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Scanning tunneling microscopy observation of surface reconstruction of GaN on sapphire and 6H-SiC

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ABSTRACT

We report studies of the surface structure of MBE-grown GaN layers on sapphire (0001) and 6H-(0001) SiC substrates. A different set of reconstructions is observed for nitrogen-face and gallium-face layers. The gallium-face has so far only been grown on MOCVD GaN/ sapphire substrates, while the nitrogen-face has been obtained on SiC and bare sapphire substrates.

INTRODUCTION

It is well known that the quality of GaN epitaxial layers is strongly influenced by the initial stages of growth. Recent work has shown that several types of inhomogeneities are generated in the initial stages of growth. Zincblende GaN has been detected near the initial interface [1] and also crystallites which are tilted with respect to the surface [2]. Typically these structures do not propagate through the film. However, under some conditions inversion domain boundaries (IDB) can be formed which can result in rough surfaces, while under other circumstances layers of a single polarity result [3]. Consequently, it is important to understand the factors which determine the polarity of GaN layers.

In this paper, we will summarize our recent studies of the surface structure of GaN layers with differing polarity. Nitrogen-face and gallium-face layers have been grown by MBE on bare sapphire and MOCVD GaN on sapphire surfaces, respectively. We will show that each face is characterized by a unique set of surface reconstructions which have been observed by reflection high energy electron diffraction (RHEED) and scanning tunneling microscopy (STM). Initial results on 6H-(0001)SiC substrates will also be presented.

EXPERIMENT

The studies described here were performed in a combined MBE/ surface analysis system designed and built at Carnegie Mellon. The growth chamber contains the gallium effusion cell, an SVTA RF plasma nitrogen source, and *in situ* RHEED. Samples approximately 1 cm^2 is size are mounted with spring clips on a molybdenum block. After growth, samples are transferred under vacuum to the analysis chamber for STM. The base pressures of the growth and analysis chambers were in the 10^{-11} torr range.

Growths were performed on bare (0001) sapphire substrates; sapphire substrates with a 2 μm GaN layer grown by MOCVD at 1050 °C using a low temperature GaN buffer layer; and 6H-(0001) SiC substrates. The growth procedures on the various substrates were as follows:

- Bare sapphire substrates were solvent-cleaned, heated to 1000 °C, and exposed to a nitrogen plasma for 30 minutes. After cooling to 685 °C with the plasma on, growth was initiated by turning on the gallium flux. The substrate temperature was slowly raised to 775 °C for the main part of the growth. A streaky 1×1 RHEED pattern was observed after a few hundred Ångstroms of growth. After growth of 2000 Å, the sample was annealed at

800 °C for 15 minutes, resulting in a 1×1 RHEED pattern.

- The MOCVD GaN/ sapphire substrates were loaded into the growth chamber and heated to 800 °C under a nitrogen plasma until the RHEED pattern became bright and streaky. Growth was initated at about 700 °C. Then the substrate temperature was raised to approximately 750 °C during growth of the remainder of the film.
- 6H-(0001)SiC substrates were *ex situ* hydrogen-etched at ≈1600 °C prior to loading into the chamber. This procedure has been shown to remove polishing damage resulting in surfaces with wide, atomically flat terraces [4-6]. In order to remove oxygen from the surface [7], the substrate was briefly exposed to a Ga flux in the temperature range 800-1000 °C. Then the substrate was cooled to the growth temperature of 750 °C, and the nitrogen plasma and gallium flux were turned on.

After growth, the substrates were cooled and in some cases, additional gallium was deposited on the surfaces. The gallium flux was calibrated using a water-cooled quartz crystal thickness monitor.

(0001) SAPPHIRE SUBSTRATES

We commonly observed large, flat areas after growth (≈1 μm in extent). Several different reconstructions were observed by STM on these flat areas. Figure 1 illustrates a portion of a terrace containing only the c(6×12) reconstruction. As detailed below, other reconstructions are found, depending upon the amount of gallium deposited after forming the initial 1×1 surface. Other observed features included domain boundaries, single- and multiple-bilayer steps, and spiral growth around dislocations.

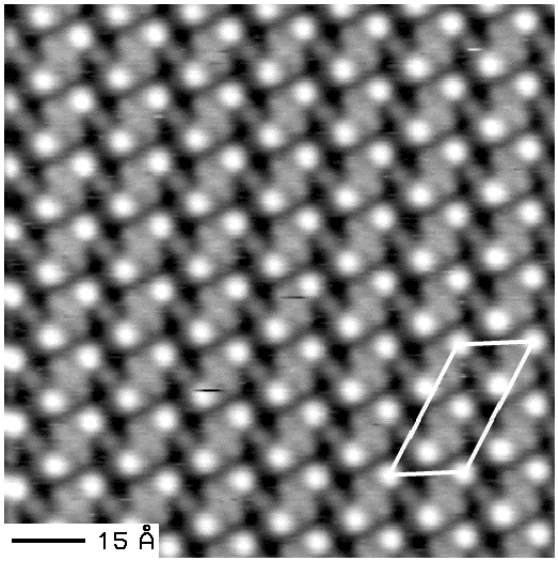

Figure 1. Empty states STM image of the c(6×12) reconstruction observed on gallium nitride grown on a sapphire substrate.

Figure 2 illustrates the sequence of reconstructions observed at 630 °C as a function of the gallium deposition time. Also illustrated is the fractional coverage corresponding to each reconstruction. All images were obtained with the substrate at room temperature. With no additional gallium exposure, only the 1×1 reconstruction is observed, where the spacing between features was consistent with the 3.19 Å GaN lateral lattice constant. A short exposure to additional gallium resulted in formation of the 3×3 reconstruction. Characteristic "glitchy" behavior, indicative of adatom motion, was occasionally seen near domain boundaries. As the gallium coverage was increased, first a 6×6 reconstruction and then the c(6×12) reconstruction were observed. No additional reconstructions were seen at higher coverages. (Presumably at very high coverage gallium droplets may be formed, although these were not observed by STM). Additional evidence for high adatom mobility is the fact that the higher-order reconstructions observed were stable only up to 100-300 °C; above this temperature there is a reversible order to disorder

transition, and a 1×1 pattern is observed by RHEED. A map of the various reconstructions observed on this surface is presented in Fig. 3.

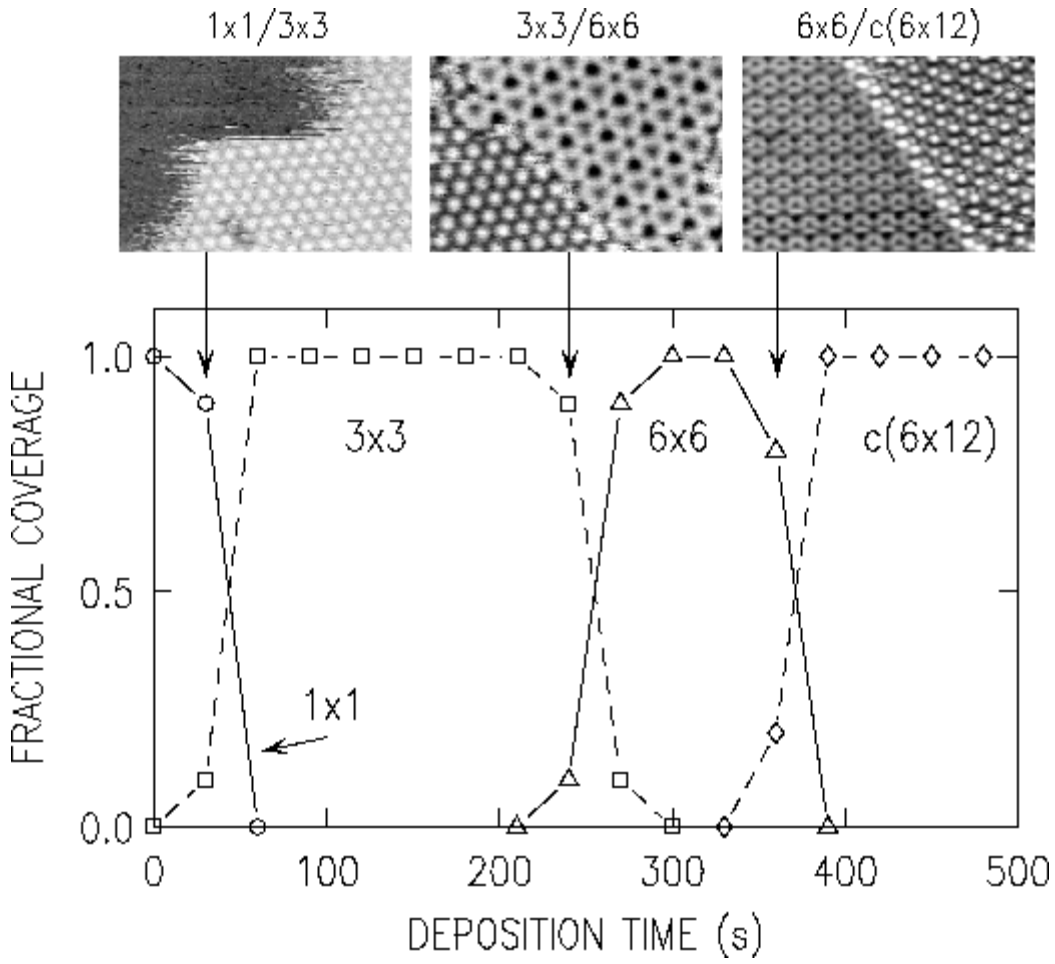

Figure 2. Reconstructions observed by STM as a function of the amount of deposited gallium.

RHEED diffraction patterns were consistent with this series of reconstructions. Along both high-symmetry directions, 1/3 order lines were clearly visible when the 3×3 reconstruction was predominant, and additional lines when the 6×6 and c(6×12) reconstructions were predominant. In order to obtain additional insight into the surface structure, the intensity of RHEED lines specific to particular reconstructions was monitored as a function of gallium deposition time. In order to make a quantitative determination of the amount of gallium required to produce a particular reconstruction, in this experiment the gallium was deposited at a sample temperature of 60 °C. The transition from 1×1 to 3×3 occurred at a coverage of 0.145±0.025 ML, which would correspond to 1.3±0.2 atoms/ unit cell if the gallium sticking coefficient were unity. Since the number of atoms/ unit cell must be an integer, and since the gallium sticking coefficient is presumably close to but less than unity, we concluded that the gallium coverage was actually 1 atom/ unit cell or 1/9 ML and that the sticking coefficient was 0.77. Assuming that this sticking coefficient is also approximately correct for high coverages, we calculate that the 6x6 corresponds to 1/3 ML and the c(6×12) to 4/9 ML. However, the sticking coefficient probably decreases with coverage and consequently the actual coverage corresponding to these reconstructions is probably less.

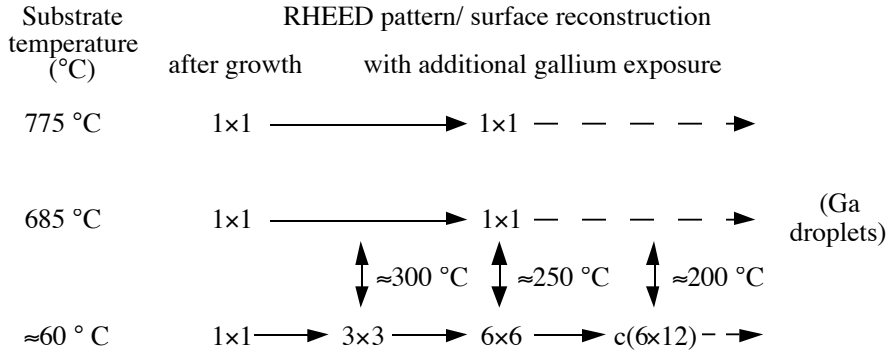

Figure 3. Map of various reconstructions observed for growth directly on sapphire surfaces.

In order to interpret these results, we begin with the 1×1 surface. We have recently reported first principles total energy calculations [8] which have been performed in order to gain some insight into the GaN surface structure. Briefly, we found that none of several 1×1 reconstructions considered were energetically favorable on the GaN(0001) (gallium-face) surface. Instead, an energetically favorable model for a 1×1 was found to consist of a monolayer (or adlayer) of Ga atoms sitting directly above the N atoms of the last GaN bilayer. As discussed above, the 3×3 reconstruction was found to form upon the deposition of approximately 1/9 ML of Ga atoms on top of the 1×1. This suggests that the 3×3 is an adatom-on-adlayer structure consisting of one additional Ga adatom per 3×3 unit cell. Such a structure is favored by the theoretical calculations [9]. Although the 6×6 and c(6×12) unit cells are too large for first principles calculations at the present time, schematic models, consistent with the STM images, known surface coverages, and rotational and translational symmetries of the reconstructions, have been constructed [9]. In these models, the 6×6 is composed of six-membered rings of Ga adatoms, while the c(6×12) is composed of slightly rearranged six-membered rings plus two additional adatoms per ring.

HOMOEPITAXIAL GROWTH ON MOCVD GaN

We discuss first the result of RHEED studies on homoepitaxial GaN. Figure 4 shows the RHEED patterns observed along the $[11\bar{2}0]$ and $[1\bar{1}00]$ azimuths. In common with some previous work [10], we designate a RHEED pattern as "n×m" if it exhibits (1/*n*)th order streaks along the $[11\bar{2}0]$ azimuth and (1/*m*)th order streaks viewed along the $[1\bar{1}00]$ azimuth.[1]

In contrast to the observations of Iwata et al. [11], we did not observe a 2×2 RHEED pattern during growth although we did observe the 2×2 after nitridation at the growth temperature (Fig. 4a). Instead, a 1×1 RHEED pattern was observed during growth, which changed to a 1×2 pattern (Fig. 4b) when the sample was annealed at 800 °C and then cooled. Unlike the case of deposition onto the nitrogen-face 1×1, deposition of additional Ga at temperatures in the range 100-300 C caused the 1/2 order streak to disappear and no additional streaks appeared. However, annealing at 600 °C followed by cooling resulted in two additional RHEED patterns, 5×5 and 6×4 (Fig. 4c and 4d, in order of increasing gallium exposure). Additional Ga deposition and annealing resulted in a "1×1" RHEED pattern with split-off fringes along the $[11\bar{2}0]$ azimuth (Fig. 4e).

These surfaces have been generally more difficult to image by STM, in part due to surface conductivity problems. So far, atomic-resolution images have been obtained only on the "1×1" and 5×5 surfaces (not presented here). Even so, it is clear both from the annealing behavior and the RHEED patterns that a different class of reconstructions are observed after homoepitaxy on

[1] We note that this usage is not consistent with the conventional notation, since, for the hexagonal system, the $[11\bar{2}0]$ and $[1\bar{1}00]$ azimuths are *not* primitive basis vectors for the surface unit cell. Future measurements by LEED and STM will reveal the surface symmetry more correctly, and may lead to some small changes in our symmetry assignment.

MOCVD GaN. Several of the higher-order RHEED patterns we see have been reported previously by other groups [12].

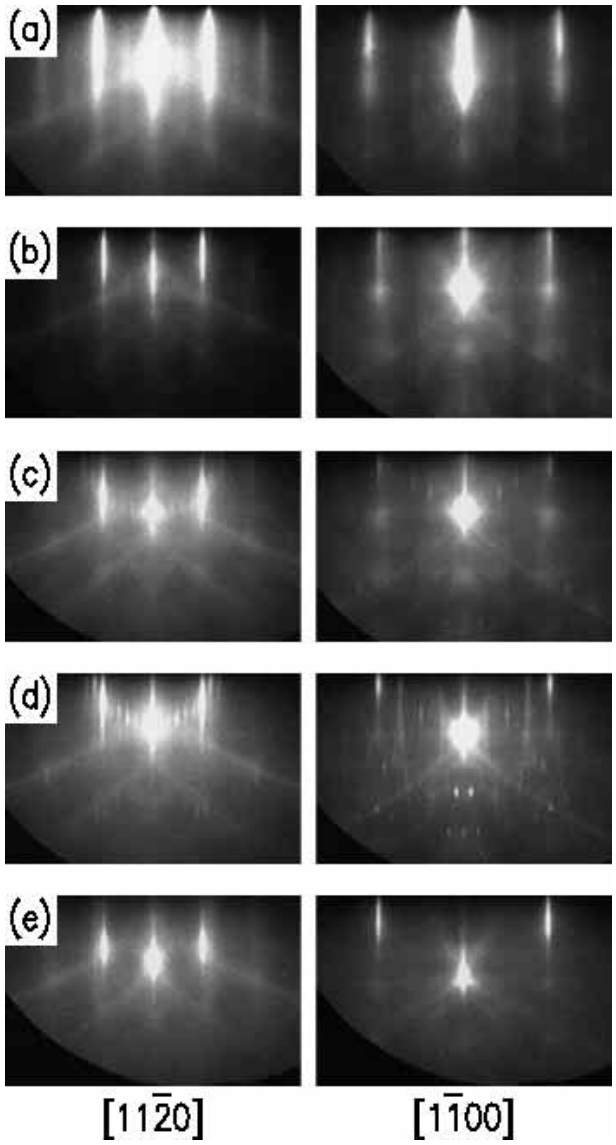

Figure 4. RHEED patterns observed along the and azimuths for homoepitaxy on MOCVD GaN. Details are presented in the text.

6H-(0001)SiC SUBSTRATES

Finally, we report our initial results obtained on 6H-SiC substrates. These studies were not as extensive as those performed on sapphire substrates. After initiation of growth as described earlier, a 1×1 RHEED pattern was observed. STM imaging of this surface after cooling to room temperature revealed a c(6×12) reconstruction.

DISCUSSION

We have observed two different classes of surface reconstructions for wurtzite GaN surfaces (Table I). One set has been observed for MBE growth directly on bare sapphire and on 6H-SiC. The second set has been observed only for MBE homoepitaxy on MOCVD-grown GaN.

We believe that the first class of surface reconstructions is formed on nirogen-face surfaces while the second is formed on gallium-face surfaces. This conclusion is supported by a number of observations. First, theoretical calculations do not find any stable 1×1 reconstruction on the gallium-face surface; and in fact no true 1×1 reconstruction was observed. Preliminary

convergent-beam electron diffraction studies suggest that the layers grown on bare sapphire are nitrogen-polar [13]. Finally, it has been reported that smooth MOCVD-grown layers are gallium-polar [3,14], and that homoepitaxial layers follow the polarity of the underlying surface [14,15].

substrate	sapphire	MOCVD GaN/sapphire	6H-SiC(0001)
during growth	1×1	1×1	1×1
no Ga	**1×1**	1×2	1×1
(with	**3×3**	**5×5**	
increasing	**6×6**	6×4	**c(6×12)**
Ga exposure)	**c(6×12)**	**"1×1"**	
(rarely)	$4\sqrt{3}\times4\sqrt{3}$-R30°		

Table I. Summary of observations on various substrates. Boldface indicates surface structures observed both by RHEED and STM, and "1×1" indicates the presence of satellite lines not characteristic of a true 1×1.

In the case of the nitrogen face, the surface layer consists of an adlayer of gallium with additional gallium adatoms. At low temperatures these gallium adatoms may form higher order reconstructions if the gallium coverage is high enough. However, at higher temperatures (T>300 °C), the adatoms become disordered and mobile on the surface. As the adatoms tend to disorder far below typical growth temperatures, this suggests that there can be an appreciable excess of gallium on the surface before gallium droplets are formed. The gallium-rich growth regime has been generally preferred because the surface becomes rough in the nitrogen-rich regime. Our picture of the surface of the gallium face is less complete but it appears likely that gallium adatoms order on this face also.

The observation that we only grow nitrogen-face GaN directly on bare sapphire and 6H-(0001)SiC (silicon face) substrates is intriguing. This may be a consequence of our growth initiation procedure in MBE, which, unlike the procedure used by some other investigators, does not use a low-temperature (≈500 °C) buffer layer. Further investigations are in progress which should yield insight into the polarity observations, and also a more detailed understanding of the Ga face.

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REFERENCES

1. W.H. Wu et al., *Appl. Phys. Lett.* **68**, 1371 (1996).
2. N. Grandjean et al., *J. Cryst. Growth* **178**, 220 (1997).
3. B. Daudin et al., *Appl. Phys. Lett.* **69**, 2480 (1996).
4. V. Ramachandran et al., (submitted to *J. Electron. Mater.*)
5. C. Hallin et al., *Inst. Phys. Conf. Ser.* **142**, (IPO Publishing Ltd, 1996).
6. T.L. Chu et al., *J. Electrochem. Soc.* **112**, 955 (1965).
7. R. Kaplan and T. M. Parrill, *Surface Science* **165**, L45-L52 (1986).
8. A.R. Smith et al., *Phys. Rev. Lett.* **79**, 3934 (1997).
9. A.R. Smith et al., *Proc. STM-97 Conference* (to be published)
10. W.C. Hughes et al., *J. Vac. Sci. Technol.* **B13**, 1571 (1995)
11. K. Iwata et al., *Jpn. J. Appl. Phys.* **35**, Part 2, L289 (1996).
12. A.R. Smith et al. (submitted to *J. Vac. Sci. Technol.*)
13. C. Hu and M. DeGraef (unpublished measurements).
14. F.A. Ponce et al., *Appl. Phys. Lett.* **67**, 337 (1996).
15. T. Sasaki and T. Matsuoka, *J. Appl. Phys.* **64**, 4531 (1988].