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Determination of Wurtzite GaN Lattice Polarity Based on Surface Reconstruction

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Abstract

We identify two categories of reconstructions occurring on wurtzite GaN surfaces, the first associated with the N-face, $(000\bar{1})$, and the second associated with the Ga-face, (0001). Not only do these two categories of reconstructions have completely different symmetries, but they also have different temperature dependence. It is thus demonstrated that surface reconstructions can be used to identify lattice polarity. Confirmation of the polarity assignment is provided by polarity-selective wet chemical etching of these surfaces.

The potential applications for blue light emitting devices continue to drive research efforts to understand the growth of GaN. In the fabrication of most nitride-based devices, epitaxial growth occurs on the c-plane of wurtzite GaN. A key characteristic of wurtzite GaN is its polarity. No symmetry operation of the crystal relates the [0001] to the $[000\bar{1}]$ direction, and so the (0001) and $(000\bar{1})$ surfaces are inequivalent. The former surface is known as the Ga-face, and the latter as the N-face. While the atomistic details of surface structure are known to govern growth kinetics, little has been understood, until recently, about the surface structures of wurtzite GaN. Remarkably, a few groups have reported the inability to observe any surface reconstructions at all on wurtzite GaN other than a 1×1.[1,2] At the same time, a number of other groups have reported a variety of reflection high energy electron diffraction (RHEED) patterns, including 1×1, 2×1, 2×2, 2×3, 3×2, 3×3, 4×4, and 5×5.[3-9] However, the polarities of the surfaces which gave these diffraction patterns were unknown.

Recently, we have identified the surface reconstructions which belong to the N-face of wurtzite GaN, which include 1×1, 3×3, 6×6, and c(6×12).[10] In this paper, we summarize those findings and identify, in addition, the surface reconstructions which belong to the Ga-face, showing that these include most of those which had been observed using RHEED and a few additional ones which had not previously been observed. In particular, we find 2×2, 5×5, 6×4, and "1×1" reconstructions, with the latter not being a true 1×1, as discussed in more detail below.[11] Thus, there is no overlap in the symmetries of these two categories of reconstructions. The assignment of the lattice polarity in our studies is based primarily on the results of theoretical total energy calculations.[10] Additional confirmation is provided by performing a polarity-selective chemical etching experiment; the results are in good agreement with those of Seelmann-Eggebert *et al.*[12]

We grow both film polarities in the same molecular beam epitaxy (MBE) chamber using different growth procedures. The reconstructions are determined using RHEED, low energy electron diffraction (LEED), and scanning tunneling microscopy (STM). All of the surface analysis is done *in-situ* on clean MBE-grown surfaces. The etching experiments are performed *ex-situ* by dipping the samples into a 1.8 M NaOH solution for 3 minutes and then rinsing them in distilled water.

The N-face [$(000\bar{1})$ surface] is prepared by nucleating and growing GaN directly on sapphire using MBE with an RF plasma source. The sapphire substrate is first solvent-cleaned *ex-situ* and then loaded into the growth chamber where it is exposed to nitrogen plasma at 1000 °C for 30 minutes. Growth of GaN begins at 685° C, after which the substrate temperature is gradually raised to 775 ° C for the main part of the film growth. The RHEED pattern becomes a streaky 1×1 after the first few hundred Å's of growth. The resulting film surface has a plateau-valley morphology with large, atomically flat terraces. We also occasionally observe growth spirals on this surface.[13]

A schematic phase diagram for the four main surface reconstructions observed for GaN films grown directly on sapphire is shown in Fig. 1(a). Also shown are the corresponding RHEED patterns, as viewed along the $[11\bar{2}0]$ azimuth. The 1×1 has the lowest Ga concentration; it is produced by heating the as-grown film surface to high temperature (~ 800 °C) in order to remove excess Ga adatoms (heating to higher temperatures causes a spotty RHEED pattern to develop, indicating surface roughening). First principles total energy calculations demonstrate that this 1×1 consists of a Ga monolayer (or adlayer) bonded to the uppermost N-terminated bilayer.[10] This adlayer is under tensile stress due to a smaller preferred Ga-Ga bond length compared to the GaN lattice constant. The 3×3, 6×6, and c(6×12) reconstructions are produced by depositing sub-monolayer quantities of Ga onto this 1×1. These additional Ga adatoms reduce the stress in the adlayer, thus forming energetically favorable adatom-on-adlayer structures.[10] These higher order reconstructions, however, only exist below ~ 300° C, as illustrated in Fig. 1. As the temperature is increased, the structures undergo reversible order-disorder phase transitions, and the non-integral RHEED features disappear.[14]

We prepare the Ga-face [(0001) surface] by performing MBE homoepitaxy of GaN on an MOCVD-grown GaN/sapphire substrate. This substrate is used as an atomic-scale template for growing the Ga-face based on the fact that high-quality MOCVD-grown GaN films have been shown to have Ga-polarity.[15,16] The MOCVD substrate is first solvent-cleaned *ex-situ*, then loaded into the growth chamber and heated to 775° C under a nitrogen plasma. Growth commences once the 1×1 RHEED pattern becomes bright. If the growth is allowed to become too N-rich, a spotty RHEED pattern will develop, indicating three-dimensional growth; on the other hand, if Ga-rich conditions are maintained, a smooth 1×1 RHEED pattern will be observed, as also reported by Tarsa *et al.*[17] The resulting film surface is characterized by large, atomically flat terraces and growth spirals.[13]

A schematic phase diagram for the four main surface reconstructions observed for GaN films grown on MOCVD/sapphire substrates is shown in Fig. 1(b). Also shown are the corresponding RHEED patterns, as viewed along the $[11\bar{2}0]$ azimuth. After terminating the growth of the film under Ga-rich conditions and cooling, the 1×1 which is observed during growth converts to a "1×1" at $\sim 350°C$. We refer to this structure as "1×1" (with quotation marks) because of the appearance of satellite lines just outside the integral order lines when viewed along the $[11\bar{2}0]$ azimuth. As determined by our own *in-situ* Auger spectroscopy measurements, this "1×1" surface has the highest Ga/N Auger intensity ratio out of all of the reconstructions we have observed on both the Ga-face and the N-face. Structural models for the "1×1" are currently being explored; the temperature dependence of the satellite features is suggestive of a fluid layer of Ga adatoms on top of the Ga-terminated bilayer.[18]

Several higher order structures can be formed on the Ga-face. First, the "1×1" is annealed to 750°C to remove excess Ga atoms; the RHEED pattern then changes to a 1×2 (not shown in Fig. 1), with a weak 1/2 order streak. If Ga is deposited onto this 1×2 surface at room temperature, the weak 1/2 order streak will disappear, and no fractional order streaks will appear (this behavior is very different from the N-face, where Ga deposition at low temperatures results in the 3×3 and other higher order reconstructions). However, by depositing 1/2 ML Ga, annealing the surface to 700°C, and cooling, the 5×5 reconstruction will be formed; and after depositing an additional 1/2 ML Ga, annealing to 700 °C, and cooling, the 6×4 reconstruction will be formed. Continuation of this deposition and annealing process ultimately results in the Ga-rich "1×1." The 5×5 structure is observed up to 700 °C, at which temperature it disappears. The 6×4, on the other hand, undergoes a reversible phase transition at $\sim 250°C$.

A number of groups have reported 2×2 RHEED patterns during growth.[3-6] While we have not observed a 2×2 during growth, we have obtained a 2×2 by annealing the 5×5 at $\sim 600°C$. We also obtained a 2×2 by nitriding the surface at $\sim 600°C$. It is interesting to note that the best 2×2 patterns have been observed for growth with ECR plasma sources as opposed to RF plasma sources,[4-6] although Hughes *et al.* observed a weak 2×2 during growth using an RF plasma source.[3] They also occasionally observed 2×3, 3×2, 5×5, and 2×1, in agreement with our own observations. We conclude that we have the same polarity in our homoepitaxial growth as Hughes *et al.* and that they have the same polarity as the other groups who also observe 2×2 patterns during growth. First principles total energy calculations indicate that both 2x2 Ga-adatom (T4) and 2x2 N-adatom (H3) structures could be stable within the allowed ranges of the Ga and N chemical potentials.[10] While it is not known which of these two structures corresponds to the experimentally observed RHEED patterns, it is clear that the Ga-face exhibits a 2x2 surface reconstruction.

While the theoretical calculations provide a convincing means of assigning the polarity of the two different faces of wurtzite GaN,[10] an independent confirmation of this assignment is desirable. Chemical etching of nitrides has been studied for a variety of etchants.[19] Recently, a method of distinguishing the polarity of wurtzite GaN films based on their chemical etching behavior in hydroxide solutions has been reported by Seelmann-Eggebert *et al.*[12] They found that films having N-polarity were etched in a solution of KOH while films having Ga-polarity were resistant to etching in the same solution. They established the polarity of their films using hemispherically scanned x-ray photoelectron diffraction (HSXPD). To check these results against our own polarity identification, we have performed a similar study of the etching behavior of the GaN films which were grown by MBE directly on sapphire, which we believe have N-polarity, and those which were grown by MBE on the MOCVD GaN/sapphire substrates, which we believe have Ga-polarity. Figure 2(a) is an atomic force microscopy (AFM) image of a film grown directly on sapphire prior to etching, illustrating the characteristic plateau-valley morphology commonly observed for these films. Fig. 2(b) shows the change in morphology which occurs upon etching in a 1.8 M NaOH solution for three minutes. While a hint of the original morphology remains, the surface is primarily composed of smaller, rounded features; apparently this film is highly reactive with the NaOH solution. Figures 2(c) and 2(d) are a similar pair of AFM images for a homoepitaxial GaN film grown on an MOCVD GaN/sapphire substrate. As can clearly be seen, there is no change in the surface morphology after etching, indicating that this surface is resistant to etching in the NaOH solution. Our etching results are therefore consistent with those of Seelmann-Eggebert *et al.* This consistency confirms our previous polarity assignment.[10]

In addition to being useful for determining polarity, knowledge of surface reconstructions is also important for understanding kinetics of growth. For the N-face, it seems clear that the structure which is present on the surface during MBE growth is quite similar to the 1x1 Ga-adlayer. On the other hand, for the Ga-face the qualitative nature of the structure which is present during growth remains unclear. The existence of a number of higher order reconstructions which are apparently stable at or near the growth temperature makes it important to obtain further clarification of their atomic structure.

In summary, 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 completely different surface reconstructions. Moreover, the temperature dependence of the intensity of the non-integral RHEED features is very different for the two faces. These reconstructions can thus be used as a means of determining the lattice polarity of wurtzite GaN. Our polarity assignment for the two faces has been confirmed by polarity-selective wet chemical etching.

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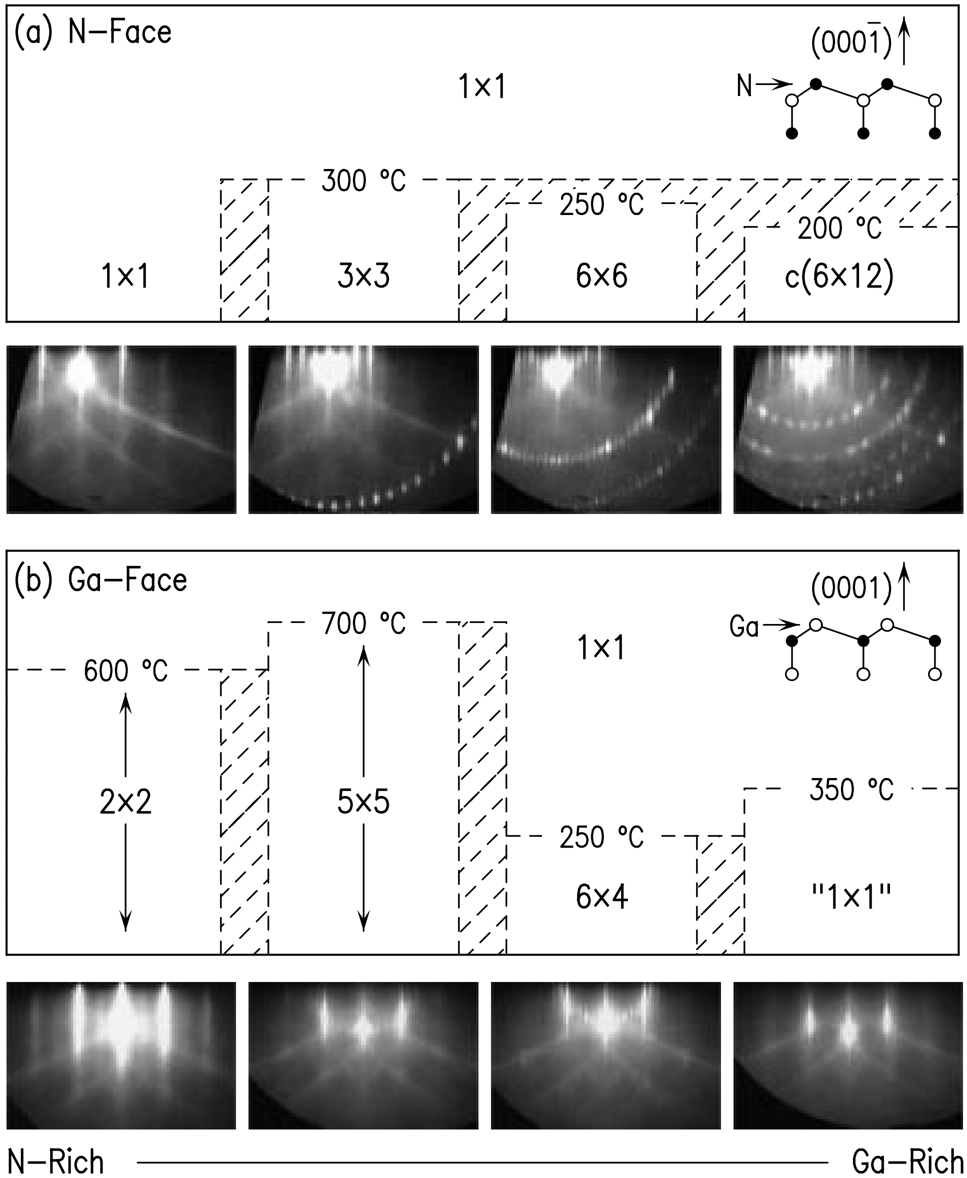

Figure 1 Schematic phase diagrams illustrating the coverage and temperature dependence of the reconstructions existing on the (a) N-face, and (b) Ga-face. Ga coverage increases from left to right in both diagrams. Temperatures given correspond to either order-disorder phase transitions or annealing transitions (see text). Cross-hatched regions indicate either mixed or intermediate phases. RHEED patterns for both the Ga- and N-face, as viewed along the [$11\bar{2}0$] azimuth, are also shown.

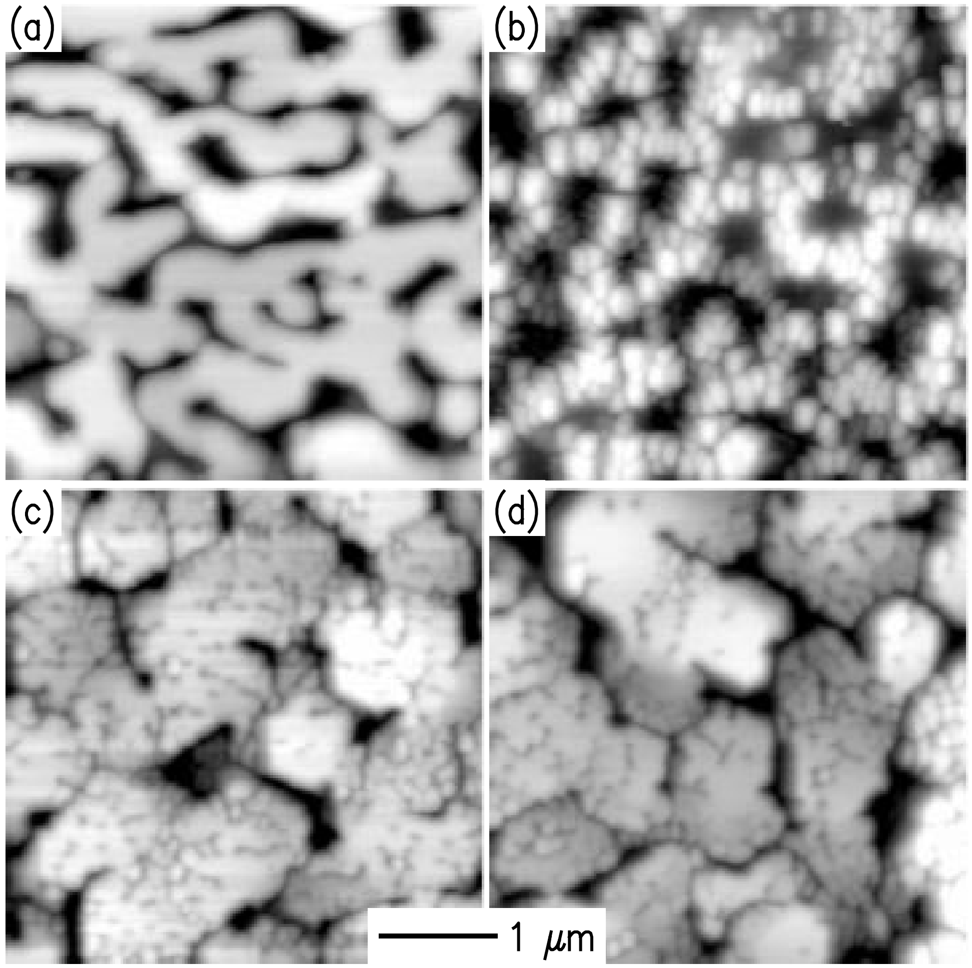

Figure 2 AFM images of GaN grown directly on sapphire (a) before etching, and (b) after etching for 3 minutes in a 1.8 M NaOH solution. Similarly displayed are AFM images of GaN grown on an MOCVD GaN/sapphire substrate (c) before etching, and (d) after etching. All images are 5 μm × 5 μm, and gray-scale ranges are 450 Å, 530 Å, 260 Å, and 260 Å, respectively.