Wurtzite GaN surface structures studied by scanning tunneling microscopy and reflection high energy electron diffraction

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We report studies of the surface reconstructions for both the Ga-face and the N-face of wurtzite GaN films grown using molecular beam epitaxy. N-face reconstructions are primarily adatom-on-adlayer structures which can be formed by room temperature submonolayer Ga deposition. These structures undergo reversible order–disorder phase transitions to 1×1 in the temperature range of 200–300 °C. Ga-face reconstructions, on the other hand, require annealing to high temperatures (600–700 °C) in order to form, and in most cases they are stable at those temperatures. The film polarity is found to be determined by the initial nucleation stage of the film growth. © *1998 American Vacuum Society.* [S0734-2101(98)52903-X]

I. INTRODUCTION

In order to achieve a better understanding of the growth of GaN, it is important to develop a thorough knowledge of the surface structures since growth is fundamentally a surface phenomenon. Although numerous surface studies of wurtzite GaN have been performed, progress in determining the true surface structures has been slow. A few experimental groups reported the inability to produce any surface reconstructions on GaN other than a 1×1.[1–3] On the other hand, a variety of reflection high energy electron diffraction (RHEED) patterns have been observed including: 1×1, 2×1, 2×2, 2×3, 3×2, 3×3, 4×4, and 5×5.[4–9] Using scanning tunneling microscopy (STM), Packard *et al.* observed striations and other defect-line features which they ascribed to N vacancy structures.[10] It should be emphasized that since the wurtzite structure lacks a center of inversion symmetry, there are two structurally inequivalent surfaces. These are referred to as the (0001) or ''Ga-face'' and the $(000\bar{1})$ or ''N-face.'' A film with its outward surface being the Ga-face is said to have ''Ga-polarity,'' and vice versa for ''N-polarity.'' In most of the aforementioned studies, the film polarity was unknown. Two separate studies on the effect of polarity on morphology and crystal structure, one using single-crystal GaN platelets and the other using metal organic chemical vapor deposition (MOCVD)-grown GaN/sapphire films, have indicated that the highest quality films have Ga-polarity.[11,12] Whether this is true for molecular beam epitaxy has yet to be determined. Regardless of the growth method, it is important to examine the surface structures of both faces of wurtzite GaN.

Recently, we determined the reconstructions belonging to the N-face using STM and RHEED.[13] These include 1×1, 3×3, 6×6, and $c(6\times12)$. Our assignment of the polarity was based primarily on comparison of our experimental data with the results of theoretical total energy calculations. Here we report a different set of reconstructions and show that these belong to the Ga-face. In particular, we observe 2×2, 1×2, 5×5, and 6×4 RHEED patterns, in substantial agreement with the previous results mentioned above. We have also on occasion seen 3×2 and 2×3 patterns. In addition, we observe a structure having predominantly 1×1 character, but which we denote as ''1×1'' (with quotation marks) due to the existence of diffraction fringes in the RHEED pattern. This observation is consistent with the theoretical calculations, which do not find an acceptable model for a true 1×1 structure on the Ga-face.[13] Additional support for our polarity assignment of these two qualitatively different, polar faces is provided by polarity-selective wet chemical etching experiments.[14,15]

II. EXPERIMENT

The studies of GaN surfaces presented here are performed using a combination molecular beam epitaxy surface analysis system. Base pressures of both the growth chamber and analysis chamber are in the 10^{-11} Torr range. *In situ* surface analysis capabilities include RHEED, low energy electron diffraction, and scanning tunneling microscopy (STM). All

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of the STM work is done by first preparing a clean surface in the MBE chamber, after which the sample is transferred directly under UHV to the adjoining analysis chamber for study.

To study the reconstructions belonging to the two opposite faces of wurtzite GaN, we have developed procedures for preparation of both film polarities. N-polar films are prepared by nucleating the GaN directly on sapphire using MBE with a rf plasma source. The sapphire substrate is first solvent-cleaned *ex situ* and then loaded into the growth chamber where it is heated to 1000 °C and bombarded with a nitrogen plasma for 30 min. GaN growth begins at 685 °C, after which the substrate temperature is gradually raised to 775 °C for the main part of the film growth. During growth, we use a nitrogen flow rate of about 0.8 sccm and a rf forward power of 550 W. The Ga flux is about 4×10^{14} atoms/cm^2 s. The RHEED pattern becomes a streaky 1×1 after the first few hundred Å's of growth (however, if the growth is too N-rich, a spotty RHEED pattern will develop). Details of the preparation of the individual reconstructions which occur on this face are discussed elsewhere.[13,16]

To grow the Ga-polar surface, we begin with a GaN/sapphire substrate which was grown using MOCVD. The MOCVD GaN substrate is first solvent-cleaned, then loaded into the growth chamber and heated to 775 °C under a nitrogen plasma. This temperature is held constant, and growth commences once the RHEED pattern becomes bright and streaky, which usually takes about 5 min. Nitrogen and gallium fluxes are the same as for growing the N-polar film. We also observe two basic growth regimes for the Ga-face, N-rich, and Ga-rich, similar to the observations of Tarsa *et al.*[17] N-rich growth leads to a spotty RHEED pattern, whereas Ga-rich growth leads to a streaky 1×1 RHEED pattern (we have also occasionally observed weak $5\times$ lines in RHEED during growth, at a growth temperature of 680 °C and under slightly N-rich conditions).

III. RESULTS AND DISCUSSION

This section is divided into two parts. In part A, we discuss STM results for the N-face of GaN, providing examples of two of the most commonly observed reconstructions, the 3×3 and $c(6\times12)$. An interesting demonstration of adatom mobility on this surface will also be shown. In part B, we discuss the RHEED patterns and STM results for the films grown on MOCVD GaN substrates. We will show that these films have Ga-polarity, preserving the polarity of the MOCVD layer, in agreement with prior observations.[5]

A. N-face

Shown in Fig. 1 is a 750 Å×750 Å STM image of a spiral growth front on a freshly prepared GaN surface. Dislocations such as this are fairly common on these films; their areal density is at least 10^8 cm^{-2}. Since the measured step heights at the two spiral growth fronts are each one bilayer, the Burgers vector for this dislocation is $c[000\bar{1}]$ with $c=5.185$ Å. This surface has the $c(6\times12)$ reconstruction. The $c(6\times12)$ reconstruction breaks the threefold symmetry

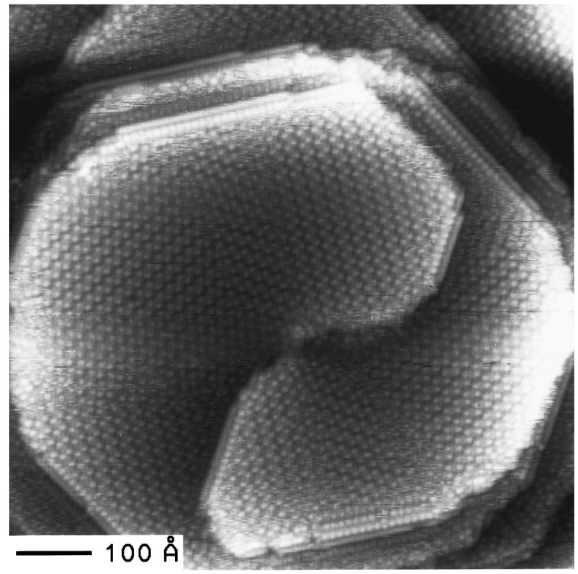

FIG. 1. 750×750 Å STM image of a screw-type dislocation with a Burgers vector of $c[000\bar{1}]$ on the N-face. The reconstruction is $c(6\times12)$, sample bias was 1.0 V, and tunnel current was 0.05 nA. The $c(6\times12)$ row directions correspond to $\langle 1\bar{1}00\rangle$.

of the underlying wurtzite structure, giving a total of six different types of domains, several of which are seen here. One will observe that domains on opposite sides of the dislocation core have their rows aligned along the same crystallographic directions. As the $c(6\times12)$ is disordered above about 200 °C, this effect cannot be directly related to the growth. Rather, this is likely a consequence of local strain in the vicinity of the dislocation which influences the nucleation and growth of $c(6\times12)$ domains as the surface cools.

It is more common to observe large, flat dislocation-free areas on these films. Such an area is shown in Fig. 2 which is a 750 Å×750 Å STM image of the 3×3 reconstruction appearing on three adjoining terraces separated by single bilayer-height steps. Single bilayer-height steps are quite common. However, we have also observed steps with heights of two, three, four, or more bilayers. The 3×3 reconstruction consists of 1/9th monolayer of Ga atoms (or 1 Ga adatom per 3×3 unit cell) sitting on top of an adlayer structure. This adlayer structure itself consists of a monolayer of Ga atoms sitting directly atop the N atoms of the last GaN bilayer. These structures have been determined to be the lowest energy structures based on first-principles total energy calculations.[13] In this image, a few defects are also seen. They may simply be missing Ga adatoms, or they could be impurity atoms. Also seen is a translational domain boundary emanating from the step edge onto the upper left terrace, as marked by the arrow in the image.

In previous work, we have reported the variation of the surface reconstructions with Ga adatom coverage.[13] The coverages for each reconstruction were determined by depositing a known amount of Ga onto the annealed 1×1 surface (Ga adlayer) at very low surface temperatures (60 °C). Even at such low deposition temperatures, the higher order recon-

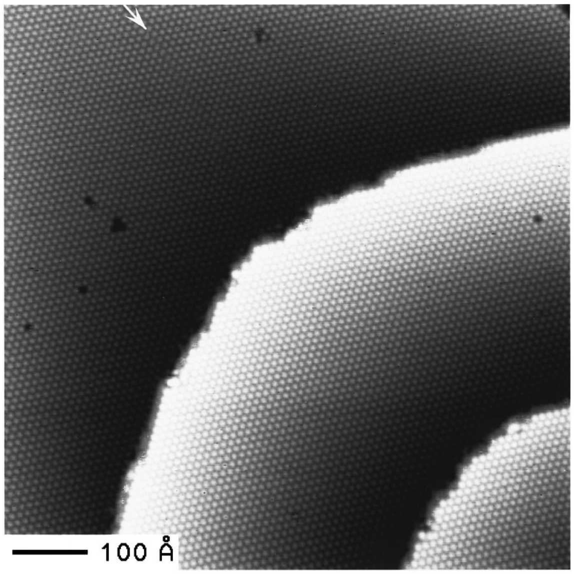

FIG. 2. 750×750 Å STM image of 3×3 reconstruction. Sample bias was 2.0 V, and tunnel current was 0.05 nA. The arrow marks a boundary between domains of the 3×3 which are translationally inequivalent.

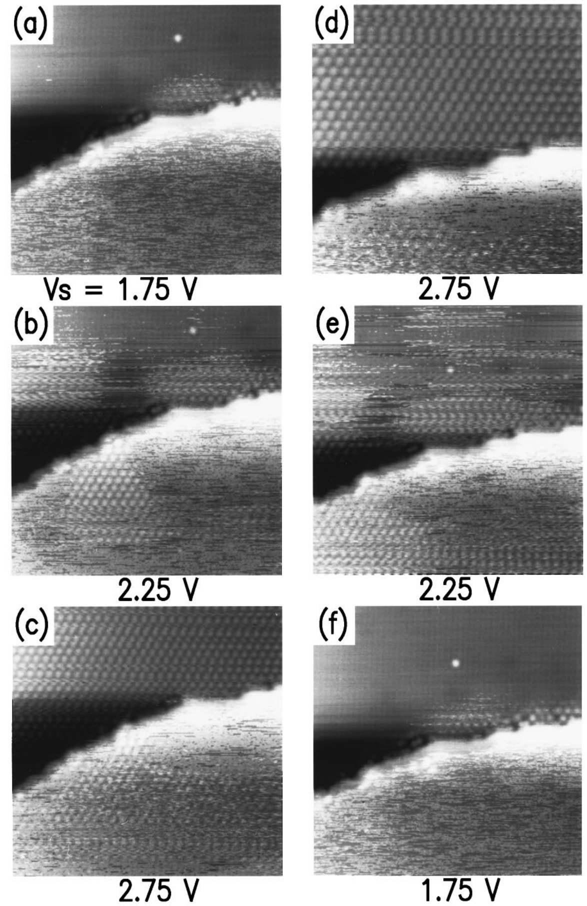

FIG. 3. Sequence of STM images for increasing sample bias (a–c) and decreasing sample bias (d–f). For all images, the tunnel current was 0.05 nA. Two terraces are seen in each image. A line-by-line background subtraction has been performed (average of each line set to zero), so that both terraces are clearly visible.

structions will form. As mentioned above, the 3×3 forms at a coverage of 1/9 ML of Ga adatoms. But if we deposit less than 1/9 ML, there are not enough Ga atoms to form a complete 3×3 over the entire surface. Shown in Fig. 3(a) is a STM image of such a surface in the vicinity of a step edge. The lower terrace (at top of image) has the 1×1 reconstruction, although it is not resolved at this sample bias (1.75 V) The upper terrace (at bottom of image) has a somewhat glitchy, disordered appearance. The glitchiness is a sign that there are extra Ga adatoms diffusing on this terrace. There also appear to be a few stable features on the lower terrace near the step edge.

Increasing the sample bias causes an unusual ordering process to occur. By increasing the sample bias to 2.25 V, as shown in Fig. 3(b), small patches of 3×3 appear on both terraces. By further increasing the bias to 2.75 V, as shown in Fig. 3(c), most of the lower terrace appears to be completely ordered in the 3×3 arrangement. The sequence beginning in Fig. 3(d) shows the reverse process. In Fig. 3(d), the lower terrace shows 3×3 ordering at a sample bias of 2.75 V. After lowering the bias to 2.25 V, as shown in Fig. 3(e), much of the lower terrace appears disordered again. In Fig. 3(f), the bias is reduced back to 1.75 V, where very little 3×3 reconstruction remains. This reversible process was repeated several times with the same results.

We interpret these observations in terms of high Ga adatom mobility on the 1×1 surface and the influence of the STM tip electric field. We have seen in other STM experiments that the edges of 3×3 domains are typically unstable. Ga adatoms at these 3×3 domain edges are easily displaced. In this case, the atoms in the vicinity of the STM tip apparently feel a force due to the tip electric field. At a sufficiently high field strength, the Ga atoms are attracted together and form a localized region of 3×3 reconstruction. At lower fields, the atoms disperse across the surface since there are not enough of them to form a permanently stable domain. This high adatom mobility observed at room temperature is consistent with the reversible order–disorder phase transitions to 1×1 which occur for the higher order reconstructions [3×3, 6×6, and $c(6\times12)$] in the range 200–300 °C.[16]

B. Ga-face

We will now show that the Ga-face is obtained by performing homoepitaxial growth on the MOCVD GaN film. RHEED patterns for this face are displayed in Fig. 4 in order of increasing Ga content from top to bottom. Contrary to a number of published results, we do not observe a strong 2×2 pattern during growth. Iwata *et al.* have suggested that the use of ion-removal magnets is important for obtaining a well-defined 2×2 reconstruction.[6] In any case, we do obtain a 2×2 RHEED pattern by nitriding the surface at the growth temperature. The 2×2 pattern remains as the sample is cooled. This 2×2 has somewhat broad 1/2-order streaks, as shown in Fig. 4(a). It is worth noting that a 2×2 RHEED

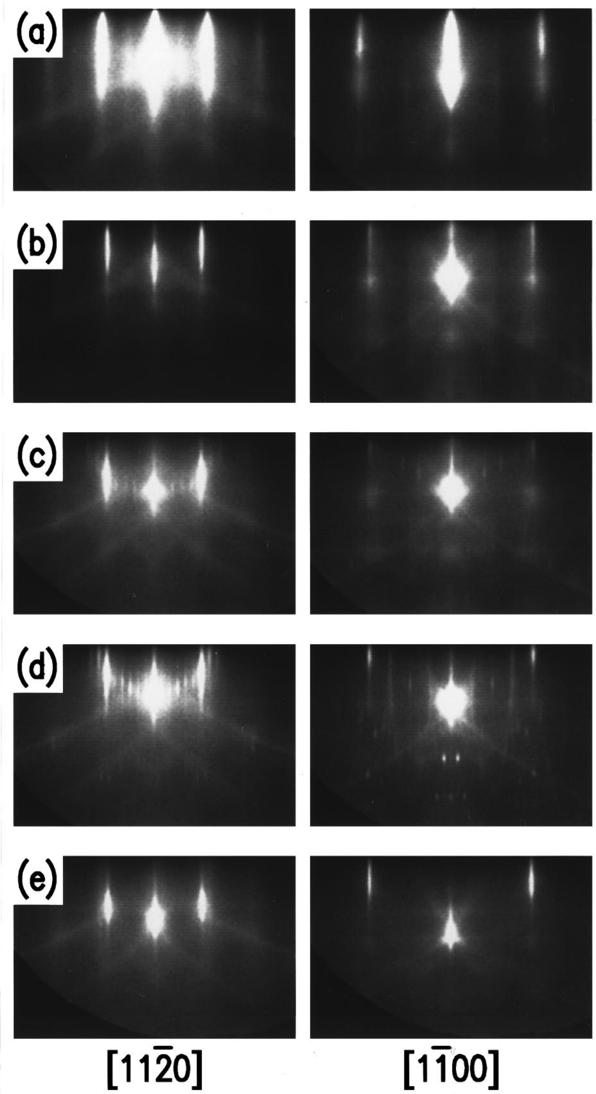

FIG. 4. RHEED patterns for the Ga-face reconstructions: (a) 2×2; (b) 1×2; (c) 5×5; (d) 6×4; and ''1×1.'' Note the addition of diffraction fringes in the case of the ''1×1.''

pattern is never observed on the N-face. This 2×2 pattern by itself is already strong evidence for the Ga-polarity.

If the as-grown film is annealed to 750 °C and then cooled, the RHEED pattern will change to a 1×2, as shown in Fig. 4(b), although the 1/2-order streak is quite weak. If Ga is then deposited onto this surface at temperatures less than a few hundred degrees C, this weak 1/2-order streak will disappear, and no additional streaks will appear (this is quite different from the N-face, where Ga deposition at similar temperatures results in higher order reconstructions such as 3×3 and 6×6). However, subsequent annealing of this surface to 700 °C followed by cooling will result in at least two additional RHEED patterns, the 5×5 and the 6×4, depending on Ga coverage. These are displayed in Fig. 4(c) and Fig. 4(d). Further Ga deposition followed by further annealing ultimately leads to a Ga-rich ''1×1'' surface. This is not a true 1×1 since split-off fringes appear along the

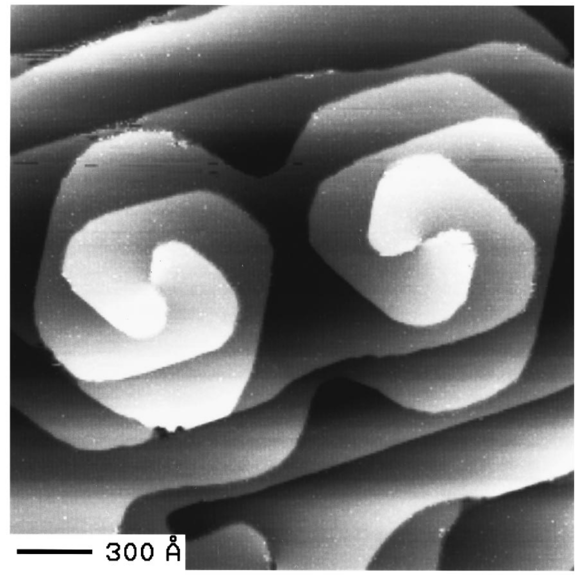

FIG. 5. 2300×2300 Å STM image of two adjacent screw-type dislocations on the Ga-face; the total Burgers vector is $2c[0001]$. No reconstruction is resolved in this image. Sample bias was -2.0 V, and tunnel current was 0.1 nA.

$[11\bar{2}0]$ azimuth as the sample cools, as shown in Fig. 4(e). This structure can also be obtained by terminating the growth under Ga-rich conditions. An atomic model for the ''1×1'' reconstruction will be presented elsewhere.[18] It is likely that it consists of one or more relaxed Ga monolayers on top of the Ga-terminated bilayer.

In Fig. 5 is shown a 2300 Å × 2300 Å STM image of the surface of a Ga-polar film. As on the N-polar films, we find that dislocations are not uncommon; in this case we observe two adjacent screw-type dislocations. One will note that the growth direction of each of the two spirals is counter-clockwise so that the total Burgers vector is $2c[0001]$, opposite to that on the N-face shown in Fig. 1. This surface was prepared in a manner which should result in the ''1×1.'' This structure has been resolved in other STM images. However, STM imaging of the other Ga-face reconstructions has been hampered by an apparent surface conductivity problem. Efforts to solve this problem are currently in progress. Nonetheless, it is very clear that the reconstructions observed on this face cannot belong to the N-face; therefore, they must belong to the Ga-face.

IV. CONCLUSIONS

In conclusion, we have investigated the reconstructions which occur on wurtzite GaN surfaces. We find that the two structurally inequivalent faces, the Ga-face and the N-face, have unique groups of reconstructions. Observation of these reconstructions permits the identification of the film polarity. N-face reconstructions include 1×1, 3×3, 6×6, and $c(6\times12)$. We have also observed a novel field-induced ordering of Ga adatoms into the 3×3 arrangement as a function of the applied electric field. Apparently, Ga atoms can easily diffuse on the N-face.

By performing homoepitaxy on a MOCVD-grown GaN film, we find a set of reconstructions with entirely different symmetries than those on the N-face. Through various nitridation, Ga deposition, and annealing steps on this surface, we have observed 2×2, 1×2, 5×5, and 6×4 RHEED patterns. A ''1×1'' has also been seen which occurs at a very high surface Ga coverage. We surmise that a true 1×1 structure does not exist on the Ga-face, in agreement with theoretical expectations.[13] Finally, since Ga-polar and N-polar films can each be grown in the same system and under nearly identical growth conditions, we deduce that film polarity is determined in the initial nucleation stage of the growth.

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