

Reconstructions of GaN(0001) and (000 $\bar{1}$) surfaces: Ga-rich metallic structures

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Reconstructions of GaN(0001) and (000 $\bar{1}$) surfaces are studied by scanning tunneling microscopy and spectroscopy, by electron diffraction, by Auger electron spectroscopy, and using first-principles theory. Attention is focused on Ga-rich reconstructions for each surface, which are found to have a metallic character involving significant overlap between Ga valence electrons. The electron counting rule is thus violated for these surfaces, but they nonetheless form minimum energy structures. © 1998 American Vacuum Society. [S0734-211X(98)05404-3]

I. INTRODUCTION

Much effort in the past five years or so has been devoted to the study of gallium nitride, since its relatively large band gap (3.4 eV) makes it ideal for both optical applications in the blue-to-ultraviolet spectral range and in high power/high temperature electronic applications. Surface science studies of this material are just beginning, with recent reports of surface reconstructions for both cubic (zinc blende) and hexagonal (wurtzite) material.¹⁻⁹ A common theme regarding the growth of these surfaces (in the absence of hydrogen) is that stable growth occurs under *metal-rich* or *near-metal-rich* conditions, suggesting that GaN surfaces are stabilized by Ga atoms.⁵⁻¹³ This behavior can be viewed as arising from the small size of nitrogen compared to gallium, so that reconstructions on the GaN surface are possible which involve purely Ga layers with Ga-Ga separations small enough to produce highly dispersive metallic bands, thereby producing low total energies (a similar situation has been reported recently for Sb-rich GaSb surfaces¹⁴). Such metallic surfaces violate the simple electron-counting rule,¹⁵ but of course this rule is only meant to give a rough guide to the existence of minimum energy structures, and the highly dispersive metallic bands discussed here provide an alternative means of lowering the energy of a system.

In this article we discuss details of the structural and electronic properties of two reconstructions for wurtzite GaN: the 1×1 structure of the GaN(000 $\bar{1}$) surface (or N face), and a pseudo-1×1 structure, denoted by “1×1,” of the GaN(0001) surface (or Ga face). On the basis of scanning

tunneling microscopy (STM) measurements and first-principles theory, the former reconstruction has recently been shown to consist of a single monolayer of Ga bonded to the outermost N atoms of the N-terminated bilayer on the GaN(000 $\bar{1}$) face.⁶ Not surprisingly, this structure, pictured in Fig. 1(a), is found to be metallic; theoretical and experimental evidence for this metallicity is presented in Sec. III A, including scanning tunneling spectroscopy (STS) measurements. This 1×1 arrangement of the GaN(000 $\bar{1}$) surface is *not* the most Ga-rich structure possible on this surface—adding additional Ga adatoms produces a 3×3 arrangement [shown in Fig. 1(b)] and also 6×6 and *c*(6×12) arrangements.

The second structure discussed in this work, the “1×1” arrangement of GaN(0001), is less well understood than the GaN(000 $\bar{1}$)1×1. Experimental evidence will be presented in Sec. III B based on STM, reflection high energy electron diffraction (RHEED), low energy electron diffraction (LEED), and Auger electron spectroscopy (AES) that this surface contains at least 2 monolayers (ML) (1 ML=1.14×10¹⁵ atoms/cm²) of Ga residing on top of a Ga-terminated bilayer of the GaN(0001) surface. These Ga adlayers are found to have a structure well characterized by a discommensuration-fluid phase, similar to that observed on Au(111) and Pt(111).¹⁶⁻¹⁸ Model calculations confirm that an incommensurate structure of Ga, containing about 7×7 unit cells of Ga in a 6×6 region of the GaN lattice, is energetically quite reasonable, although a structural model based on first-principles calculations has not yet been obtained. This “1×1” structure of GaN(0001) is the most Ga-rich structure found on this surface, and it is highly metallic, as

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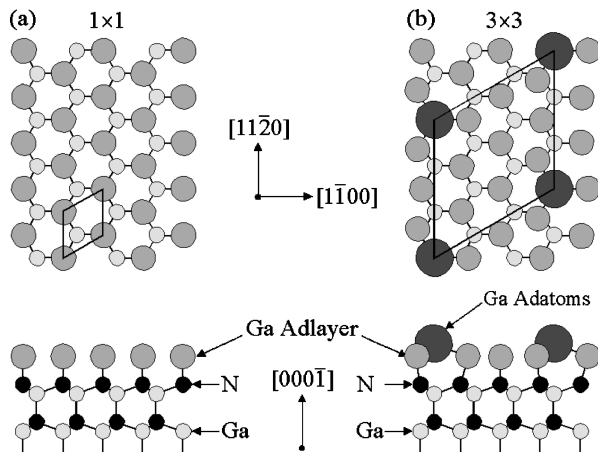


FIG. 1. Model structures determined for the (a) 1×1 Ga adlayer structure and (b) 3×3 adatom-on-adlayer structure of GaN(000 $\bar{1}$). The Ga adlayer is under tensile stress since the Ga atoms are stretched further apart compared to their spacing in bulk Ga (3.19 Å compared ~ 2.7 Å). For the 3×3 structure, the adlayer atoms are able to get closer together by moving in the in-plane (lateral) direction away from the Ga adatoms by 0.51 Å, thus relieving the stress. All other lateral or vertical displacements of the adlayer atoms are less than 0.1 Å.

revealed by STS. Various other reconstructions containing less Ga have also been observed, and will be discussed in more detail elsewhere.¹⁹

II. EXPERIMENTAL DETAILS

The studies of GaN surfaces presented here are performed using a combination molecular beam epitaxy (MBE)/surface analysis system. Base pressures of both the MBE growth chamber and the analysis chamber are in the 10^{-11} Torr range. GaN films are grown using a standard Knudsen cell for the Ga and a rf plasma source to activate the N_2 (both built by SVT Associates). *In situ* surface analysis capabilities include RHEED, LEED, AES, and STM. GaN surfaces prepared in the MBE chamber are transferred under ultrahigh vacuum (UHV) conditions directly into the adjoining analysis chamber for investigation.

We have developed procedures for preparing both the GaN(0001) and GaN(000 $\bar{1}$) faces of wurtzite GaN. Details of the growth of these two structurally inequivalent faces as well as the preparation of the individual reconstructions are discussed elsewhere.⁶⁻⁹ Briefly, the (000 $\bar{1}$) face is grown by nucleating the GaN directly on a solvent-cleaned and plasma-nitrided sapphire substrate. The 1×1 is then prepared by annealing the as-grown film at 800 °C, which removes excess Ga atoms. The (0001) face is grown by performing homoepitaxy on a metalorganic chemical vapor deposition (MOCVD)-grown GaN/sapphire substrate where the substrate is briefly nitrided prior to the homoepitaxial growth. The “ 1×1 ” is typically observed after termination of the homoepitaxy under Ga-rich conditions. The “ 1×1 ” can also be prepared by annealing the (0001) face at 750 °C, which removes Ga atoms, and subsequently redepositing ~ 2 ML of Ga, followed by a quick anneal to 700 °C.

III. RESULTS AND DISCUSSION

A. GaN(000 $\bar{1}$) 1×1 surface

The structure of the GaN(000 $\bar{1}$) 1×1 reconstruction is shown in Fig. 1(a). As discussed elsewhere, first-principles total energy calculations have been performed for this structure, along with calculations for a variety of other models for surfaces having either (0001) or (000 $\bar{1}$) polarity.⁶ The calculations are performed with the Ga 3*d* electrons included as valence electrons, and with a plane wave cutoff of 60 Ry. This approach has been employed in studies of the GaN(10 $\bar{1}$ 0) surface,¹ the *c*-plane surfaces of AlN,² and for surfaces of cubic GaN.³ The GaN(000 $\bar{1}$) 1×1 Ga adlayer model is the only 1×1 structure, of either polarity, which we have found that can account for a stable 1×1 symmetry structure in equilibrium conditions.⁶ A similar result has been found for the *c*-plane AlN surfaces.²

The relative stability of this 1×1 adlayer structure arises in part from the strong Ga–Ga interaction within the adlayer itself. To see this, consider the following hypothetical reaction. Starting from a GaN(000 $\bar{1}$) 1×1 N-terminated bilayer and a bulk Ga reservoir, form the 1×1 Ga adlayer by removing atoms from the Ga reservoir and forming bonds with the N atoms on the GaN surface. The energy required to remove the Ga from the reservoir, thereby creating free Ga atoms, is the experimental cohesive energy of Ga (2.8 eV/atom). The energy released by forming the Ga–N bond is the bond strength of the Ga–N bond, 2.2 eV/atom. If these were the only two bonding mechanisms involved in the reaction, the reaction would be endothermic by 0.6 eV/atom. What is still missing from the analysis is the bonding within the Ga adlayer itself. The energy reduction due to the bonding of the Ga within the adlayer may be determined by a direct calculation of the formation energy of a free-standing hexagonal monolayer with a lattice constant of 3.19 Å. This calculation gives a formation energy of 1.0 eV/atom relative to bulk Ga, and so the cohesive energy of the monolayer is $-2.8+1.0 = -1.8$ eV/atom. Thus the net reduction in energy in the formation of the Ga adlayer on GaN(000 $\bar{1}$) is -1.2 eV/atom. The key point to be made here is that the bonding of the Ga within the adlayer is as important to the stability of the structure as the formation of the Ga–N bond itself. We also note that this estimate of the energy difference between the N-terminated bilayer and the Ga adlayer (1.2 eV/ 1×1) is almost identical to that determined by our direct calculation reported earlier.⁶ Now a similar analysis may be performed for the GaAs($\bar{1}\bar{1}\bar{1}$) surface. However, in that case the Ga–Ga separation within an adlayer is much larger (4.0 Å). For such a Ga–Ga separation, calculations show that the cohesive energy of the adlayer is only -0.8 eV/atom. Since the Ga–As bond strength is 1.6 eV, the total reaction energy is $2.8-0.8-1.6=0.4$ eV/atom, and so the reaction is endothermic. It is therefore clear that the reduced Ga–Ga separation possible on the surfaces of GaN plays an important role in establishing the stability of Ga adlayer structures. A similar situation arises for the GaN(001) surface.³

The surface electronic structure has been calculated for

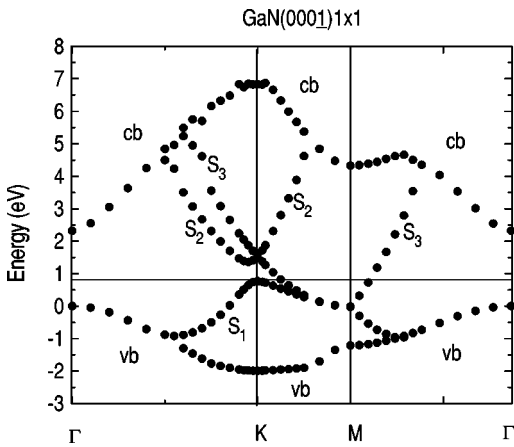


FIG. 2. Band structure for the GaN(000 $\bar{1}$)1 \times 1 Ga adlayer based on local density functional calculations. Energies are plotted relative to the VBM. The Fermi level is located 0.75 eV above the VBM. The plot shows the valence and conduction band edges and three surface states: S_1 , S_2 , and S_3 . The computed bulk band gap of GaN is less than the experimental value (3.4 eV).

the GaN(000 $\bar{1}$)1 \times 1 Ga adlayer model and is shown in Fig. 2. This system is metallic, and the Fermi energy is located about 0.75 eV above the valence band maximum (VBM). There exist three highly dispersive surface states inside the band gap. These states are derived from the three p -state orbitals of the Ga adlayer atoms. The band labeled S_1 is fully occupied and has a predominantly p_z character with respect to the Ga atom. A remaining one-quarter electron per cell occupies the bottom of the S_3 band, which exhibits a p_x, p_y, p_z character with respect to the Ga adlayer atom. The S_2 band exhibits a minimum located about 0.6 eV above the Fermi level near the K point of the Brillouin zone. Such a minimum in $E(\mathbf{k})$ gives a step function contribution to the density of states, and it is therefore possible that the onset of tunneling for a bias voltage larger than 0.6 V could give rise to structure in the tunneling I - V spectrum near this energy.

Experimental evidence for the metallicity of the GaN(000 $\bar{1}$)1 \times 1 surface has been obtained from STS measurements. The STM probe tip is positioned over a well-ordered region of the 1 \times 1 surface, and then the tip-sample separation is held fixed while the tip-sample voltage (V) is varied and the tunnel current (I) is measured. Results are shown in Figs. 3(a)-3(f), where three representative spectra acquired using three different probe tips are displayed. The I - V curves are shown on the left with the derived $(dI/dV)/(I/V)$ (normalized conductance) curves shown on the right. As is evident from the data, the three spectra are significantly different from each other. This largely represents differences between probe tips, none of which were well characterized for the purpose of spectroscopy.²⁰ However, the three spectra do have one very important feature in common, namely, that they all have a minimum in the normalized conductance at zero voltage which is very nearly equal to unity (as indicated in Fig. 3 by dashed lines). Such a feature is a defining characteristic of a metallic surface.²¹ For a semiconducting surface, this minimum in the normal-

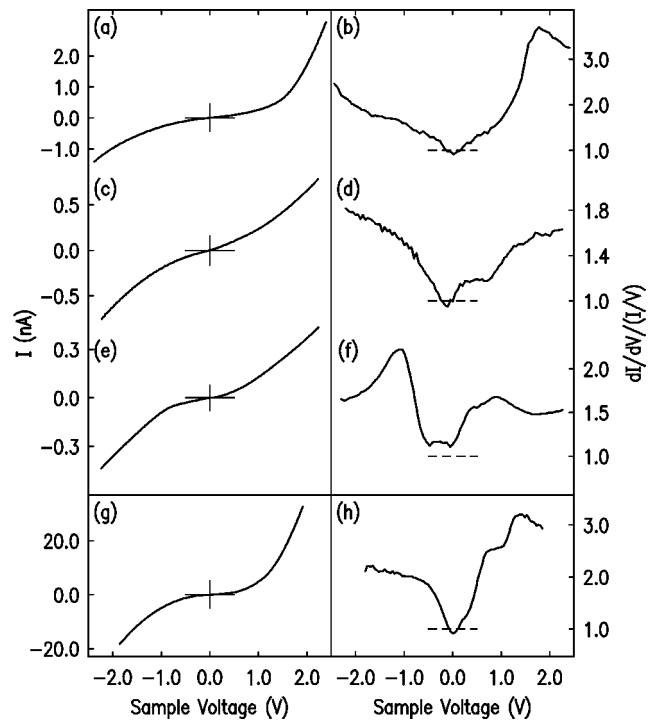


FIG. 3. Averaged tunneling spectroscopy results from three separate experiments (three different tips) on the GaN(000 $\bar{1}$)1 \times 1 surface (a)-(f) and a single experiment on the GaN(0001) "1 \times 1" surface (g) and (h). I - V curves are shown on the left with the corresponding normalized conductance curves shown on the right. Crossmarks represent the origins for the I - V curves, while dashed lines indicate where the normalized conductance=1.

ized conductance will be near zero. Thus, despite the variation in probe tips, the STS measurements clearly show that the 1 \times 1 surface is metallic. In addition, we find that this 1 \times 1 surface can be routinely imaged at tip-sample biases as low as 0.1 eV, also indicating its metallic character.

B. GaN(0001) "1 \times 1" surface

We now turn to a discussion of the most Ga-rich reconstruction of the GaN(0001) surface, prepared as described in Sec. II. The diffraction patterns of this Ga-rich surface show mainly 1 \times 1 streaks (RHEED) or spots (LEED), with sidebands in RHEED or satellite spots in LEED as described below. Hence we refer to this structure as "1 \times 1," using the quotation marks to indicate that the symmetry is not truly 1 \times 1. For this surface, the RHEED pattern at the growth temperature shows only 1 \times 1 streaks, as illustrated in Fig. 4(a). However, as the surface is cooled down to <350 $^{\circ}$ C, distinct sidebands appear on the high wave vector sides of the first-order streaks along the [1120] azimuth, as shown in Fig. 4(b). Depending on the Ga coverage, the spacing of the sidebands from the first-order streaks at room temperature is either 0.16 ± 0.01 ($\approx 1/6$) or 0.08 ± 0.01 ($\approx 1/12$) of the 1 \times spacing $k_1 = 2.28 \text{ \AA}^{-1}$, as illustrated by the two LEED patterns shown in Figs. 4(c) and 4(d). For lack of better terminology, we refer to these structures as "1 + $\frac{1}{6}$ " and "1 + $\frac{1}{12}$," respectively; the precise difference between these structures is not well understood at present. As shown in Fig.

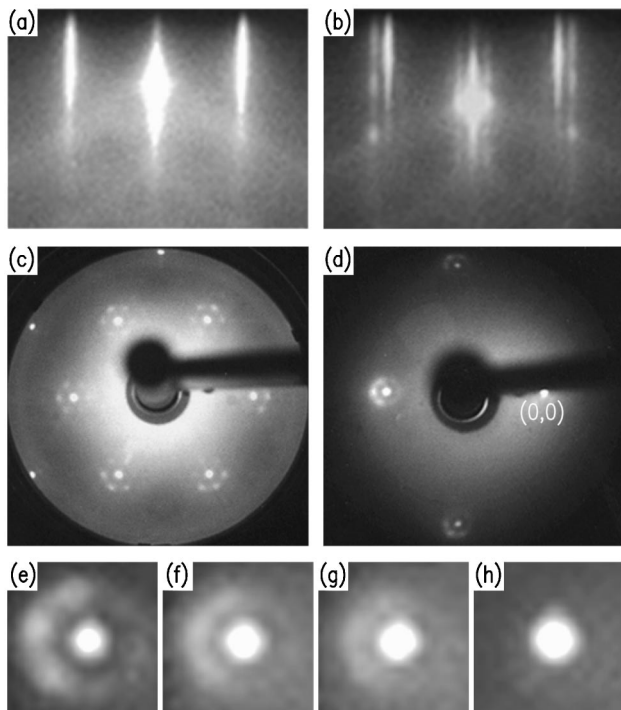


Fig. 4. 1×1 RHEED pattern for GaN(0001) (a) during growth, and (b) after cooling to below 350°C , where it converts to a $1 + \frac{1}{6}$ pattern. The $1 + \frac{1}{6}$ LEED pattern ($E_{\text{inc}} = 100 \text{ eV}$) is shown in (c). For most “ 1×1 ” surfaces (see the text), a $1 + \frac{1}{12}$ pattern is observed below 200°C , as shown in (d) ($E_{\text{inc}} = 40 \text{ eV}$). LEED in the vicinity of the (0, 1) spot ($E_{\text{inc}} = 40 \text{ eV}$) at various temperatures: (e) room temperature– 100°C , (f) 100 – 150°C , (g) 150 – 200°C , and (h) above 350°C .

4(c), the $1 + \frac{1}{6}$ structure can exist down to room temperature for a narrow range of Ga coverage (just above that needed to form the 6×4 , described elsewhere^{8,9}), but for all higher coverages, the $1 + \frac{1}{6}$ converts to $1 + \frac{1}{12}$ as the temperature is reduced to about 200°C .

The temperature dependence of the “ 1×1 ” surface is illustrated in Figs. 4(e)–4(h), focusing on the vicinity of the integral order (0, 1) spot. Between room temperature and about 100°C , as seen in Fig. 4(e), a modulated ring of intensity with radius $0.08k_1$ is observed around the (0, 1) spot with modulation at 60° intervals. This ring has greater intensity on the high wave vector side of the spot. Similar asymmetric, modulated ring patterns have been seen for Pt(111) and Au(111).¹⁶ As the temperature is increased to about 150°C , the ring modulation decreases slightly [Fig. 4(f)]. As the surface temperature increases further to around 200°C , the ring modulation decreases further [Fig. 4(g)]. It is also seen that the radius of the ring appears to have decreased slightly to about $0.07k_1$. As the temperature is raised past 200°C , the pattern converts to $1 + \frac{1}{6}$ (although not observed in this particular LEED experiment, the conversion from $1 + \frac{1}{12}$ to $1 + \frac{1}{6}$ in this temperature range has been observed consistently in RHEED experiments). Above 350°C , one sees only the (0, 1) integral order LEED spot [Fig. 4(h)]. This sequence of phase transitions is reversible. Thus we find that the ring modulation decreases with increasing temperature. At the same time, the ring radius decreases slightly from

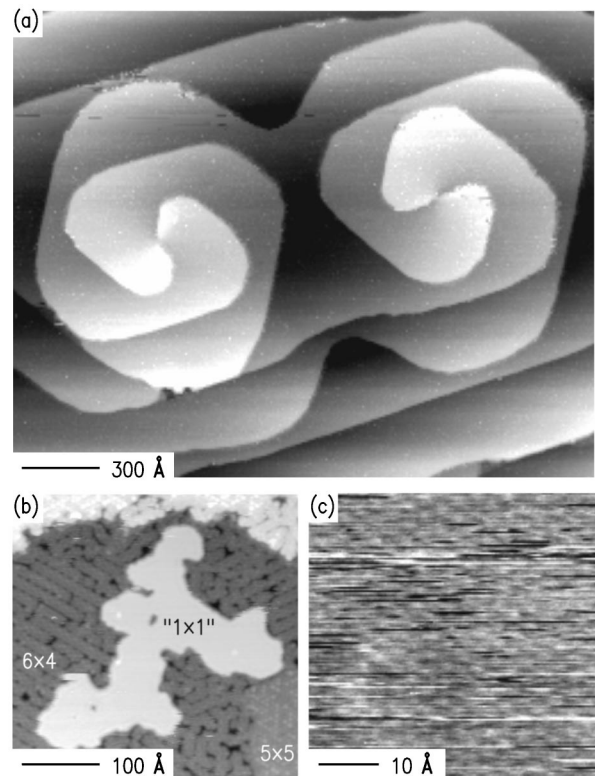


Fig. 5. STM images of (a) GaN(0001) “ 1×1 ” surface showing spiral growth, (b) (0001) surface with mixed 5×5 , 6×4 , and “ 1×1 ” reconstructions (“ 1×1 ” island height = 2.1 \AA), and (c) “ 1×1 ” reconstruction showing atomic resolution [lateral spacing = GaN lattice constant (3.19 \AA) to within $< 1\%$]. The tunnel parameters are (a) -2.0 V at 0.1 nA , (b) -2.5 V at 0.075 nA , and (c) -0.25 V at 0.1 nA . The atomic steps seen in (a) are single bilayer high (2.59 \AA) (line-by-line background subtraction has been applied to permit viewing of many terraces). The gray scale ranges are (b) 4.0 and (c) 0.27 \AA , respectively.

$0.08k_1$ to $0.07k_1$ with increasing temperature until about 200°C , at which point it increases by a discrete amount to $0.16k_1$. Identical diffraction patterns having the same temperature dependence have been reproducibly observed on numerous “ 1×1 ” surfaces prepared on grown films with various morphologies. Thus, the “ 1×1 ” patterns do *not* correlate with or depend on faceting or periodic step arrangements on the surface; instead, they suggest an incommensurate surface structure. Moreover, the modulated ring structure and its temperature dependence indicate that this incommensurate structure possesses a considerably dynamic, fluidlike character, even at room temperature. Thus, we infer that the “ 1×1 ” surface at room temperature is best characterized by a discommensuration-fluid phase, similar to that seen for Au(111) and Pt(111) at elevated temperatures ($T > 0.64T_m$ for Au and $T > 0.65T_m$ for Pt).¹⁷ We note that since the melting point of bulk Ga (29.8°C) is very near room temperature, such a structural phase for a Ga-rich surface is most reasonable. Furthermore, we also infer that, as temperature increases, the discommensuration-fluid phase converts to a disordered, fluid phase.

STM images acquired at room temperature for the GaN(0001) “ 1×1 ” surface are shown in Fig. 5. Since we

have not observed any difference between the $1+\frac{1}{6}$ and $1+\frac{1}{12}$ surfaces in the STM studies, we shall refer to them collectively as “ 1×1 ” here. Generally the “ 1×1 ” surface appears featureless (i.e., no corrugation) in the images, although small-scale images with a sharp tip do reveal atomic corrugation. Figure 5(a) shows a large-scale view of a surface which was imaged directly following Ga-rich growth without any further surface processing. It shows a typical spiral growth morphology where two dislocations, each with a screw component of their Burgers vector of $c[0001]$, are seen intersecting the surface and producing atomic steps. This surface was completely covered by the “ 1×1 ” arrangement and had a relatively high Ga coverage (at least 2 ML based on the Auger spectroscopy measurements discussed below). In contrast, the surface of Fig. 5(b) had a Ga coverage of only ~ 1 ML and was prepared by the annealing, redeposition, and reannealing procedure. For this lower Ga coverage, the surface contains islands of “ 1×1 ” surrounded by areas of 5×5 and 6×4 reconstruction. The precise structures of these latter two reconstructions are not known at present, although the 5×5 arrangement is thought to contain a combination of Ga adatoms, N adatoms, and possibly Ga vacancies.¹⁹ Evidence suggesting a relatively high Ga coverage for the “ 1×1 ” reconstruction is also contained within the STM image of Fig. 5(b). The height of the “ 1×1 ” island above the surrounding 6×4 and 5×5 regions is 2.1 \AA . Electronic effects can of course influence this height, but typically by only a few tenths of \AA . The 5×5 and 6×4 regions are believed to contain adatoms with height (from theory) of 1.7 \AA above the Ga atoms in the outermost GaN bilayer. Thus, we would estimate a thickness of the “ 1×1 ” Ga layer of 3.8 \AA , corresponding to 1.8 ML. While this estimate is somewhat crude, it does suggest that the “ 1×1 ” reconstruction contains around 2 ML of Ga atoms.

For either the $1+\frac{1}{6}$ or $1+\frac{1}{12}$ surfaces, high resolution images reveal atomic corrugation, as seen in Fig. 5(c). However, the signal to noise ratio for these images is typically $\sim 4\times$ smaller than that found on the GaN(0001) 1×1 surface. Such a weak atomic corrugation is consistent with a highly metallic surface. Indeed, STS measurements reveal the surface metallicity, with a minimum in the normalized conductance at zero voltage very close to 1, as shown in Figs. 3(g) and 3(h). Careful measurements of the lateral period of the atomic corrugation, using tips which were calibrated on the GaN(000 $\bar{1}$) 3×3 reconstruction,²² reveal that the period is identical to a $1\times$ spacing (3.19 \AA) to within $<1\%$.

Auger spectroscopy measurements with an incident electron energy of 3 keV have been performed on the (0001) “ 1×1 ” surfaces, as well as on all other (0001) and (000 $\bar{1}$) reconstructions which we have studied, as a routine probe of Ga coverage. Experimental measurements for the (000 $\bar{1}$) surfaces are plotted in Fig. 6(a), and those for the (0001) surfaces are plotted in Fig. 6(b). For almost all of the surface reconstructions, the ratio of intensities of the Ga (1055 eV) to N (379 eV) lines is in the range 0.6–0.9, with the exception being the “ 1×1 ” surface where this ratio is signifi-

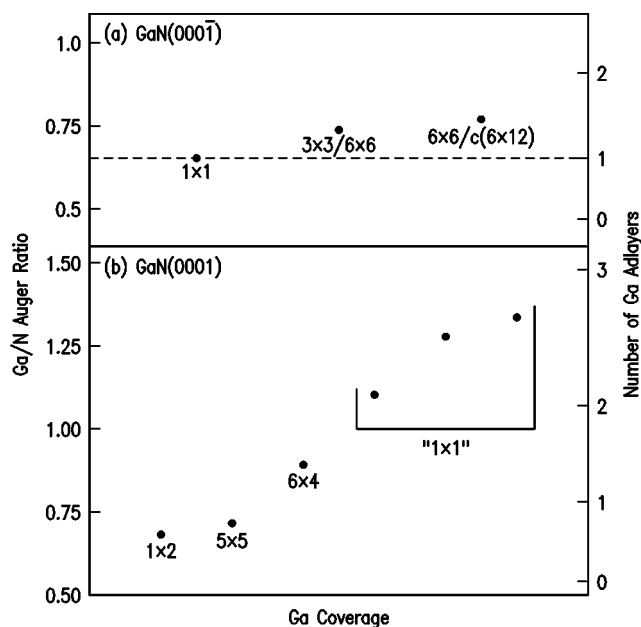


FIG. 6. Plots of Ga/N Auger intensity ratios for (a) GaN(000 $\bar{1}$) reconstructions and (b) GaN(0001) reconstructions. The scales on the right are based on model calculations and represent the number of Ga monolayers sitting on top of the bulk-terminated bilayer for each polarity. Dashed line in (a) shows fit of 1×1 Auger ratio to 1 Ga adlayer on right-hand scale.

cantly higher (1.1–1.4). To interpret these measured intensity ratios, we perform model computations by summing intensity contributions from individual atomic layers over a sufficient number of layers extending into the surface to obtain convergence of the Ga/N ratio. We utilize Auger sensitivity factors of 0.12 for Ga and 0.33 for N (taken from Ref. 23). We choose electron escape depths of 14.0 and 9.7 \AA for the 1055 and 379 eV electrons, respectively. These escape depths are chosen such that the Ga/N ratio for the GaN(000 $\bar{1}$) 1×1 reconstruction [indicated by the dashed line in Fig. 6(a)] corresponds to exactly one Ga adlayer located at a height of 1.99 \AA above the nitrogen atoms of the last GaN bilayer, which is the known structure of this surface.⁶ Using these values, Ga/N Auger intensity ratios are then computed for surfaces of either polarity having 0, 1, 2, and 3 layers of Ga sitting on top of the bulk-terminated bilayers. In the model computations for the (0001) surface, we assume a first additional layer of Ga 2.5 \AA above the Ga-terminated bilayer, and successive Ga monolayers at 2.1 \AA intervals, with all values based on theoretical results. For the GaN(000 $\bar{1}$) surface, successive Ga monolayers after the first monolayer are also spaced at 2.1 \AA intervals. The results of the model computations are given by the scales on the right-hand side of Fig. 6. As evidence for the success of the modeling, we note from Fig. 6(a) that the mixed $6\times 6/c(6\times 12)$ surface corresponds to a Ga coverage of 1.45 ML while the measured Ga coverage for the $c(6\times 12)$ was (after correction for sticking coefficient) 1.44 ± 0.02 ML, as reported previously⁷ [this surface, while containing a few isolated patches of 6×6 , was predominantly $c(6\times 12)$, as observed by sweeping the RHEED beam laterally across the surface]. Thus the

agreement between the Auger data and the model calculations is quite good.²⁴

Consider now the results for the (0001) surface, shown in Fig. 6(b). As discussed elsewhere,⁹ the ordered 5×5 is formed by depositing $1/2$ ML Ga onto the annealed 1×2 surface and then briefly annealing that surface. Since the 1×2 is known to be disordered,¹⁹ it is not unreasonable that the Ga/N Auger ratios of these two are similar. The 6×4 surface is similarly produced by depositing $1/2$ ML Ga onto the 5×5 and briefly annealing that surface. Repeating this deposition and annealing cycle one or two more times results in a “ 1×1 ” surface. As seen from Fig. 6(b), this sequence of Ga deposition steps is in good agreement with the increase in Ga coverage from one reconstruction to the next, as deduced from the computed scale on the right-hand side. Based on these Auger results, it is quite clear that the (0001) “ 1×1 ” surfaces contain 2–3 additional monolayers of Ga above the Ga-terminated bilayer.

With all of the above experimental data on the “ 1×1 ” structure, let us now discuss possible structural models. For the GaN(0001) surface, the most stable structure we have theoretically obtained in the Ga-rich limit is the 2×2 Ga adatom model. In this model, the Ga adatom resides in the $T4$ site. Any proposed model for the high Ga coverage “ 1×1 ” phase should be more stable than the 2×2 $T4$ Ga adatom model in Ga-rich conditions. All of the true 1×1 structures that we have examined up to now, and which contain one additional monolayer or bilayer of Ga, are unstable with respect to this 2×2 adatom structure. This result is, of course, consistent with the apparent incommensurate, fluid-like nature of the “ 1×1 ” inferred from the diffraction analysis. Calculations performed for free-standing Ga monolayers or bilayers indicate that there is a driving force for a reduction in the in-plane Ga–Ga separation. Given this, and the experimental information discussed already, we consider a laterally contracted bilayer model for the “ 1×1 ” consisting of a Ga bilayer where the in-plane separation of the Ga atoms in the layers is contracted to a smaller value. We note that such a laterally contracted structure is not unreasonable for this system, since the GaN lattice constant of 3.19 Å is substantially greater than the typical Ga–Ga spacing of 2.7 Å in bulk Ga, so that a 1×1 arrangement of Ga is under considerable tensile strain.⁶ We have performed total energy calculations for a free-standing Ga bilayer and have determined the formation energy $\Omega(a) = E(a) - 2\mu_{\text{Ga(bulk)}}$ as a function of a , the hexagonal lattice constant. The minimum in $\Omega(a)$ occurs for $a = 2.7$ Å where Ω is equal to 0.46 eV/pair. Thus a free-standing hexagonal Ga bilayer is less stable than bulk Ga by about 0.23 eV/atom. In the contraction from $a = 3.19$ to $a = 2.7$ Å, the energy/pair of the bilayer is reduced by about $\Delta\Omega = 0.68$ eV/pair.

We may employ these results to estimate the surface energy for a structure consisting of a 7×7 bilayer in approximate registry with a 6×6 GaN(0001) substrate. Such a structure would contain the equivalent of 2.7 Ga layers above the Ga-terminated bilayer, in agreement with that estimated from the Auger analysis. The estimated change in surface energy,

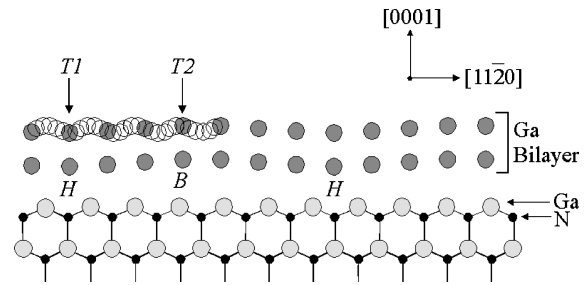


Fig. 7. Side view of possible structural model for the “ 1×1 ” surface (at a given instant in time) consisting of 2.7 ML of Ga sitting on top of the Ga-terminated bilayer. The open circles represent the various possible positions of first-layer Ga atoms plotted with respect to each of several GaN unit cells, and illustrate the time-averaged height of the first-layer Ga atoms and thus the 1×1 contour which the STM tip will follow. At a given instant in time, however, this incommensurate structure will manifest itself in diffraction as satellites surrounding the integral order peaks.

relative to a 1×1 bilayer structure, may be broken down into three terms. The first term, E_1 , is the cost of adding $13 = 7 \times 7 - 6 \times 6$ additional pairs of Ga atoms to each 6×6 unit cell. The second term, E_2 , is the energy benefit of the reduced lattice constant of the bilayer. The third term, E_3 , is the energy cost of the imperfect registration of the incommensurate overlayer with the GaN(0001) substrate. E_1 is approximately $13 \times \Omega(a = 2.7) = 6.0$ eV. E_2 is approximately $36 \times \Delta\Omega = -24.5$ eV. From calculations for bilayers having different registrations with respect to the substrate, we estimate E_3 to be approximately 3.2 eV. The net effect is a reduction in surface energy of 0.43 eV/ 1×1 in the Ga-rich limit. This is close to the energy difference between the 2×2 adatom model and the best 1×1 bilayer model, 0.39 eV/ 1×1 in the Ga-rich limit. Thus it is plausible that such a laterally contracted bilayer structure could be stable under very Ga-rich conditions.

A schematic view of our proposed structure for the “ 1×1 ” surface is shown in Fig. 7. We consider the Ga bilayer (shown in dark gray circles), with uniform lateral spacing of the atoms of about 2.7 Å. In Fig. 7, the first layer atoms are positioned directly atop the second layer atoms. However, the energy difference between the top and hollow site registrations computed for free-standing Ga bilayers is very small. We expect that such a layer would be slightly buckled on the GaN surface since Ga atoms residing above hollow sites of the GaN surface (e.g., $T4$ sites above fourth layer nitrogen atoms), indicated by H in Fig. 7, would be slightly displaced towards the GaN, while Ga atoms residing in between such hollow sites, such as at position B in Fig. 7, would be slightly displaced away from the GaN. Such a model at this point is analogous to that used for the Au(111) surface,¹⁷ except that we further assume, based on the diffraction results, that the structure is dynamic, with the Ga atoms moving around rapidly (this would probably imply the presence of vacancies or domain boundaries in the structure to allow the Ga bilayer space for such movement). The model shown in Fig. 7 is thus a picture of the structure at a given instant in time. Let us then consider what the appearance of this dynamic structure would be in STM images. A

surprising aspect of the STM results is the observation of precisely $1\times$ periodicity with $a=3.19\text{ \AA}$, which appears to be inconsistent with the $1+\frac{1}{6}$ or $1+\frac{1}{12}$ inverse periods seen in diffraction. However, these STM measurements may be reconciled by taking into account the dynamic, fluidlike nature of the Ga bilayer. Consider a sharp STM tip as it scans over this structure. We assume that the time scale for the Ga bilayer motion is much shorter than the time the tip spends at each sampling point in the image. Hence, during the time that the tip is sitting over a given point on the surface, it senses a time average of the vertical positions of the first-layer Ga atoms as they move beneath the tip. This time average will include all possible translations of the incommensurate structure, and is illustrated conveniently by plotting the various possible positions of top Ga bilayer atoms with respect to each of several unit cells of the GaN lattice. These positions are indicated in Fig. 7 by the open circles. Thus, with the tip at position $T1$ over the hollow site H , the time-averaged height is relatively small (i.e., a corrugation minimum). Alternatively, with the tip at position $T2$ over an in-between site B , the time-averaged height is relatively large (i.e., a corrugation maximum). Thus, the STM image will appear to have a true 1×1 periodicity, as seen by the resulting contour of circles, arising from the periodicity of the top bilayer of GaN.

The diffraction patterns and their temperature dependence are accounted for in this model by the different orientational relationships for the surface discommensurations. For discussion purposes, we can define the discommensurations in our case as being associated with the B sites in Fig. 7, where the binding site of the Ga adatoms is in between two hollow sites. Below $100\text{ }^\circ\text{C}$, the data indicate that the discommensurations have a preferred spacing, and that they are aligned along particular crystal directions but, for $100\text{--}200\text{ }^\circ\text{C}$, they begin to lose their orientational ordering. Above $200\text{ }^\circ\text{C}$, the system converts into the $1+\frac{1}{6}$ structure, which may indicate a sudden change in the spacing of the discommensurations. Finally, above $350\text{ }^\circ\text{C}$, the system becomes further disordered, and the surface is then characterized by a completely disordered, fluid phase.

IV. CONCLUSIONS

In conclusion, we have investigated the reconstructions which occur on GaN(0001) and (000 $\bar{1}$) surfaces. We emphasize that the energetically stable structures exhibit partially occupied surface states and are in direct violation of the electron counting rule (ECR). The ECR asserts that a semiconductor surface is stable only if all anion dangling bonds are doubly occupied and all cation dangling bonds are empty. It is further assumed that all cation dangling bonds are high in energy (close to the conduction band) and all anion dangling bonds are low in energy (close to the valence band). The calculated band structure shown in Fig. 2 for the GaN(000 $\bar{1}$) 1×1 surface shows that both assumptions are violated: while the Ga adlayer structure consists solely of cations, the occupied surface states ($S1$) are close in energy to the valence band maximum. The small lattice constant

gives rise to strong Ga–Ga bonding even without bringing surface atoms together and forming, e.g., dimers, as commonly observed on other semiconductor surfaces. The strong Ga–Ga bonding thus not only stabilizes the 1×1 structure as discussed above, but it also significantly increases the dispersion of the cation surface states. In fact, the energetically lowest surface states are close to the valence band, and occupying these bands gives rise to energetically stable structures.

We have focused in particular on the 1×1 and “ 1×1 ” structures, respectively, which are both metallic in nature based on both experiment and theory. The “ 1×1 ” structure exhibits satellite peaks in the diffraction patterns below $350\text{ }^\circ\text{C}$, suggesting an incommensurate surface structure. The STM measurements, on the other hand, reveal a lateral atomic periodicity consistent with the surface GaN lattice constant. This apparent discrepancy is resolved by modeling the surface as a dynamic, fluidlike, discommensurate Ga bilayer structure with an increased surface atom density, and where mobile defects enable the motion to occur. Auger spectroscopy measurements reveal that this “ 1×1 ” structure is the most metal-rich structure out of all possible (0001) or (000 $\bar{1}$) structures. Modeling of the Auger Ga/N peak intensity ratios as well as STM measurements of “ 1×1 ” island step heights also suggest a structure consisting of at least 2 ML of Ga on top of the Ga-terminated bilayer.

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