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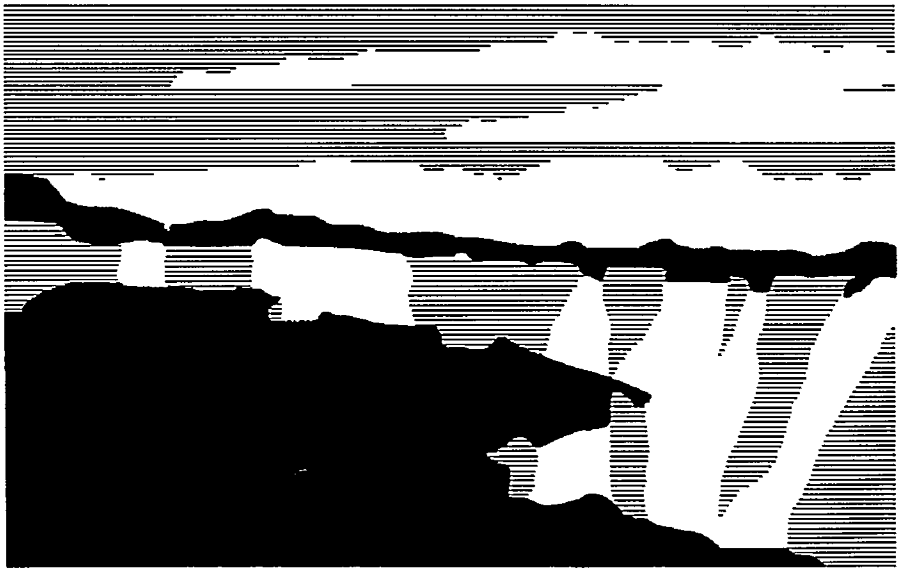

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ABSTRACT

Low-pressure metal-organic chemical vapor deposition (MOCVD) has been used to deposit unnucleated and self-nucleated GaN thin films on (00.1) sapphire substrates. For the self-nucleated films, initial layers were grown at 540°C using trimethylgallium and ammonia as elemental sources and either nitrogen or hydrogen as the carrier gas. Using these same gas phase conditions, overlayers on native (00.1) sapphire substrates or the GaN-nucleated (00.1) sapphire substrates were deposited at 1025°C. The surface morphology and mosaic dispersion of these unnucleated and self-nucleated GaN thin films have been surveyed by a combination of real space images from atomic force microscopy and reciprocal space intensity data from X-ray scattering measurements. As expected, the unnucleated GaN films show a large-grained hexagonal relief, typical of three-dimensional island growth. However, the self-nucleated films are shown to be dense mosaics of highly oriented islands, emblematic of a more two-dimensional growth.

INTRODUCTION

MOCVD has emerged as one of the leading synthetic methods for thin films of GaN [1-7] and its alloys. Generally common to the technique as practiced in various laboratories are: (1) utilization of trimethylgallium as the elemental source for the group IIIA gallium; (2) ammonia as the source for group V nitrogen; (3) deposition temperatures in the range 1000 - 1050°C; and, (4) low temperature [500 - 600°C] nucleation layers, typically comprised of 20 - 50 nm of AlN or GaN (self nucleation).

Of special interest here is that hydrogen has almost universally been selected as the carrier gas used to assist in transport of the gaseous precursors to the heated susceptor. It worthwhile recalling , however, that a variety of carrier gasses were successfully employed in the early CVD growth of unnucleated GaN. For example, Maruska and Tietjen employed hydrogen [8], Ilegems utilized helium [9], and Wickenden and coworkers [10] used nitrogen as the carrier gas.

In this report, the surface morphologies and mosaic dispersion for unnnucleated and self-nucleated growth of (00.1) GaN on (00.1) sapphire using nitrogen or hydrogen as carrier gas are contrasted.

EXPERIMENT

Films were prepared on basal-plane [(00.1)CP] sapphire substrates using trimethylgallium and ammonia as reactants and nitrogen or hydrogen as the carrier gas in a vertical spinning disc MOCVD reactor operating at 70 torr. The nucleation layers (~20 nm for hydrogen and 50 nm for nitrogen) were deposited using a trimethylgallium gas flow of 40 μmole/min, an NH_3 gas flow of 22 x 10^{-3} mole/min, height, but many were outside the maximum vertical and horizontal scan limits (120 µm x 4.5 µm) of the atomic force microscope. Smaller subunits on prismatic faces appear to be layered (like stacked sand dollars), with an average height of tens of nm high and on average about 400 nm across.

Unnucleated films grown in nitrogen as the carrier gas also exhibit [Figure 1 (B)] large hexagonal prisms, but in this case the prisms are only 10 to 20 µm across the base and 200 to 400 nm high. Even the crystallites that appear flat have a shallow pyramidal top. Here, the smaller subunits are 120 to 145 nm across and are more crystalline in appearance that those for unnucleated growth in hydrogen and the prisms also appear to be less closely packed.

Self-Unnucleated Growth. The pseudo two dimensional growth surfaces of the self-nucleated GaN films [Figure 2 (A) and (B)] are expectedly smooth [1-7, 11] compared to those for the island growth of the unnucleated films. These self-nucleated films are, however, still made up of islands 8 to 10 µm across. A few of the islands give the appearance of being as large as 30 µm across, but these are more likely comprised of clusters of smaller islands. The individual islands have terrace steps as small as 0.3 to 0.4 nm high and 150 to 300 nm across depending on the region of the film scanned. In many cases, the tops of the grains appear to end in a spiral; and in other cases some shallow holes are seen to be present. Even though the islands are not well faceted, the terrace edges do have straight edges and the overall appearance of some of the upper half of the islands are suggestive of the same 6-fold symmetry more obviously displayed by the large grains of the unnucleated films.

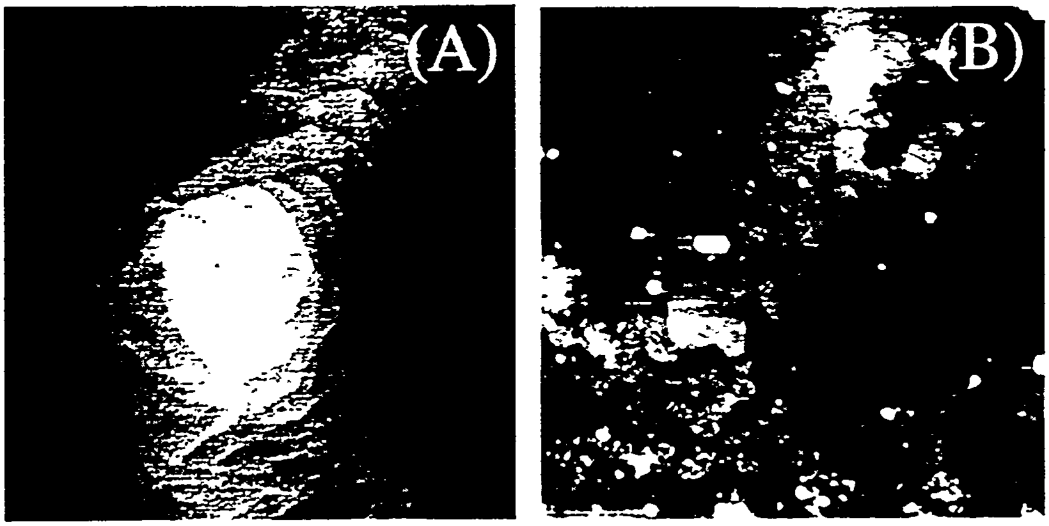

Figure 2. AFM images (4 µm x 4 µm) for: (A) self-nucleated growth in hydrogen as the carrier gas; and, (B) self-nucleated growth in nitrogen as the carrier gas.

X-Ray Scattering: Structural Coherence and Mosaic Dispersion

Out-of-plane Coherence and Dispersion. Moderate resolution θ/2θ X-ray diffractometer scans through the (00.2)GaN reflection are presented in Figure 3 (A) and (B). The very small difference in the structural coherence across the series of films laboratories [12]. In contrast, for growth in nitrogen, FWHM values near 0.2° are found for unnucleated films and even larger values, 0.25 to 0.45°, for self-nucleated films.

Finally, X-ray rocking curves for the (00.6) reflection from the sapphire substrate were also measured and typical scans are shown in Figure 4 (B). The rocking curve for a native (00.1) sapphire substrate shows an expectedly small FWHM of ~11 arcseconds), typical of a largely unstrained single-crystal substrate. As is indicated in Figure 4, the inhomogeneous strain and resulting mosaic spread in the (00.1) sapphire substrate has measurably increased along the film growth direction when either nitrogen (~18 arcsec) or hydrogen (~50 arcsec) is employed as the carrier gas. The larger increase occurs for either nucleated or unnucleated growth in hydrogen.

In-plane Coherence

Variations in the in-plane structural coherence were probed by measuring the X-ray scattering from {hh.0} reciprocal lattice vectors for both the thin films and the sapphire substrate by the X-ray precession method. Zero-level precession photographs (Figure 5) of the combined scattering from the (hh.0) reciprocal lattice planes of the (00.1) sapphire substrate and the (00.1) heteroepitaxial GaN film reveal a common in-plane epitaxial relationship [{10.0}$_{GaN}$//{11.0}$_{sapphire}$]. There is, moreover, a notable improvement in signal-to-noise ratio for growth in hydrogen, which is largely achieved by a reduction in noise. Several potential processes contribute to the background level, including: fluorescence; extrinsic instrumental scattering; and Bremsstrahlung and diffuse scattering. While it might be expected that fluorescence and the extrinsic incoherent (Compton modified) fraction of the diffuse scattering are largely sample independent, the coherent scattering from various kinds of imperfections (point and line defects, stacking faults, surface roughness, and homogeneous and inhomogeneous stress) is expected to be sample dependent

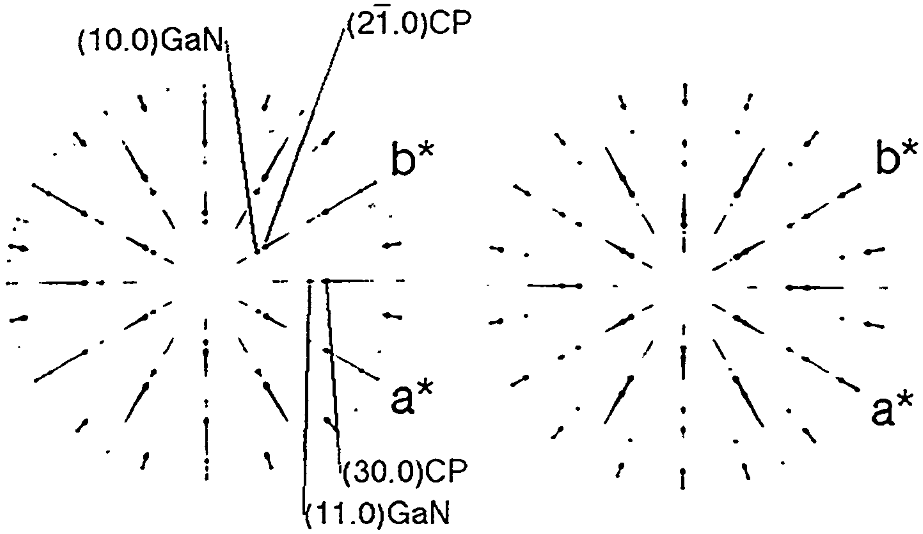

Figure 5. X-Ray precession photographs of the (hh.0) reciprocal lattice planes of (00.1)GaN on (00.1)CP for: (left) self-nucleated growth in a nitrogen and (right) self-nucleated growth in a hydrogen as the carrier gas.

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The surface morphology of these films was studied by atomic force microscopy (AFM), using a Nanoscope III instrument. Both contact and tapping mode methods were used to obtain the AFM topographs. Contact mode micrographs were acquired employing commercial 100µm long triangular cantilevers with etched Si_3N_4 tips. Imaging was carried out after the film surfaces were cleaned by dipping each sample in 1M hot HCl for 10 minutes, followed by repeated rinses in ultrapure water and reagent grade methanol, and subsequent drying under a stream of N_2. Cantilevers used for tapping mode images were 125µm long diving board type with Si tips. Typical operating parameters for the tapping mode images were 300kHz drive frequency at 120mV drive amplitude.

The out-of-plane $[\{00.1\}_{GaN}//\{00.1\}_{sapphire}]$ structural coherence was ascertained from conventional $\theta/2\theta$ X-ray diffraction scans collected on a Phillips APD powder diffractometer employing graphite-monochromatized CuKα radiation. The out-of-plane mosaic spread for these films were measured in reflection from moving-crystal/fixed-counter θ scans (rocking curves), employing a high-precision X-ray spectrometer equipped with a channel-cut, four-bounce germanium monochromator to provide aCuKα_1 beam of high spectral purity and resolution. Additionally, the in-plane $[\{10.0\}_{GaN}//\ \{11.0\}_{sapphire}]$ scattering from these films were examined in transmission using a Buerger precession camera and Zr-filtered MoKα radiation.

RESULTS AND DISCUSSION

Atomic Force Microscopy: Surface Imaging

Unnucleated Growth. As expected for a three-dimensional island growth mode [8-10], deposition of GaN onto unnucleated (00.1) sapphire yields large hexagonal prisms (Figure 1) with either hydrogen or nitrogen as the carrier gas. In the films grown in hydrogen, Figure 1 (A), these prisms range 50 to 100 µm in diameter, with a mean value clustered about 60-70 µm. Moreover, these prism were typically 1.5 to > 4 µm in

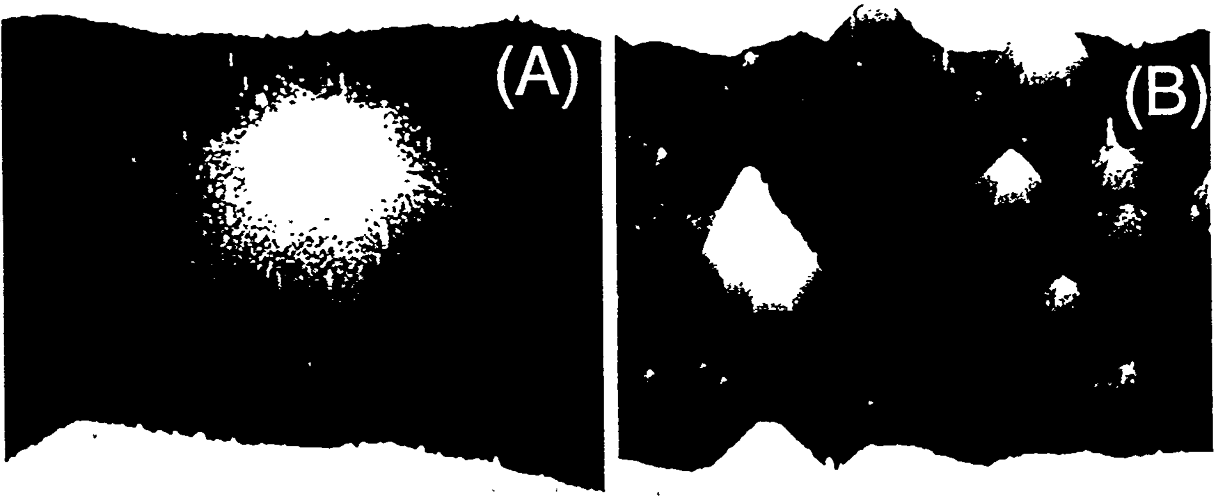

Figure 1. AFM images (100 µm x 100 µm) for unnucleated growth in: (A) hydrogen as the carrier gas and (B) nitrogen as the carrier gas.

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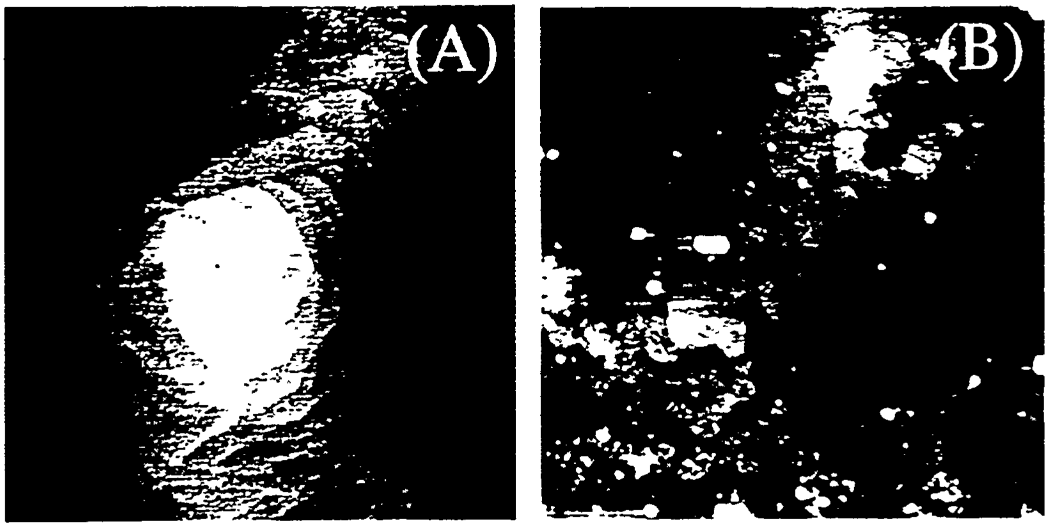

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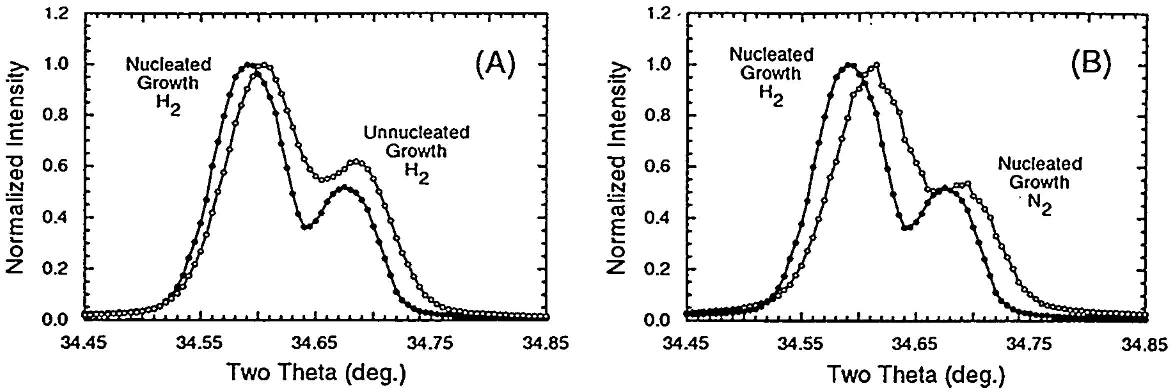

Figure 3. Normalized $\theta/2\theta$ X-ray diffractometer scans for the (00.2)GaN reflection from: (A) unnucleated and self-nucleated films grown in hydrogen as the carrier gas; and, (B) self-nucleated films grown in hydrogen or nitrogen as the carrier gas.

is well reflected in this Figure. In fact, the range of calculated d-spacing for (00.2)GaN is only from 0.2590 nm (for unnucleated growth in hydrogen) to 0.2592 nm (for unnucleated growth in nitrogen). Similarly, the spread in FWHM (full-width at half-maximum) derived from a gaussian fit to the $K\alpha_1$ component is quite small -- from 207 arcsec for nucleated growth in nitrogen to 213 arcsec for either unnucleated or nucleated growth in hydrogen. Obviously, the out-of-plane structural coherence is markedly unaffected by the nature of the carrier gas.

X-ray rocking curves for the (00.2) GaN reflection are presented in Figure 4(A). These curves very clearly differentiate between films grown in nitrogen and hydrogen. For both unnucleated and self-nucleated growth in hydrogen, the FWHM for the (00.2)GaN reflection is essentially identical at 0.10° (360 arcsec) and is very similar to that reported for films grown in hydrogen as the carrier gas in a variety of other

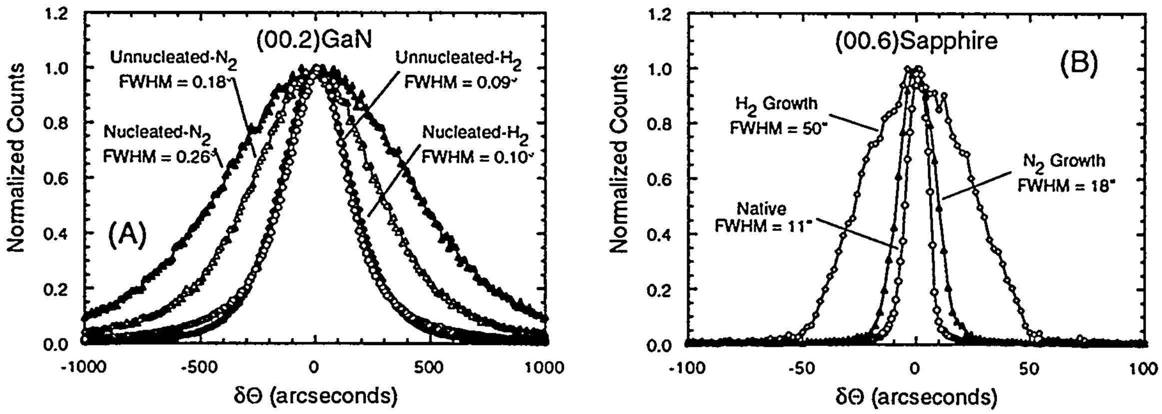

Figure 4. Comparison of X-ray rocking curves (θ scans) for: (A) the (00.2)GaN reflection from nucleated and unnucleated GaN films grown in hydrogen or nitrogen as the carrier gas; and, (B) the (00.6) reflection from the companion sapphire substrates.

laboratories [12]. In contrast, for growth in nitrogen, FWHM values near 0.2° are found for unnucleated films and even larger values, 0.25 to 0.45°, for self-nucleated films.

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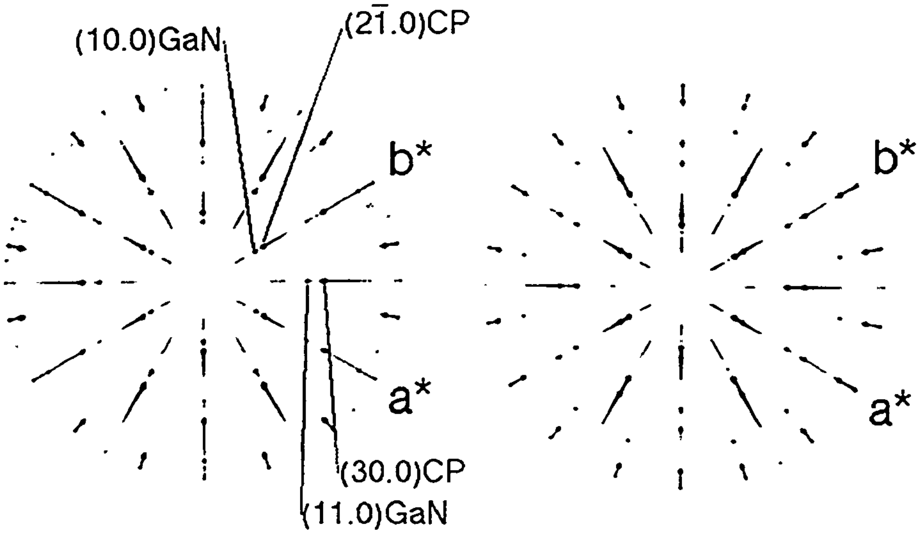

Figure 5. X-Ray precession photographs of the (hh.0) reciprocal lattice planes of (00.1)GaN on (00.1)CP for: (left) self-nucleated growth in a nitrogen and (right) self-nucleated growth in a hydrogen as the carrier gas.

Thus, the reduced background for growth in hydrogen is likely due to a decrease in the density of such imperfections.

In that context, recent transmission electron microscopy studies [13] have begun to appear for growth on a number of substrates using hydrogen as the carrier gas. In parallel, these studies have shown abrupt interfaces, a predominance of (00.1) stacking faults, interfacial misfit dislocations (with densities of order 10^{10} cm^{-2}) and loops, and defect microstructure arising from island nucleation and coalescence. The implications from the present X-ray precession study is that the defect densities could be even greater for growth in nitrogen as the carrier gas.

SUMMARY

Low-pressure MOCVD has been used to deposit unnucleated and self-nucleated epitaxial thin films of GaN on (00.1) sapphire substrates. The island growth mode of the unnucleated GaN films yields a surface morphology composed of large hexagonal grains, with prism diameters ranging from 50 to 100 µm for growth in nitrogen and 10 to 20 µm for growth in nitrogen. In contrast, the pseudo two-dimensional growth of the self-nucleated films give much smoother surface morphologies. These self-nucleated films are, however, still made up of islands 8 to 10 µm across, with minimum steps of 0.4 nm in each case. The structural coherence normal to the film surface is essentially unchanged, but the mosaic dispersion (and apparently the defect density) is measurably larger for growth in nitrogen.

ACKNOWLEDGMENTS

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