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Oxidized GaN(0001) Surfaces studied by Scanning Tunneling Microscopy and Spectroscopy and by First-Principles Theory

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Abstract

Oxidized Ga-polar GaN surfaces have been studied both experimentally and theoretically. For in-situ oxidization at 550°C using molecular oxygen, Auger electron spectroscopy indicates a saturation oxygen coverage of 2.1 ± 0.5 monolayers. For these surfaces scanning tunneling microscopy reveals two surface phases, one with $3\sqrt{3}\times3\sqrt{3}-R30^\circ$ periodicity and the other with disordered 2× periodicity. Scanning tunneling spectroscopy revealed a surface band gap with size close to that of GaN, indicating that any states of the oxide lie predominantly outside of the GaN gap. From first-principles total energy calculations of surface formation energies two models of energetically favorable surfaces structures are developed, with oxygen coverages of 1.25 and 2 monolayers, respectively. Both structures satisfy electron counting and have surface band gaps close in size to that of GaN, in agreement with experiment.

I. Introduction

The growth of oxides on GaN is a subject of considerable current activity, due in part to promising device applications [1]. Oxides are commonly used as insulators for GaN-based field effect transistors, and for such applications it is essential to investigate the trap state density at the interface between GaN and the oxide. An understanding of the electronic properties of oxidized GaN (and/or AlGaN) surfaces is also relevant to the formation of a 2-dimensional electron gas (2DEG) at AlGaN/GaN heterostructures [2-4]. In terms of structure, it has been confirmed that Ga-O bonds form at the surface for small amount of oxygen exposure, and the native oxide on GaN surfaces is of the Ga_2O_3 type [5-9]. A significant uncertainty with previous surface science studies of oxidized GaN is that the GaN films are introduced into the surface analysis system from air, so that the initial surface structure prior to oxidation was not well defined.

This work describes a study of oxidized Ga-polar GaN (0001) surfaces, using scanning tunneling microscopy / spectroscopy (STM/STS) and first-principles theory. Our starting surface consists of MBE-grown GaN surfaces terminated by a Ga-bilayer (the so-called "1×1" or pseudo-1×1 structure). The surfaces are exposed to molecular oxygen in-situ in the GaN growth chamber, either at room temperature or at elevated temperatures near 550°C. We focus on the latter set of results in this work, for which ordered (or partially ordered) structures are found to form on the surface. The oxidized GaN surfaces are found to contain two phases. One phase, which is relatively smooth in morphology, shows a $3\sqrt{3}\times3\sqrt{3}-R30^\circ$ periodicity and the other phase, which is relatively rough, displays a disordered 2× periodicity. By STS, these surfaces oxidized at elevated temperature are found to have a surface Fermi level position near the conduction band edge, i.e. corresponding to nearly *flat band* conditions in our samples, This observation, along with the appearance of a "dopant-induced" component of the tunneling current, indicates that the oxide does not introduce a significant number of states within the GaN band gap. First-principles theory is used to develop energetically favorable structural models for the oxide layer, in which the oxidation is confined to the Ga-bilayer together with one subsurface nitrogen layer. In agreement with experiment these structures are found to have a band gap nearly equal in size to the GaN gap. Thus, the surface structures formed by oxidation of GaN surface at elevated temperatures do *not* have states lying within the GaN band gap that act to strongly constrain or "pin" the Fermi level.

II. Experimental

GaN films were grown by plasma-assisted molecular beam epitaxy, in an ultra-high vacuum (UHV) growth chamber equipped with reflection high-energy electron diffraction (RHEED). Oxidation was done in-situ by exposing GaN films to molecular oxygen either at room temperature or with the samples held at 550°C, using various oxygen partial pressures (typically in the range 1.5×10^{-7} to 1.5×10^{-5} Torr for most of our experiments, with the ion gauge left on during the exposures). This temperature of 550°C is chosen so that GaN will not decompose, and so that diffusion of oxygen atoms within the Ga layers is facilitated. Ultra-pure oxygen gas (99.998%) is introduced into the growth chamber through a UHV leak valve. Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and scanning tunneling microscopy and spectroscopy (STM/STS) are performed in an UHV analysis chamber adjoining to the growth chamber.

AES was performed using a Perkin-Elmer 15-255G double-pass cylindrical mirror analyzer, at an incident electron energy of 3 keV. The observed peak-to-peak intensities were found to have some dependence on the distance from the sample to the detector, and this distance was maintained a constant between measurements by observing the maximum of the elastically scattered electron beam.

Commercial Pt–Ir probe tips are used for the 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 varying the tip-sample separation during the voltage scan [10], either by acquiring a sequence of current-voltage curves at varying fixed tip-sample separations or by continuously varying the separation during the voltage scan. In the former case the conductance dI/dV is obtained by numerical differentiation and in the latter case it is measured using a lock-in amplifier with modulation of 50 mV. Normalization of the conductance is done by multiplying the measured dI/dV by $\exp(2 ? ? s)$ where Δs is the relative change in separation and k is a *measured* value for the exponential dependence of the current (and conductance) on separation. The resulting conductances vary over many orders of magnitude and are therefore displayed on a logarithmic scale. The variation of the tunneling current I with tip-sample separation s, dI/ds, was also measured, again using a modulation method. Values of this quantity are plotted below using the quantity $0.5\, d\ln(I)/ds$ [11], which is equal to the exponential decay constant k for the tunneling process.

Determination of surface coverage values for oxygen is made using peak-to-peak intensity value from observed Auger spectra. To convert these intensity ratios into surface coverages, we make use of the Handbook of Auger Electron Spectroscopy values for the bulk sensitivity factors [12], which are converted to sensitivity factors for a layer of atoms using the known density of the standard materials and a phenomenological form for the electron escape depths [13]. Results are expressed in monolayers (ML), corresponding to one atom per unit cell or 1.14×10^{15} atoms/cm^2. In order to perform this type of analysis it is necessary to assume a particular model for the surface structure; the structure of the bare GaN surface is known (consisting of a bilayer of Ga, with the first Ga layer separated from the GaN by 2.5 Å and the second layer 2.4 Å above that [14]) but the structure of the oxygen exposed surfaces are not so well known. However, the theoretical models described below indicate that energetically favorable structures may be formed by incorporating oxygen atoms at sites approximately *between* the Ga layers on the surface (this structure can be visualized approximately as a GaN bilayer in which the N atoms have been replaced by O). Thus, in the computations below we use this structure for determining the oxygen coverages, placing one layer of oxygen atoms between the GaN and the first Ga layer above the GaN, and any remaining oxygen above that first Ga layer. By considering other structural models, we estimate that the corrections to coverage values obtained in this way should be less than about ±0.1 ML.

III. Results and Discussion

When oxygen exposure is performed with the samples held at room temperature, disordered surface structures are produced. A saturation oxygen coverage of 2.1 ± 0.5 ML is determined by AES (this coverage is larger than the value of 0.79 ± 0.1 ML reported by Janzen et al. [9] although it should be noted that their starting surface differed from the present one in that it likely did not include the terminating Ga bilayer). Diffraction (RHEED or LEED) of such surfaces does not display any additional spots, and STM images reveal a rather disordered arrangement of oxygen atoms or molecules in the Ga bilayer, as described elsewhere [15]. Annealing of such samples up to about 550°C is found by diffraction to produce ordered structures, and exactly the same structures are formed by directly performing the oxygen exposure with the sample held at 550°C. All of the results described below are obtained from such 550°C exposures, performed typically under 1.5×10^{-5} Torr of oxygen atmosphere with a total exposure of 2×10^{5} L. From AES we deduce an oxygen coverage of 2.1 ± 0.5 ML for these surfaces (i.e. the same as for the room temperature oxidation). Also, using the same model, the surface coverage of Ga atoms (i.e. excess Ga atoms, counting those in the model that are *not* bonded to nitrogen atoms) is found to be between 2 and 3 ML.

Figure 1 shows diffraction patterns of the oxidized GaN surfaces. In LEED, Figs. 1(c) and (d), a new set of diffraction spots is observed consisting mainly of six additional spots spaced symmetrically around each primary spot. In Fig. 1(d), the reciprocal lattice vectors of surface reconstruction are obtained by measuring the distance between the center spot [not visible in Fig. 1(d), but it can be deduced from the positions of the other spots] and one of the six additional spots. The magnitude of the reconstruction reciprocal lattice vector b^* equals to $a^*/(3\sqrt{3})$, where a^* is the reciprocal lattice vector of the (0001) 1×1 surface. It is also easily seen from the diffraction pattern that there is a rotation of 30º between the reconstruction spots and the 1×1 spots. The surface periodicity is thus $3\sqrt{3}\times3\sqrt{3}-R30^\circ$. All the diffraction spots in Fig. 1(c) can be accounted for using this reconstruction, and it is also consistent with RHEED patterns of Figs. 1(a) and (b). It should be noted that the arrangement of intensities of the fractional-order LEED spots is reminiscent of an incommensurate type of surface structure (as observed for the clean GaN(0001) surface [14]), and indeed the STM images below support this type of interpretation.

Figure 2 shows a large-scale STM image of the oxidized GaN surface. There are two different surface structure phases observed in the image: the majority phase (appearing brighter) is relatively smooth and shows corrugation rows with hexagonal symmetry, while the minority phase (appearing darker in the images) is relatively rough. Figure 2(b) shows a line cut across the dashed line in (a), revealing a height difference of about 1.0 Å between the smooth and rough regions (with the smooth domain being higher). Figures 3(a) and (b) show expanded views of these smooth and rough regions, respectively. The smooth regions, Fig. 3(a), show a corrugation with periodicity of ≈ 15 Å, which is consistent with the $3\sqrt{3}\times3\sqrt{3}-R30^\circ$ pattern seen by diffraction (spacing between corrugation rows of this hexagonal pattern is $3\sqrt{3}\times\sin60^\circ\times3.19\text{ Å}=14.4\text{ Å}$). In the relatively rough region, Fig. 3(b), disordered adatom or dangling bond type features can be seen with a spacing of approximately 6 Å, which is consistent with a 2× spacing. A series of what appear to be surface domain boundaries is also seen in this region, suggestive perhaps of strain relaxation in the surface layer.

Scanning tunneling spectroscopy was carried out in order to understand the electronic properties of the surfaces. Figures 4(a) show two typical spectra obtained from a smooth region of the surface displaying $3\sqrt{3}\times$ periodicity. These two spectra (shown by solid and dashed lines, respectively) are obtained using two different STM tips from two different surfaces prepared with the same oxidation process. Spectroscopy measurements were also performed on the rough, disordered 2× regions, and they show results very similar to those of Fig. 4. In both of the spectra of Fig. 4(a), an inflection point is observed at about –3 V. Additionally, the onset of the conductance at 0 V has a shape consistent with that expected for the onset of a free electron band, i.e. indicating a conduction band minimum at that voltage. This surface is thus seen to have a band gap, close in size to the GaN band gap of 3.4 eV. The inset of Fig. 4(a) shows the measured conductance vs. voltage for one data set, clearly revealing the observed band gap.

Since our oxide layers are very thin, we expect the observed gap to be bounded by the lowest-lying empty states of the oxide and/or underlying GaN and the highest-lying filled states of the oxide and/or GaN. Thus, with the observed gap being close in size to that of GaN, we do indeed interpret it as arising from the GaN band gap. The position of the surface Fermi level corresponds to zero volts in the spectra, so we find that the Fermi level is located near the conduction band minimum of the observed gap. It has been reported that the surface Fermi level is shifted from a midgap position towards conduction band edge by 1.5 eV after as-grown GaN films are exposed to air [16], and that result is consistent with our observations for our UHV-oxidized surfaces.

Another important observation from Fig. 4(a) is the presence of nonzero conductance throughout the band gap region, as seen between 0 and –3 V in the spectrum. Such nonzero conductance can arise either from surface states inside the band gap or from the presence of free electrons in the conduction band. The latter mechanism is the "dopant-induced" component of the tunnel current investigated previously [10,11]. The spectra observed on these oxidized GaN surfaces are quite invariant with respect to surface location, displaying similar features (for the midgap conductance in particular) both on the rough and smooth regions of the surface. For this reason, we associate the midgap conductance with a dopant-induced component, i.e. arising from the presence of free electrons in the conduction band. However, we believe that this presence of free electrons in the conduction band is *not* an intrinsic property of oxidized GaN surfaces, since otherwise a much larger midgap conductance would be expected [10,11]. Rather, during the STS experiments, the semiconductor bands are bent downwards because of the negative voltage applied to the sample relative to the probe tip. This downwards band bending leads to the electron accumulation in the conduction band for our n-type GaN samples. Thus, the important conclusion based on the appearance of the “dopant-induced” component of the tunneling current is that this oxidized surface has only a low number of surface states, less than about 0.01 ML, such that the Fermi level is not strongly pinned at the surface and its position can be varied by the applied sample-tip voltage in the STS experiments.

In short, nearly flat band conditions have been deduced from spectroscopy measurements. The valence band maximum is found to be about 3.0 eV below the Fermi level, which is consistent with photoelectron spectroscopy results on n-type Ga-polar GaN surfaces which are cleaned using ammonia-based chemical vapor cleaning [17]. The observation of near flat band condition, along with the appearance of “dopant-induced” component of the tunneling current, indicates a low density of surface states inside the GaN band gap.

Additional data relating to the tunneling characteristics is displayed in Fig. 4(b), where the separation dependence of the tunneling current, $0.5\, d\ln(I)/ds$, is shown. This quantity is equal to k in the expression for the s-dependence of the tunnel current, $\exp(-2\,?\,s)$, i.e. under the assumption that any s-dependence of k can be neglected. For an ideal tunnel junction, without any tip-induced band bending or other complicating effects, k would have a value given by $\sqrt{2m\bar{f}}/\hbar$ where $\bar{f}$ is the average work function of tip and sample, with $k = 1.0\ \text{Å}^{-1}$ for $\bar{f} = 4\ \text{eV}$. Two sets of data in Fig. 4(b) (shown by solid lines and dashed lines respectively) correspond to the spectra of Fig. 4(a). As seen in Fig. 4(b), we obtain values for k somewhat greater than $1.0\ \text{Å}^{-1}$ for negative voltages around –2 V, but for positive voltages the observed k values are much less than expected. These k values can be interpreted by detailed simulations of the tunneling current, of the type discussed elsewhere [10,11,18]. In brief, we interpret the enhanced k values at negative voltage as arising from the dopant-induced component of the current; moving the tip towards the surfaces affects the tip-induced band bending in such a way so as to increase this component in the current. For the reduced k values at positive voltages (and negative voltage near 0 V), we believe that transport of the carriers in the semiconductor is somewhat limited, since the carriers for these voltages are confined to midgap states localized at the surface. Any limitation in transport in the semiconductor will produce a decrease in k, arising from voltage drops (spreading resistance) associated with this transport limitation [19].

IV. First-Principles Theory

First-principles total energy calculations were performed to acquire insight into atomic structures that could be produced by interaction of oxygen with the GaN(0001) surface. As in earlier work for clean GaN surfaces [14], calculations of surface formation energies were performed within the pseudopotential density functional theory. In the present work the plane wave cutoff energy is 60 Ry, and a 4×4×1 **k**-point sampling of the Brillouin zone is employed. The Ga 3d states are included in the valence band. The structures considered have 2×2 symmetry.

Previous theoretical investigations of GaN(0001):O were restricted to structures having one monolayer of O or less [20-22]. In the present investigations we have also considered the possibility of more O-rich structures. The most O-rich surface structures possible are those which would exist in equilibrium with Ga_2O_3 precipitates. We therefore calculate chemical-potential dependent formation energies, and focus on the O-rich limit defined by the onset of precipitation of bulk Ga_2O_3. Our studies show that in such conditions it is possible to form stable two-dimensional phases having ~2 monolayers of O.

The relative stability of surface structures depends on the chemical potentials of the atomic constituents [14,23,24]. We employ the condition that the system is in equilibrium with bulk GaN. In other words we assume that $\mu_{Ga} + \mu_N = E_{bulk}(GaN)$. This allows us to eliminate the chemical potential of N as a variable. The chemical potential of O is bounded from above by the formation of Ga_2O_3. Specifically, for any given Ga chemical potential, the chemical potential of oxygen must be such that the $2\mu_{Ga} + 3\mu_O \leq E_{bulk}(Ga_2O_3)$. One may then determine the lowest energy surface for any pair of values of μ_{Ga} and μ_O. A similar approach is discussed in Ref. [24].

The results of the total energy calculations are summarized in Fig. 5. In this diagram there are three regions corresponding to stable surface phases having oxygen coverages of 0.25, 1.25 and 2 monolayers of oxygen. The O adatom model, studied previously by Zywietz et al. [21], has an oxygen coverage of 0.25 monolayers. The two structures with 1.25 and 2 ML O are discussed in more detail below. These O-rich structures could co-exist with Ga_2O_3 precipitates.

Of the structures considered, the one having a Ga adatom on top of an O-Ga-O trilayer emerges as the lowest in energy for a large region of the phase space. A schematic model of this structure, which contains two monolayers of oxygen, is shown in Fig. 5. We will refer to this structure as the trilayer + adatom model. The stacking sequence of the O-Ga-O trilayer is A-B-C, and the Ga adatoms are then located in position A. The threefold coordinated Ga adatoms are located 1.49 Å above the O layer, and the Ga atoms in the central layer are sixfold coordinated. The question of whether or not the 2× array of protrusions seen by STM in disordered regions of the surface can be accounted for by such Ga adatoms requires additional work to answer.

The band structure for the trilayer + adatom model, as calculated in the local density approximation (LDA), is shown in Fig. 6. An interesting feature of this structure is that the Ga dangling bond orbitals are each occupied by two electrons. Nevertheless, these states are located in energy close to the top of the bulk GaN valence band (within ~0.1 eV). In the LDA the bulk energy gap of GaN is about 1.9 eV, instead of the experimental value of 3.4 eV. The energy gap obtained for the trilayer + adatom structure is also close to 1.9 eV, and there are no surface states present that would pin the Fermi level in mid-gap.

It may seem unusual to find stability for a structure with a doubly occupied cation dangling bond, because this is not the usual case for surfaces of standard III-Vs such as GaAs [25]. The present situation, however, is somewhat different. In the paradigmatic case the Ga atoms adopt an sp^2 coordination, have an empty p_z orbital, and are bonded to three As atoms. In the present case the Ga atoms are p^3 coordinated, have a doubly occupied dangling bond orbital with a significant amount of s-character, and are bonded to three *oxygen* neighbors. We note also that a similar structure was found to be energetically favorable for oxygen-rich GaN($10\bar{1}0$) surfaces [24].

The remaining low energy structure appearing in the phase diagram is obtained by adding a Ga-O bilayer to the ideal surface, and replacing one of the subsurface N atoms by an O atom in order to provide electrons to fill the O lone pair orbitals. This structure contains 1.25 monolayers of O, and is shown schematically in Fig. 5. As seen in Fig. 5 this structure is preferred in somewhat more Ga-rich and less O-rich conditions. The Ga-Ga bonds have length 2.55 Å and the top layer of oxygen is 0.70 Å above the Ga layer. A structure similar to this, but with only 1.0 ML of oxygen, was studied by Elsner *et al.* [20].

In order to account for the $3\sqrt{3}\times 3\sqrt{3}-R30^\circ$ symmetry it is necessary to rearrange the adatoms in the 2×2 trilayer + adatom structure. The most straightforward way to do this is to construct a $3\sqrt{3}\times 3\sqrt{3}-R30^\circ$ cell consisting of the O-Ga-O trilayer decorated by 7 Ga adatoms. Each Ga adatom is bonded to three O atoms in the top layer of the trilayer. There are then 6 oxygen rest-atoms in each cell. The ratio of Ga adatoms to O rest-atoms is 7/6 in this structure, compared to 1/1 in the 2×2 version of the structure. In this way the $3\sqrt{3}\times 3\sqrt{3}-R30^\circ$ structure comes very close to satisfying electron counting:

there are just 0.25 electrons per cell that would occupy a conduction band resonance. We note also that strain relaxation in the oxide layer could produce a nearly incommensurate type of surface structure as suggested by the LEED intensities discussed in Section III. Further work, both experimental and theoretical, is needed to test these types of models.

V. Summary

Ga-polar GaN films were oxidized in situ at both room temperature and elevated temperatures. These surfaces were studied by STM, STS and other surface analysis tools. For GaN films oxidized at elevated temperatures, two distinct surface phases were observed, one of which is relatively smooth and the other of which is rougher. Tunneling spectra obtained from both phases were similar, displaying a band gap of size close to that of bulk GaN (3.4 eV) and with the surface Fermi level located near to the conduction band edge.

Our observation of a surface Fermi level position near the conduction band edge corresponds to nearly *flat band* conditions in our samples (since they are n-type). Thus, from this observation and the existence of “dopant-induced” component of the tunneling current, we find that the surface structures formed by oxidation of GaN surface, at elevated temperatures, do *not* have states lying within the GaN band gap that act to constrain or “pin” the Fermi level. Specifically, this observation implies that any normally empty states of the oxide overlayer (i.e. conduction band states, or acceptor states) must have energy above the GaN conduction band edge. First-principles total energy calculations of surface formation energies demonstrate that it is possible to form this type of semiconducting surface structure, having oxygen coverage of about 2 ML.

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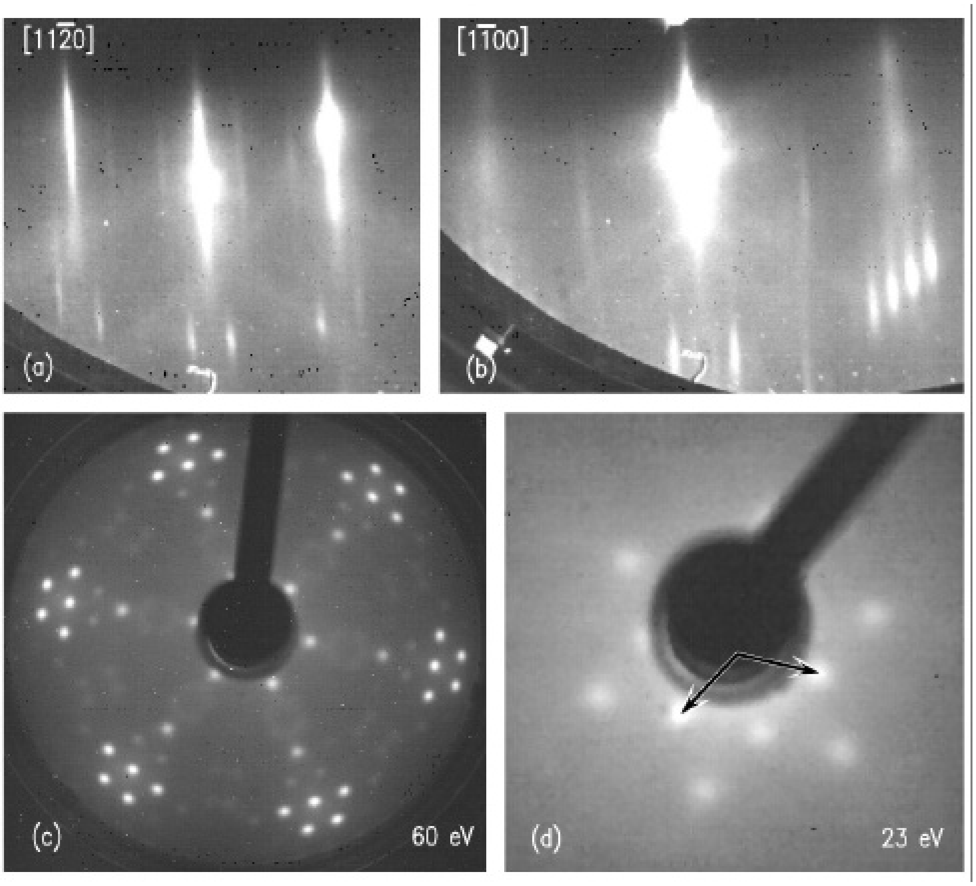

Figure 1. RHEED and LEED pattern of GaN surfaces oxidized at 550ºC. (a) RHEED pattern along $[11\bar{2}0]$ direction. (b) RHEED pattern along $[1\bar{1}00]$ direction. (c) LEED pattern at 60 eV. (d) LEED pattern at 23 eV. Denoting the reciprocal lattice vector of the GaN (0001) surface by a^*, then the distance from the center to the outer 6 spots is $a^*/3$ and the distance from the center to the inner 6 spots is $a^*/(3\sqrt{3})$. Two of these latter reciprocal lattice vectors for the surface reconstruction are shown.

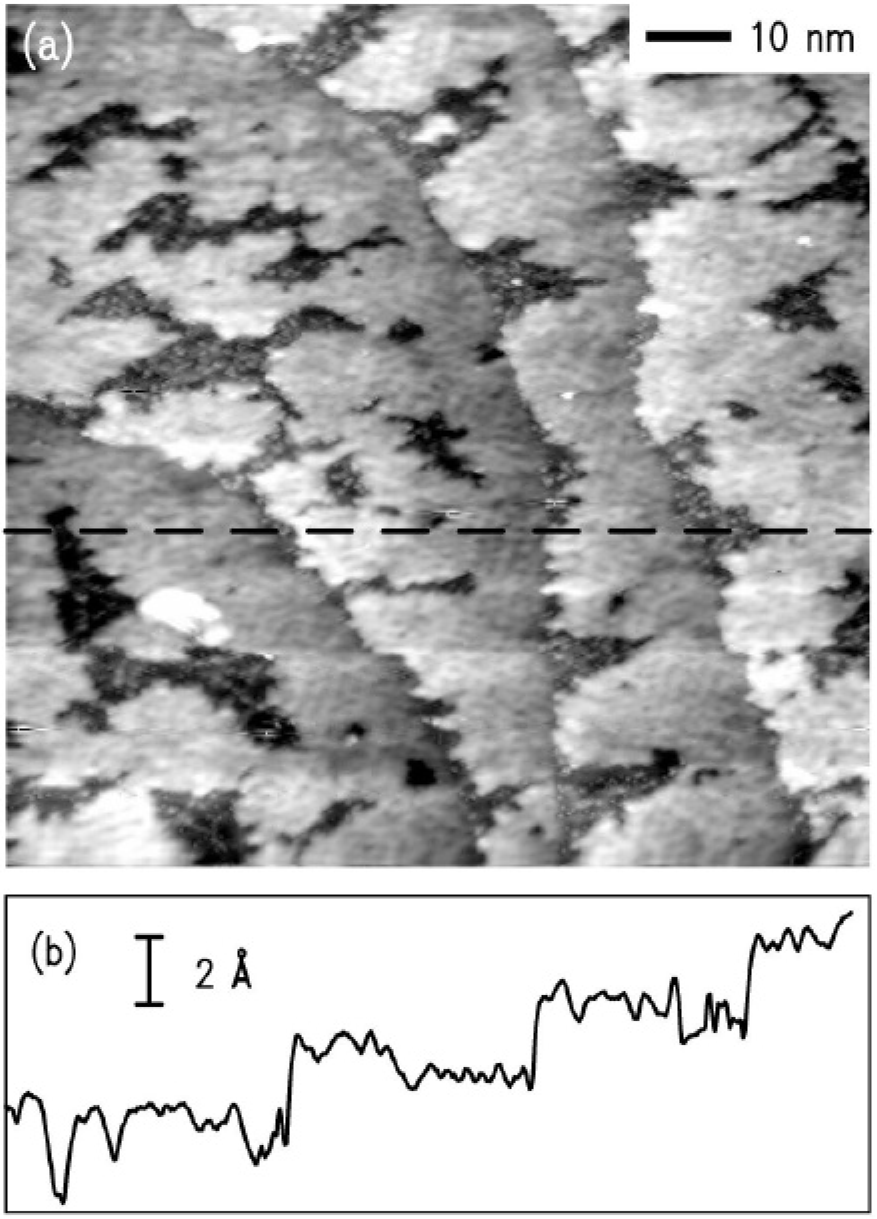

Figure 2. (a) a STM image of a GaN surface oxidized at 550ºC, acquired at +2 V. The image is displayed with a gray scale of 7.4 Å. Patches showing relatively rough morphology (appearing darker) decorate the relatively smooth ordered terraces. A horizontal black dashed line indicates the position where a line cut is performed, as shown in (b). The step height between two smooth ordered terraces is found to be 2.6 Å. The smooth regions are higher than the relatively rough ones by 1.0 Å.

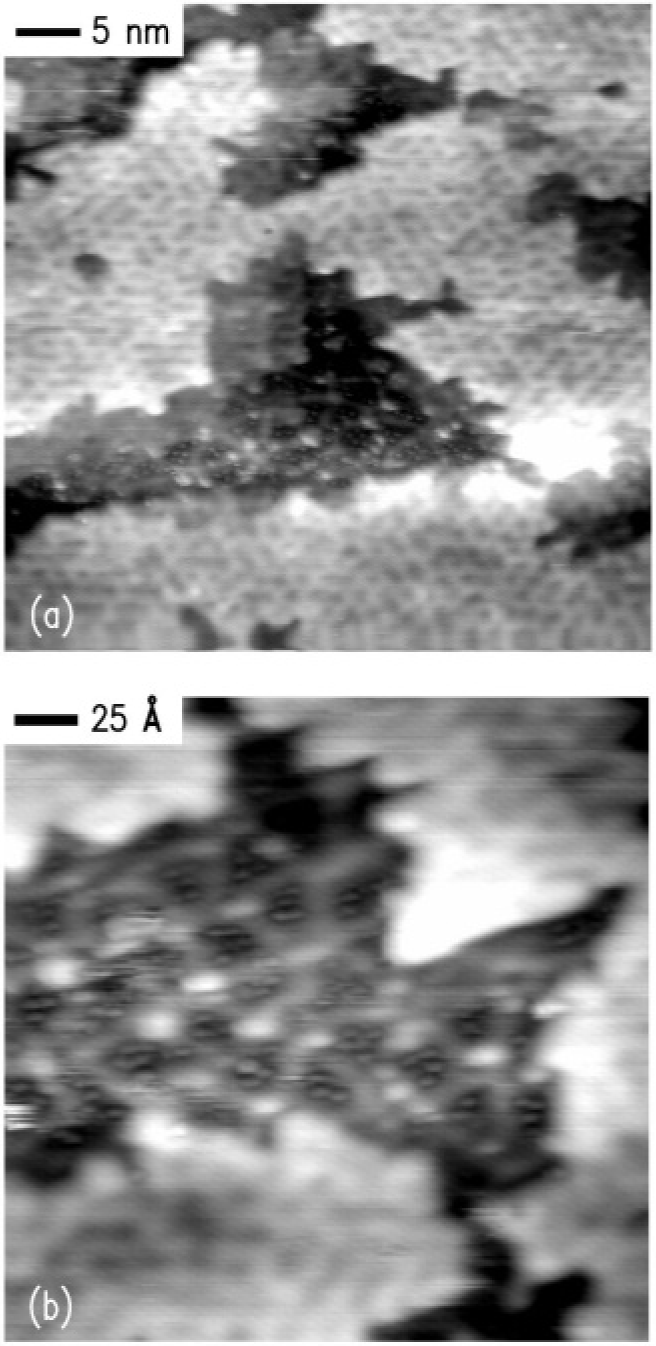

Figure 3. STM images of GaN films oxidized at 550ºC, acquired at a sample voltage of +2 V. Images (a) and (b) are displayed with a gray scale of 6.1 and 4.1 Å, respectively. Both images reveal a relatively smooth ordered phase that appears brighter, as seen most clearly in (a), and a relatively rough phase that appears darker, as seen most clearly in (b). [In image (a) some blurring of the step edges occurs, presumably because of convolution with the STM probe tip, but this effect does not affect the images further from the step edges].

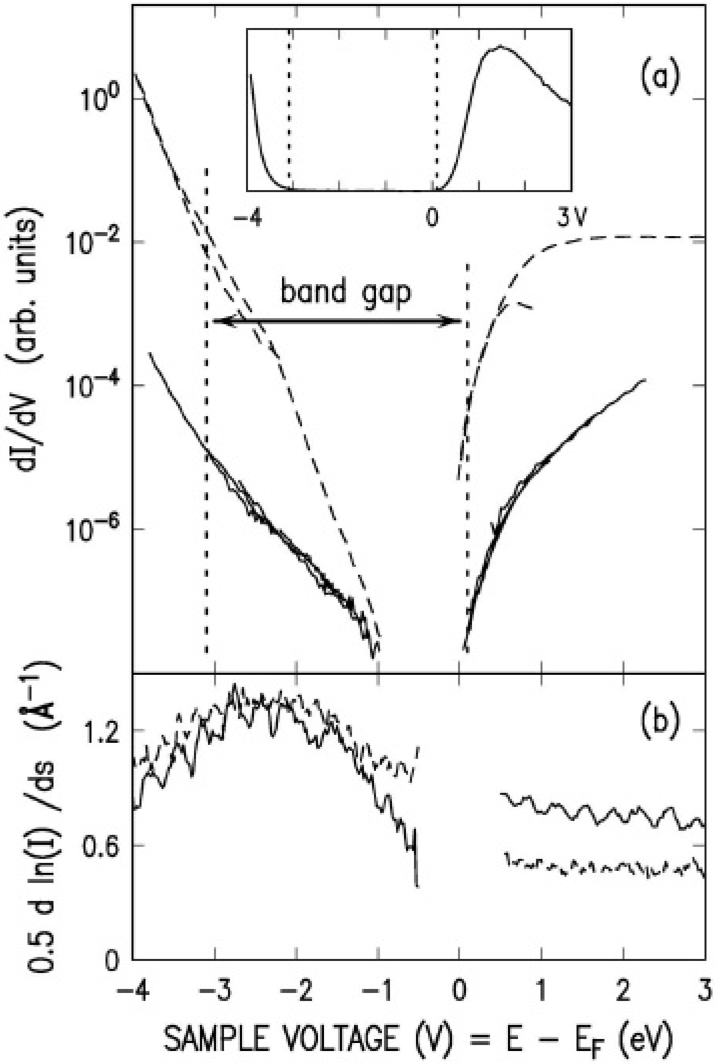

Figure 4. (a) Two sets of tunneling spectra obtained from GaN surfaces oxidized at 550°C. Each set is composed of a series of individual measurements, made with different tip-sample separation, and they are normalized to the same separation and overlaid on each other. One set is shifted from the other by three orders of magnitude, for ease of viewing. The inset shows the raw data (not normalized to constant separation) for one conductance curve, on a linear scale. (b) Separation dependence of the tunneling current, $0.5\, d \ln(I) / ds$, acquired from the same surfaces as for the spectra of (a).

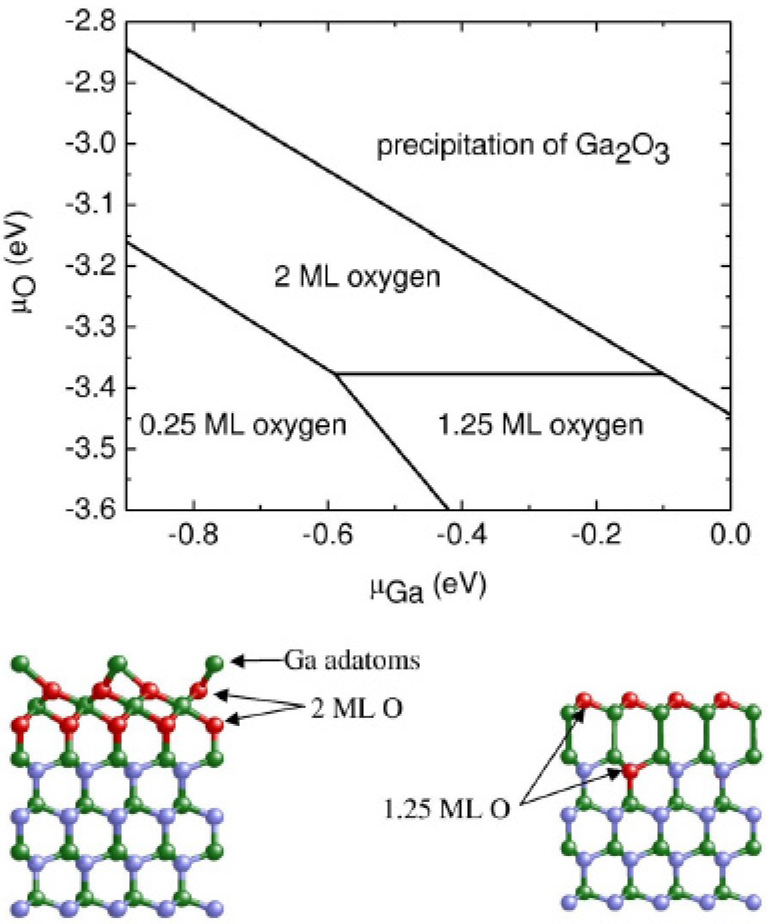

Figure 5. (color online) A two-dimensional phase diagram is shown. It indicates the most stable structures as a function of the Ga and O chemical potentials. The region labeled 2 ML oxygen corresponds to the trilayer + adatom model shown in the inset. The region labeled 1.25 ML oxygen corresponds to the O-terminated structure shown in the inset. These two surfaces could co-exist with Ga_2O_3 precipitates in the O-rich limit. The zero of oxygen chemical potential corresponds to the energy/atom of molecular oxygen (O_2). The zero of the Ga chemical potential corresponds to the energy/atom of bulk Ga.

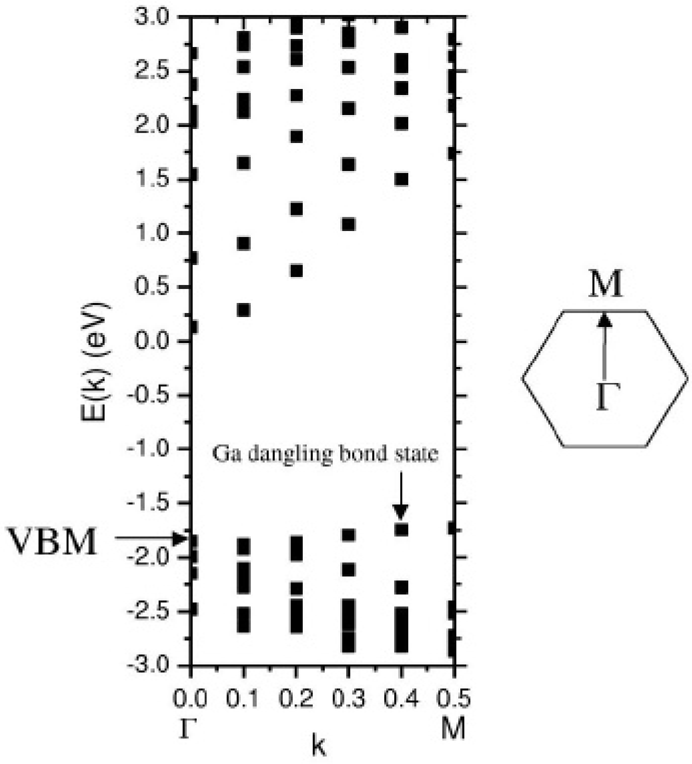

Figure 6. The band structure for the trilayer + adatom model along the G-M direction of the 2×2 surface Brillouin zone as calculated using the local-density-approximation. The calculated surface band gap is similar to the band gap of bulk GaN obtained in the LDA. If the difference between the LDA band structure and the true band structure is primarily a rigid upward shift of the unoccupied states relative to the occupied states, then there will be no deep states in the gap that could pin the Fermi level. Occupied surface states near the valence band maximum are derived from the Ga adatom dangling bonds.