indicated. Each spectrum is composed of a series of measurements at different tip-sample separations. The spectra for the three different oxygen exposures are displaced vertically for ease of viewing. The values on the voltage axis equal the energy of a state relative to the Fermi level (0 V). Locations of the GaN valence and conduction band edges, E_V and E_C, respectively, are shown for spectra (a) and (c), as determined in Ref. [10] (see text).

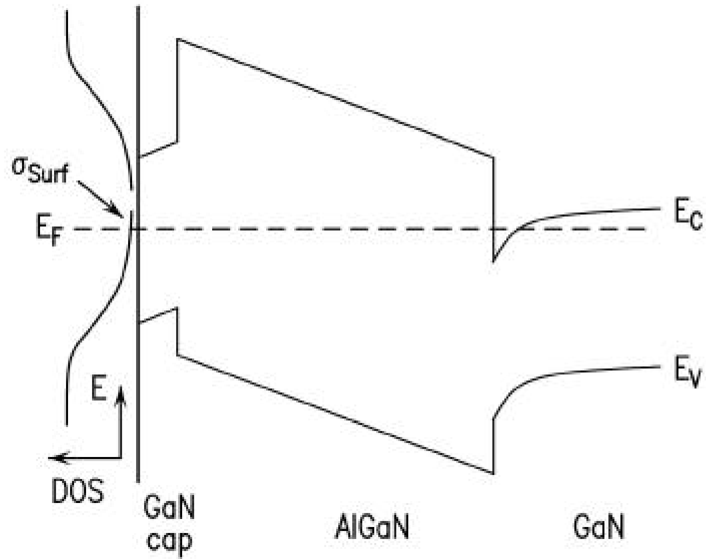

FIG 3. Schematic band diagram for band bending near a AlGaN/GaN heterostructure covered by a thin GaN cap layer. The electric field in the semiconductor includes contributions from the polarization charges, the electron charge in the channel, and the positive surface charge s_{Surf} from the empty surface donor states. The density of surface states shown (DOS) is deduced from the STS spectrum of Fig. 2.