Characterizing the thickness dependence of epitaxial GaN grown over GaN nanocolumns using X-ray diffraction

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ABSTRACT

The crystal quality, as determined by X-ray diffraction, of GaN epitaxial films synthesized by MOCVD overgrowth of oriented GaN nanocolumns on Si(111) is studied as a function of film thickness and compared with control films grown on sapphire substrate. Samples were characterized using a three-beam X-ray diffraction technique from which depth-dependent rocking-curve widths (for the (0113)/(0112) crystal plane) are obtained as functions of depth. Through the examination of four samples prepared under conditions spanning key growth parameters it is found that optimizing for overgrowth at higher substrate temperatures can lead to coalesced films with significantly narrower rocking-curve widths. The results indicate that initially disconnected crystal domains stemming from individual columns do merge under the right conditions and that the coalesced crystal improves with increasing thickness. Overgrowth with the substrate temperature at 1000 °C (the highest of the study) resulted in a GaN overgrowth with properties superior to those of the control sample, a standard high-quality 2 μm MOCVD GaN thin-film grown on sapphire substrate.

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1. Introduction

GaN nanocolumn (NC) growth on sapphire or silicon substrates has been useful for investigating the optical properties of strain-relaxed GaN free of threading dislocations [1–3] and for forming structures for increasing the indium content in InGaN/GaN quantum wells [4]. However, the fabrication of optoelectronic or photonic devices directly into or on a NC structure is difficult and insufficient for many applications. Therefore, GaN with comparatively small dislocation densities formed by the overgrowth of GaN NCs has been explored as an alternative technique for preparing large-area GaN templates suitable for device fabrication [5,6].

During the overgrowth process, we observe that crystal domains stemming from the NCs expand into a horn-shaped structures as the growth extends from the tips of the NCs. When such a structure becomes sufficiently large in the lateral dimension to touch the neighboring domains and when the crystal orientations of two neighboring domains are close, they can merge to form a connected domain and result in a continuous

crystal surface. When the alignment is not close, distinct domains with clear boundaries are observed at the surface of the overgrown layer. To optimize the overgrowth parameters for forming large continuous surfaces, it is important to understand the evolution of growth conditions throughout the overgrowth process. In particular, the understanding of the dependence of crystal quality on the overgrowth thickness and the associated transitions to coalesced film growth are critical for optimizing the process.

In this paper, we report the results of depth-dependent X-ray diffraction (XRD) measurements based on a three-beam XRD technique taken on four overgrowth samples and correlate the XRD measurements with images obtained by cross-section scanning electron microscopy (XSEM). The depth-dependent XRD rocking-curve widths indicate that the crystal quality is comparatively poor during the early stages of overgrowth before adjacent domains have merged. This is consistent with the XRD measurement sampling many disconnected crystal grains. After coalescence, the rocking-curve widths decrease with sampling along the overgrowth thickness owing to improved crystal quality consistent with a continuous film. In Section 2 of this paper, the procedure for sample preparation and the theory behind the depth-dependent XRD measurement are described.

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The depth-dependent measurement results are presented and discussed in Section 3. Finally, the conclusions are drawn in Section 4.

2. Sample preparation and measurement procedures

The samples were overgrown with metalorganic chemical vapor deposition (MOCVD) on GaN NCs (on Si (111) substrates), which were grown with molecular beam epitaxy (MBE). The MBE growth conditions for NCs have been reported previously [3]. The cross-sectional dimension of the NCs is approximately 100 nm and the NC number density is estimated to be 10^9 cm^{-2} . The overgrowth was performed with MOCVD at 800 (sample A), 900 (sample B), and 1000 °C (samples C1 and C2). For samples A, B, and C1, the overgrowth duration was 40 min, leading to an estimated growth thickness of 700–800 nm. For sample C2, the overgrowth duration was 140 min and the growth thickness is estimated to be slightly larger than 2 μm . Two GaN thin-film control samples of about 2 μm in thickness, but different known crystal qualities (good crystal quality = GaN1 and poor crystal quality = GaN2) on sapphire substrate were prepared for comparison.

X-ray multiple-diffraction can occur when an incident beam simultaneously satisfies more than one Bragg condition in different lattice planes of a crystal [7]. In the three-beam case, i.e., two Bragg diffractions, normally one of the lattice planes is parallel to the crystal surface. Therefore, depending on the incident angle (skew angle) of the X-ray beam, the three-beam XRD signal mainly comes from a certain depth of the sample. In other words, the three-beam XRD technique has the capability of monitoring relative crystal properties at different sample depths [8]. For the XRD measurement in the $(01\bar{1}3)/(0\bar{1}\bar{1}2)$ plane, which is the case of this study, the relationship between the measurement sample depth, t , and the skew angle, θ , can be derived to give [9]

$$t = \frac{1}{u} [\sin \theta_{(0001)} \cos \theta_1 + \sin(\theta_{(01\bar{1}3)} + \theta_{(01\bar{1}3)/(0001)}) \cos \theta_2] \quad (1)$$

Here, θ_1 and θ_2 are defined as

$$\cos \theta_1 = 1 - \sin^2 \theta_{(01\bar{1}3)/(0001)} (1 - \cos \theta) \quad (2)$$

and

$$\cos \theta_2 = 1 - \sin^2 \theta_{(0\bar{1}\bar{1}2)/(0001)} (1 - \cos \theta) \quad (3)$$

In the above equations, u is the X-ray absorption coefficient in the crystal under measurement, $\theta_{(0001)}$ is the angle satisfying the Bragg condition in the (0001) plane, $\theta_{(01\bar{1}3)}$ is the angle satisfying the Bragg condition in the $(01\bar{1}3)$ plane, $\theta_{(01\bar{1}3)/(0001)}$ is the angle between the $(01\bar{1}3)$ and (0001) planes, and

Fig. 1. Geometry of the three-beam XRD measurement.

$\theta_{(0\bar{1}\bar{1}2)/(0001)}$ is the angle between the $(0\bar{1}\bar{1}2)$ and (0001) planes. In our study on GaN thin films, u is set to be $0.029 \mu\text{m}^{-1}$ [9].

Fig. 1 shows the geometry of the three-beam XRD measurement, including the definitions of those angles. The X-ray diffraction measurement was performed on a Bede D1 system with a Si (220) channel-cut crystal utilized as the collimator and monochromator. The beam divergence angle was about 25 arcsec. The beam was confined to an aperture of 1 mm in diameter before illuminating the sample. For the three-beam measurement, the sample and detector stages were adjusted to exactly match the Bragg condition in the GaN (0001) plane. By rotating the sample normal (φ axis), we could observe several peaks in detected intensity, which correspond to different sets of multiple-diffraction. The condition of $\varphi = 0$ corresponds to the $[10\bar{1}0]$ direction. The peak corresponding to the $(01\bar{1}3)/(0\bar{1}\bar{1}2)$ diffraction condition, which is the case of our concern, could be observed at $\varphi = 19.655^\circ$. φ scans were performed over 10° for each skew angle, θ , as shown in Fig. 1. To guarantee sufficient signal-to-noise ratio, a long signal accumulation time was used such that it took 15 min for the φ scan of a θ value.

3. Measurement results and discussions

Fig. 2 shows the (0002)-plane rocking curves of the six samples based on the two-beam XRD measurement (the conventional method). The full-widths at half-maximum (FWHMs) of samples A, B, C1, C2, GaN1, and GaN2 are 1274, 1435, 2653, 6245, 201, and 1012 arcsec, respectively. Here, one can see the large difference between the good- (GaN1) and poor-quality (GaN2) GaN thin-film control samples. Normally, the overgrown samples have much broader rocking-curve widths compared with sapphire substrate growth because the X-ray penetration is sufficiently deep to sample not just the overgrown crystal surface, but also the NCs and growth transition regions during data accumulation. The various crystalline orientations at different depths and in different domains result in a broad rocking curve. The thickest overgrown layer of sample C2 results in the largest FWHM.

Figs. 3(a,b) and 4(a,b) show the XSEM images of samples A, B, C1, and C2. Based on the records of overgrowth duration and the estimated overgrowth rates, arrows at the right ends of these images are marked to show the starting points of overgrowth. Below these points, part of NCs is thickened or merged during MOCVD overgrowth. During this stage of the growth process, GaN also fills in the gaps between NCs to form a dense combination

Fig. 2. Two-beam (conventional) XRD rocking curves in the (0002) plane of the six samples for comparison.

Fig. 3. XSEM images of samples A (a) and B (b).

with the NCs near the substrate. Near the top, the growth stemming from the NCs has started to merge and leads to the formation of a continuous layer at a depth of around 300 nm (measured from the surface), as shown in Figs. 3(a,b), and 4(a). In the samples of short duration overgrowth, the overgrowth formations are all similar (overgrowth formation forms the first 400 nm followed by connected film thicknesses of approximately 300 nm). This occurs even though the substrate temperatures are different among the growths. The long duration overgrowth performed for sample C2 resulted in a connected growth thickness greater than 2 μm.

While the overgrowth thicknesses and formation processes are only weakly dependent on substrate temperature, different overgrowth substrate temperatures do lead to significantly different crystal and optical properties. Fig. 5 plots the depth dependence of the $(01\bar{1}3)/(0\bar{1}1\bar{2})$ -plane, three-beam XRD measurements from which we obtain the rocking-curve FWHMs of the six samples as functions of skew angle. The corresponding sample depth positions are labeled below the skew angle values. In this figure, the data from both control samples GaN1 or GaN2 are weakly dependent on skew angle (depth), indicating nearly uniform crystal properties along the sample depth for typical MOCVD films on sapphire substrate. The rocking curves from data collected using the three-beam technique are always broad relative to those from the conventional two-beam measurements because of the extra diffraction process involved. The three-beam technique is not intended to collect information to be compared directly with conventional XRD, but to allow the relative comparison of the depth-dependence of the crystal structure.

In the $(01\bar{1}3)/(0\bar{1}1\bar{2})$ plane, the good-quality GaN control film (GAN1) has a rocking-curve FWHM of ~6300 arcsec, compared

Fig. 4. XSEM images of samples C1 (a) and C2 (b).

Fig. 5. Depth-dependent, three-beam XRD rocking-curve FWHMs in the $(01\bar{1}3)/(0\bar{1}1\bar{2})$ plane of the six samples.

with ~9300 arcsec in the poor-quality GaN control sample (GAN2). In sample A (filled triangles, Fig. 5), one can see that between the depths of 1324 and 700 nm, the FWHM is almost constant at ~8900 arcsec. The FWHM increases to a peak level of about ~10,300 arcsec with decreasing sample depth then drops to ~8800 arcsec near the sample surface. In sample B (filled circles,

Fig. 5), the depth dependence is similar except that the signal is noisier. As with sample A, the data from sample B show that the FWHM increases with decreasing depth at around 700 nm and peaks around 300 nm below the sample surface. The rocking-curve FWHM of sample B improves to around 7500 arcsec at the surface.

The overgrowth performed at a substrate temperature of 1000 °C leads to significantly smaller rocking-curve FWHMs than those of samples A and B grown at lower substrate temperatures. As shown in Fig. 5, the basic trends of the data from sample C1 are the same as those of samples A and B except that the feature around 700 nm present for A and B is not noticeable for C1. Nevertheless, the FWHM peak around 300 nm in depth is quite consistent with those of samples A and B.

The FWHM data from sample C2 are different from those of all other overgrown samples because of the large sample thickness. Because sample C2 is very thick, the data are all collected at depths after the overgrown film has started to improve in crystal quality so the FWHM is continuously decreasing with decreasing depth. Near the sample surface, the FWHM drops to a level below 6000 arcsec, which is lower than the level of the good-quality GaN thin-film control sample (GAN1).

Because the overgrowth thicknesses of samples C1 and C2 are estimated to be 700 nm and 2 μ m, respectively, the crystal quality evolution represented by the left end of curve C2 can be roughly connected with that of the right end of the curve C1. Based on the observations above, one can conclude that generally the crystal quality is poor at the beginning of overgrowth (at $\sim$ 700 nm in depth for samples A, B, and C1). During the early stages of overgrowth, the crystals stemming from NCs are merged individually resulting in inhomogeneously broadened XRD data corresponding to a poor-quality GaN film. After the individual columns start to coalesce, as seen by the features in FWHM at $\sim$ 300 nm in depth for samples of common thickness, the connected film subsequently improves with additional overgrowth.

There are many possible explanations for this improvement in the overgrown crystal. The domains that merge together are not perfectly aligned in the hexagonal plane or in height. After the overgrowth regions merge, the crystalline orientations become more uniform across the whole sample perhaps indicating that the strain present from minor misalignment is accommodated gradually with additional growth. Hence, the crystal quality keeps increasing as the overgrowth layer becomes thicker. Therefore, in sample C2 the rocking-curve FWHM keeps decreasing with decreasing depth. The small FWHM near the surface of sample C2, which is even smaller than that of sample GAN1, implies that the crystal quality of a thin surface layer (around 200 nm in

thickness) of the overgrown sample C2 is better than that of the good-quality GaN thin-film control sample. We have also performed photoluminescence measurement (shallow excitation) to show that the integrated luminescence intensity of this sample is seven times stronger than that of the good-quality GaN thin-film sample [6]. Hence, the overgrowth on GaN NCs at 1000 °C for a thickness over 2 μ m can lead to a high-quality GaN template for fabricating optoelectronic or electronic devices.

4. Conclusions

In summary, we have used the three-beam XRD technique described above to demonstrate the depth-dependent crystal qualities, which were indicated by the rocking-curve FWHMs in the (01 $\bar{1}$ 3)/(0 $\bar{1}$ 1 $\bar{2}$) plane, of four MOCVD-overgrown samples of MBE-grown GaN NCs. A higher MOCVD overgrowth substrate temperature led to improved crystal quality. During the overgrowth process, the crystal quality is initially poor until the domains stemming from individual columns or merged columns merge to form a larger, continuous film. After this coalescence, the crystal quality improves up to the sample surface. With the growth temperature at 1000 °C for up to 2- μ m-thick overgrown films, the crystal quality near the sample surface is shown to be better than that of a standard high-quality MOCVD GaN thin-film grown on sapphire substrate.

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