

Homoepitaxy on GaN substrate with various treatments by metalorganic vapor phase epitaxy

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ABSTRACT

This study shows the morphological, optical, and crystal characteristics of homoepitaxial GaN epilayers that were overgrown by metalorganic vapor phase epitaxy (MOVPE) on the Ga-polar face of GaN substrates that had undergone various surface treatments. The MOVPE overgrown epilayer with surface treatment was fine polished (sample C) to obtain a flat surface that exhibits two-dimensional step-flow growth. And the interface between the MOVPE overgrown epilayer and the GaN substrate was completely absent, indicating the continuous growth of GaN, and, correspondingly, the high degree of homoepitaxy. However, a network of cracks appeared in as-grown sample A (mechanically polished) and hillocks formed with the striped morphology in as-grown sample B (ICP treated). The dislocation density and full width at half maximum (FWHM) obtained by X-ray measurements of as-grown sample C were superior to those obtained by other surface treatments and the original GaN substrate. According to the photoluminescence (PL) and cathodoluminescence (CL) measurements, the decreasing FWHM of band edge emission (NBE) of the overgrown epilayers was attributable to the point defects of V_N being greatly reduced. Additionally, cross-sectional transmission electron microscopy (TEM) revealed that many threading dislocations formed in sample A by edge type dislocations and intermittently appeared due to inter-crack.

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1. Introduction

GaN substrates have great potential in the manufacturing of laser diodes (LD) [1] and high-power light emitting diodes (LEDs) [2] owing to their low dislocation density and superior thermal electrical properties. Currently, GaN substrates are formed by several methods, such as hydride vapor phase epitaxy (HVPE) [3], Na-flux method [4], and ammonothermal method [5]. The surface of a GaN substrate cannot be directly used for further epitaxial growth unless it is surface treated. GaN substrates have to be polished to make them smooth. However, lapping and mechanical polishing cause surface and subsurface damage to the GaN substrates [6]. Current methods for reducing such damage include chemical mechanical polishing (CMP) [7], chemically assisted ion beam etching (CAIBE) [8], and reactive ion etching (RIE) [9]. Since the crack-free epilayers overgrown on GaN substrates are required, the smoothness of their surfaces and their optical and crystal qualities should be further improved. In this study, we investigated the surface morphology and optical and crystal characteristics of GaN epilayers homoepitaxially overgrown on GaN substrates using various surface treatments prior to MOVPE growth.

2. Experimental procedure

In the experiment, HVPE was used to grow a thick GaN film on an MOVPE-grown *c*-plane GaN template by employing temperature ramping techniques that were developed by the authors in an earlier study [10]. Subsequently, the thick GaN film was separated from the sapphire substrate by laser lift-off (LLO) using a 355 nm Nd:YAG laser to make a free-standing GaN substrate. Then the Ga-polar face of the GaN substrate was mechanically polished using diamond slurry to planarize the surface (sample A). Another sample was mechanically polished and then underwent inductively coupled plasma (ICP) treatment under mixed Cl_2 and Ar gases that flowed constantly into the chamber (sample B). The other sample, after being mechanically polished and ICP treated, underwent fine polishing using silicon dioxide slurry in a chemical solution (sample C). In all samples, 4 μ m-thick undoped GaN epilayers were deposited on the Ga-polar face of the on-axis *c*-plane GaN substrates without a H_2 thermal clean and low temperature buffer layer by MOVPE. The growth temperature and pressure were 1100 °C and 300 mbar, respectively. Trimethylgallium and ammonia were used as the Ga and N precursors, respectively. And H_2 was used as the carrier gas during MOVPE growth.

The surface morphology of the overgrown epilayers and GaN substrates was observed under a Nomarski optical microscope, an atomic force microscope (AFM), and a scanning electronic

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microscope (SEM). Panchromatic CL images and field emission transmission electron microscope (FETEM, JEM-2100F) were performed to analyze the threading dislocations. The etching pit density (EPD) experiment was also applied under 220 °C for 20 min in a mixed solution of H_3PO_4 and H_2SO_4 at a ratio of 1:3 taken using AFM. Optical measurements were made by PL using the 325 nm line of a He–Cd laser at room temperature. High-resolution X-ray diffraction (HRXRD) was also applied to measure the FWHM variation of the epilayers. The (0 0 2) diffraction peaks in the X-ray ω -scan were identified using a Bede D1 system with a slit width of 0.5 mm.

3. Results and discussion

The Nomarski contrast images in Fig. 1 reveal the large variation among the surface morphologies of the GaN epilayers that were homoepitaxially overgrown on the Ga-polar faces of the GaN substrates. Fig. 1(a) shows a network of cracks in as-grown sample A, whose surface underwent only mechanical polishing before it was overgrown by MOVPE. This phenomenon is attributed to the fact that the strain in the overgrown epilayer is too high to cause cracking [11]. In contrast, the surfaces of as-grown samples B (mechanical polishing followed by ICP treatment) and C (mechanical polishing followed by ICP treatment and then fine polishing) were crack-free. Lee and Auh [12] found that dry etching removed the damage layer that was formed by mechanical polishing, leaving a homogeneous and smooth surface. However, the surface of as-grown sample C was smoother than that of as-grown sample B. In as-grown sample B, hillocks formed in the GaN epilayer with the striped morphology, but the morphology of as-grown sample C was flat over a large area. The insets in Fig. 1 present the treated surfaces of GaN substrates prior to overgrowth by MOVPE to elucidate the

remarkable variation among the morphologies of the overgrown epilayers. The mechanically polished surface of sample A had deep and dense scratches, but the ICP treatment of sample B reduced the density and depth of scratches. The fine polishing of sample C further reduced the scratches and replaced them with a slightly indented morphology. We suggest that the scratches or slight indentations of the treated surfaces were the favored nucleation positions for GaN overgrowth and replicated in the epilayers, resulting in the remarkable variation of the morphologies of these samples after MOVPE overgrowth. Weyher et al. [11] and Miskys et al. [13] also observed the residual work damage is replicated in the epitaxial layer.

Fig. 2 shows AFM images of the microscopic morphologies of the samples after MOVPE overgrowth. As-grown sample A showed rough and large-scale height difference surface with a root-mean-square (RMS) roughness of 12.6 nm. As-grown sample B had a strip morphology in the early stage of two-dimensional step-flow growth, and its RMS roughness was decreased to 1.9 nm. As-grown sample C shows a flat and two-dimensional step-flow grown surface with an RMS roughness of 0.5 nm. These microscopic morphologies, observed by AFM, were consistent with the macroscopic Nomarski measurements in Fig. 1. The surface treatments of sample C effectively reduced the RMS roughness of the as-grown surface to 0.5 nm compared to 1.9 nm of sample B.

Fig. 3 shows the cross-sectional SEM and corresponding panchromatic CL images of the samples after MOVPE GaN epilayers overgrew GaN substrates. The SEM images show that the interface between the MOVPE overgrown epilayers and the GaN substrate was clear, indistinct, and disappeared in samples A, B, and C, respectively. In fact, the interface was completely absent from sample C, indicating the continuous growth of GaN and, correspondingly, a high degree of homoepitaxy. Moreover, the GaN substrate and MOVPE overgrown epilayers in all of these samples

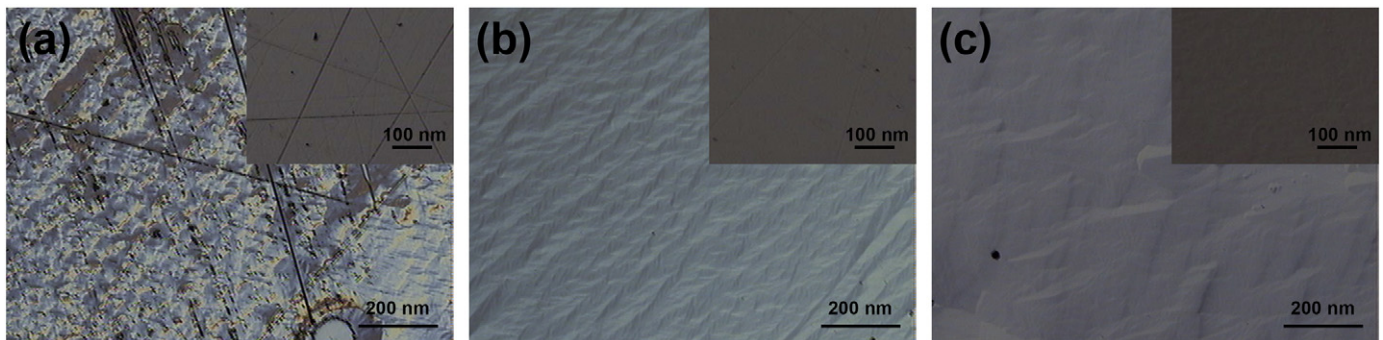


Fig. 1. Surface morphologies of MOVPE overgrown GaN epilayers on GaN substrates by a Nomarski optical microscope: (a) sample A, (b) sample B, and (c) sample C. The insets are surfaces of GaN substrate prior to MOVPE overgrowth.

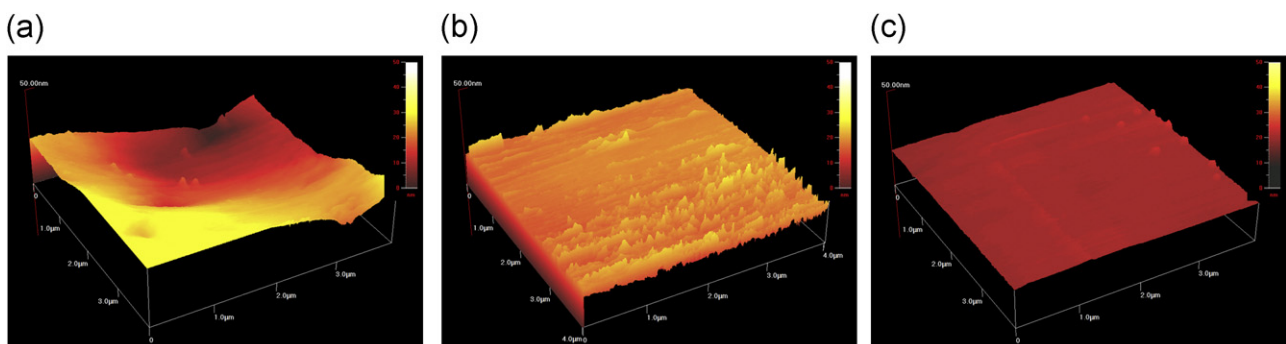


Fig. 2. AFM micrographs of MOVPE overgrown GaN epilayers on GaN substrates: (a) sample A, (b) sample B, and (c) sample C.

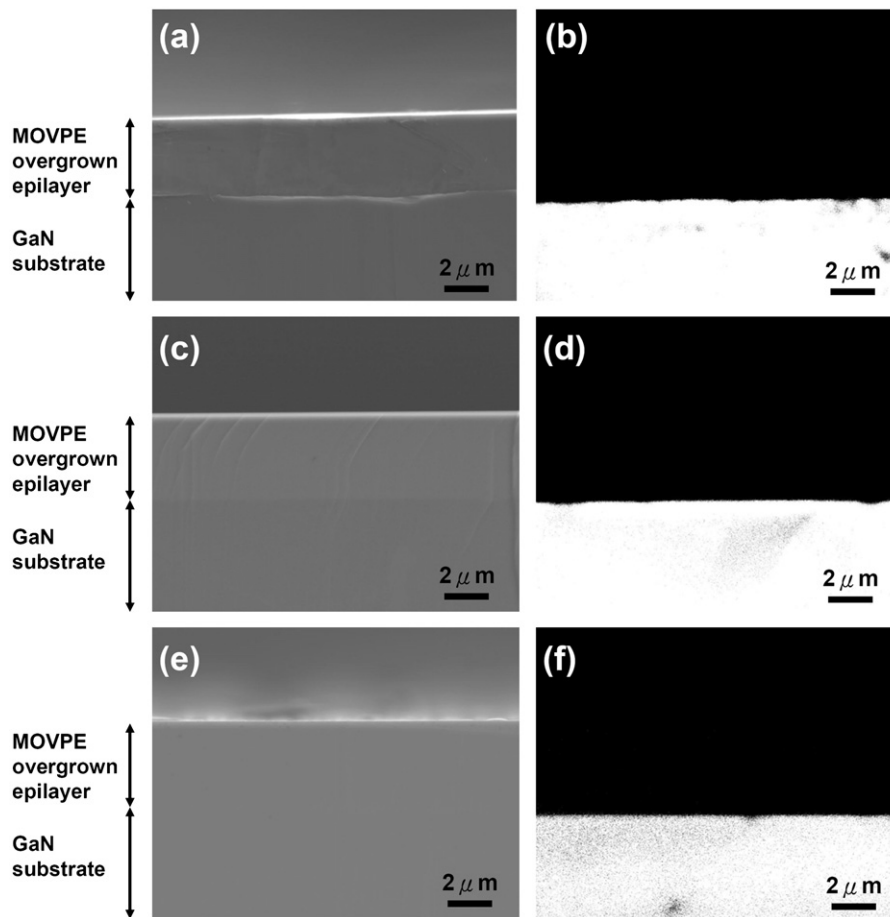


Fig. 3. Cross-sectional SEM and corresponding panchromatic CL images of MOVPE overgrown GaN epilayers on GaN substrates: (a) and (b) sample A, (c) and (d) sample B, (e) and (f) sample C.

were bright and dark regions, respectively, in the panchromatic CL images. The carrier concentration was relatively high in the GaN substrate. The origins of the carriers are discussed below with reference to the PL measurements.

Fig. 4 displays top-view panchromatic CL images of the samples after MOVPE overgrowth, from which the dislocation density was calculated. The dislocation densities of as-grown samples A, B, and C were close to 10^9 , 2.1×10^7 , and $1.7 \times 10^7 \text{ cm}^{-2}$, respectively. The dislocation density of as-grown sample A was two orders of magnitude higher than that of $2 \times 10^7 \text{ cm}^{-2}$ in the original GaN substrate. It is because the mechanical polishing induced a damage layer under the GaN substrate, forming dislocations in the interface, which extended throughout the epilayer [14]. To determine the exact cause of this reduction in quality, cross-sectional TEM $[1\ 1\ -2\ 0]$ images of as-grown sample A are obtained under two-beam conditions using different $\mathbf{g}$ vectors, $[1\ -1\ 0\ 0]$ and $[0\ 0\ 0\ 2]$, as shown in Fig. 5(a) and (b). Fig. 5(a) shows a large amount of dislocations started forming at the interface and extended into the MOVPE overgrown epilayer. Notably, some of the dislocations formed a loop near the interface, some of them intermittently induced in the growth direction, and some of the dislocations extended to the surface. Ponce et al. [15] claimed that the existence of dislocation loops is a characteristic of homoepitaxy, since the interface is fully coherent. With respect to the intermittent appearance of dislocations in the growth direction, the dislocations may have been blocked by inter-cracks in the epilayers and induced as epilayer overgrown upon inter-crack. Because most of the dislocations appeared with using $\mathbf{g}$ vectors of $[1\ -1\ 0\ 0]$, we elucidated the dislocations of MOVPE epilayer overgrown GaN

substrate with only mechanical polishing treated surface were dominated by edge type. The dislocation densities were around 3×10^9 and $2 \times 10^9 \text{ cm}^{-2}$ at the interface and the surface, respectively. Furthermore, only a few dislocations in screw type, with a density of around $5 \times 10^8 \text{ cm}^{-2}$, are observed in the MOVPE overgrown epilayer in Fig. 5(b) using $\mathbf{g}$ vectors of $[0\ 0\ 0\ 2]$. Furthermore, the EPD measurement was also applied on as-grown samples A as shown in Fig. 6. According to Albrecht et al. [16] and Lu et al. [17], the larger pits are related to screw or mixed-type dislocations and the small ones are related to edge-type dislocations. The dislocation density of screw and mixed type is $6 \times 10^7 \text{ cm}^{-2}$. The dislocation density of edge type is $8 \times 10^8 \text{ cm}^{-2}$. The total dislocation density obtained by CL, TEM, and EPD measurements is similar, which is close to 10^9 cm^{-2} . From the TEM and EPD measurements, the total dislocation density is found to be close to the edge type dislocation density. However, the screw and mixed type dislocations measured by TEM were overestimated by one order than those obtained by EPD. This inaccuracy could be due to the narrow measured region by TEM. In as-grown samples B and C, as shown in Fig. 4(a) and (b), the dislocation densities of the MOVPE overgrown epilayer were close to the value of the original GaN substrate. No dislocation was observed in the cross-sectional TEM image of either as-grown sample B or sample C (not shown here). It indicated that the surfaces of samples B and C were properly prepared, so the dislocation density of the homoepitaxial layers followed that of the GaN substrate [18]. The dislocation density of as-grown sample C was less than that of sample B, demonstrating that surface treatment of sample C was much effective. Moreover, Dwilinski et al. [19] reported that pits agglomerated mainly along

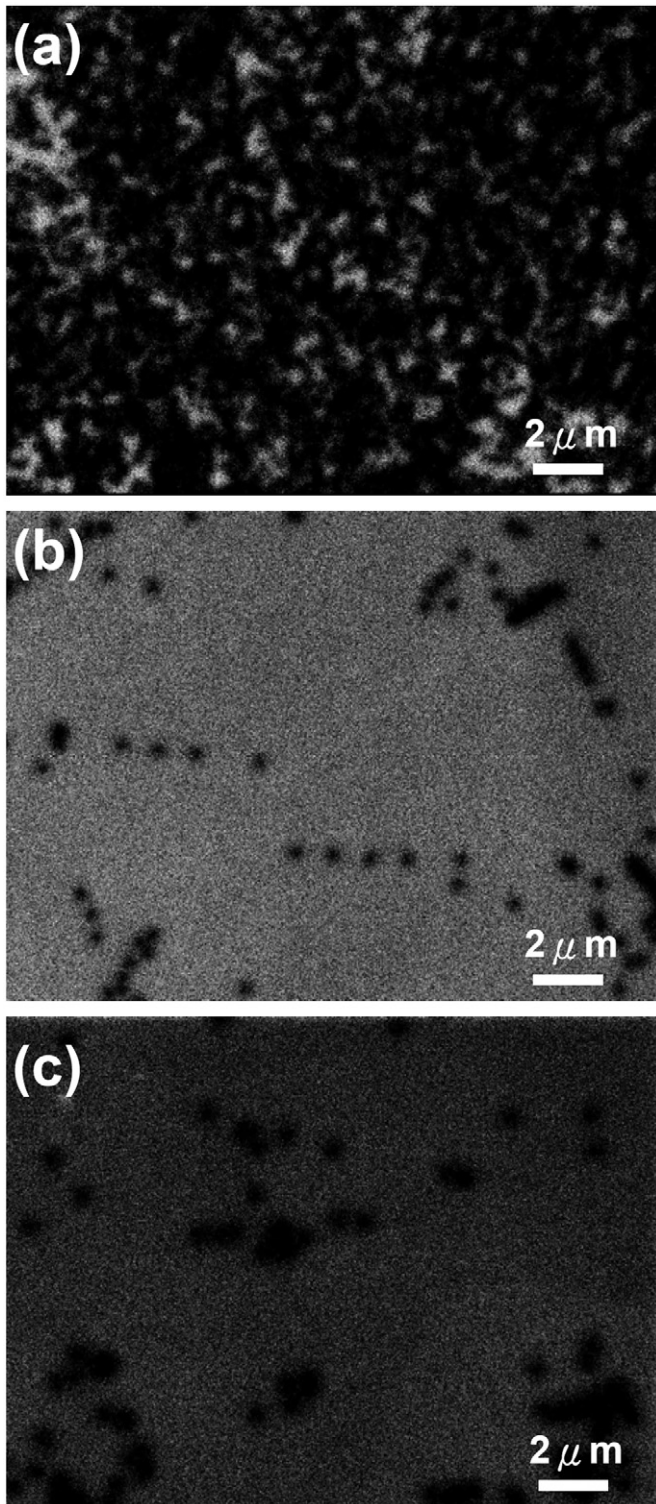


Fig. 4. Top-view panchromatic CL images of MOVPE overgrown GaN epilayers on GaN substrates: (a) sample A, (b) sample B, and (c) sample C. The dark spots show the positions of dislocations.

the traces of scratches. It was also found the pits were formed by arrays of lines and indentations in as-grown samples B and C, respectively, which are compared with each other with respect to the treated surfaces of the GaN substrates in the insets in Fig. 1.

Fig. 7(a) shows the PL spectra before and after MOVPE overgrowth. Each PL spectrum was normalized to the intensity of the

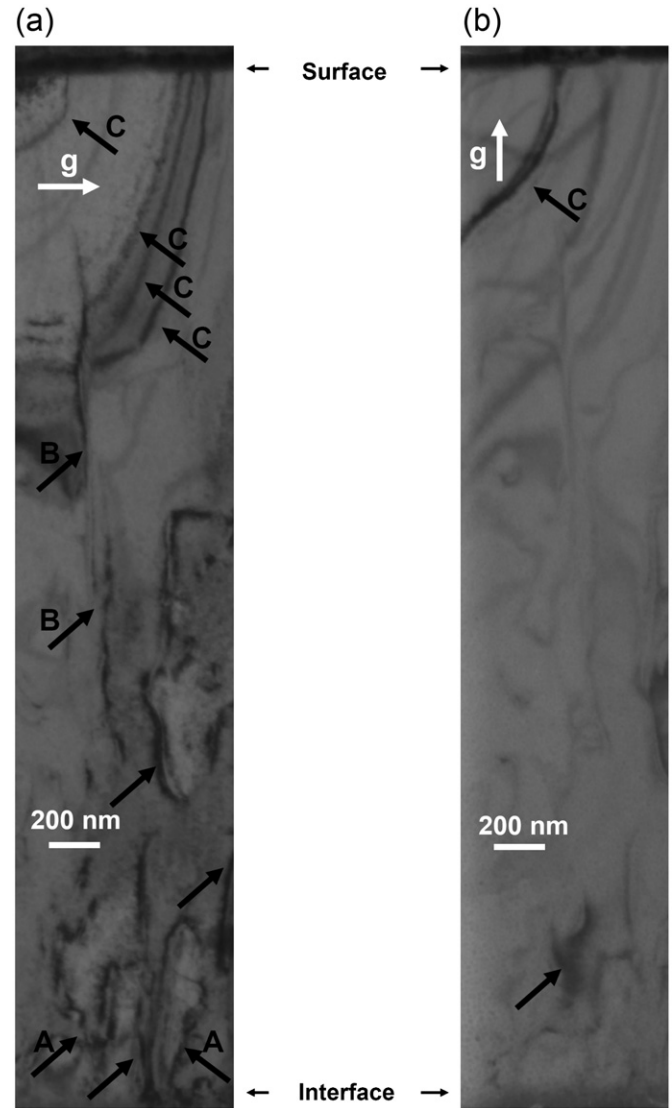


Fig. 5. Cross-sectional TEM [1 1 - 2 0] images under two-beam conditions with g vectors of (a) [1 - 1 0 0] and (b) [0 0 0 2] of as-grown sample A. The arrows indicate the dislocation. The dislocation indicated by arrow A, B, and C shows the loop of dislocation formed near the interface, intermittently in the growth direction, and extended to surface, respectively.

GaN NBE. MOVPE overgrown epilayers significantly increased the yellow band emission (YL) of all of the samples. Reshchikov and Morkoç [20] reported that $V_{Ga}-O_N$ complex defects increase the YL emission and have very low formation energies near the edge dislocations. The cross-sectional TEM measurements reveal that many edge dislocations formed in as-grown sample A. Therefore, as-grown sample A had a significantly larger YL than the other two samples. Moreover, all of the MOVPE overgrown samples exhibited blue luminescence (BL) close to 440 nm. Yang et al. [21] stated that this BL emission is the transition from the O_N donor to the $V_{Ga}-O_N$ complex acceptor. We suggest that the appearance of O_N and $V_{Ga}-O_N$ defects in MOVPE overgrown epilayers was attributable to the non-optimized overgrowth system and conditions. Furthermore, the FWHM of NBE decreased from 15.4 to 11.4, 15.4 to 7.4, and 11.4 to 6.8 nm for samples A, B, and C, respectively. Because V_N generates a shallow level below the conduction-band minimum to have a role of a donor, donor-bound excitons at the NBE are ascribed to those donor-types of defects [22]. Thus, the decrease in FWHM of NBE after MOVPE overgrowth is attributable to a significant decrease in V_N . Moreover, the NBE of all samples was

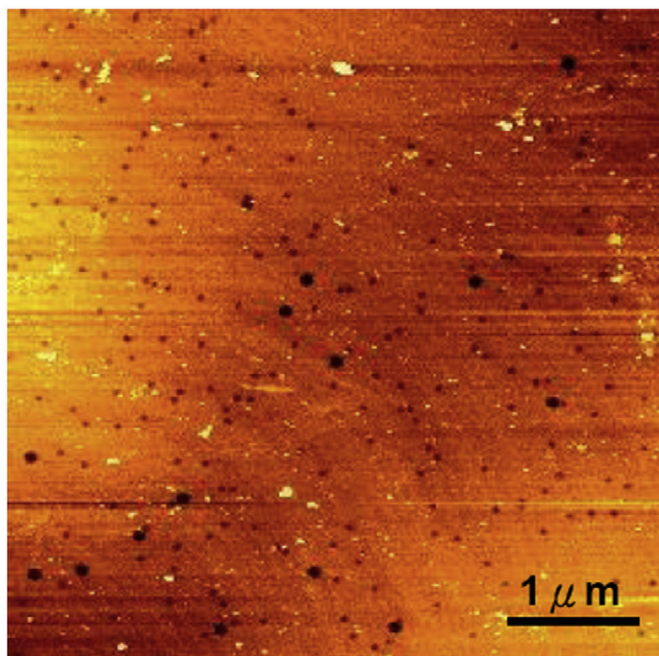


Fig. 6. EPD measurement under 220 °C for 20 min in a mixed solution of H_3PO_4 and H_2SO_4 at a ratio of 1:3 of as-grown sample A.

blue-shifted after MOVPE overgrowth. Chua et al. [23] indicated the blue-shifted of NBE is related to the significantly higher carrier concentration in GaN substrate compared to the overgrown epilayer. Based on the decrease in the FWHM of the NBE, the decrease in the carrier concentration in the MOVPE overgrown epilayer was determined to be due to V_N . Hence the GaN substrate and MOVPE GaN epilayers were observed as bright and dark regions in the panchromatic CL images in Fig. 3.

An HRXRD ω -scan of the (002) reflection of the MOVPE overgrown epilayers was performed, as shown in Fig. 7(b). The FWHM for as-grown samples A, B, and C were 248, 150, and 118 arcsec, respectively. The corresponding FWHM for the original GaN substrate was 204 arcsec. The FWHM of the as-grown sample A was clearly larger than those of the other two samples because it had many screw dislocations, with a density of around 10^8 cm^{-2} and $V_{\text{Ga-O}_N}$ point defects that were associated with YL. The FWHM of as-grown sample C was smaller than that of as-grown sample B, because as-grown sample C had fewer dislocations and $V_{\text{Ga-O}_N}$ point defects. The surface treatment of sample C was therefore much more effective than that of sample B.

4. Conclusion

In this study, GaN epilayers were overgrown by MOVPE homo-epitaxially on the Ga-polar faces of GaN substrates with various surface treatments. A network of cracks appeared in as-grown sample A (mechanically polished) and hillocks formed with the striped morphology in as-grown sample B (ICP treated). As-grown sample C (fine polished) had a flat, two-dimensional step-flow growth surface with the lowest RMS roughness of 0.5 nm. The dislocation densities of as-grown samples A, B, and C were close to 10^9 , 2.1×10^7 , and $1.7 \times 10^7 \text{ cm}^{-2}$, respectively. Cross-sectional TEM revealed that many threading dislocations in as-grown sample A were formed at the interface. The dislocations were dominated by edge type, which appeared intermittently owing to the presence of inter-cracks. Moreover, the significant decrease in V_N reduced the FWHM of NBE after MOVPE overgrowth. And the FWHM

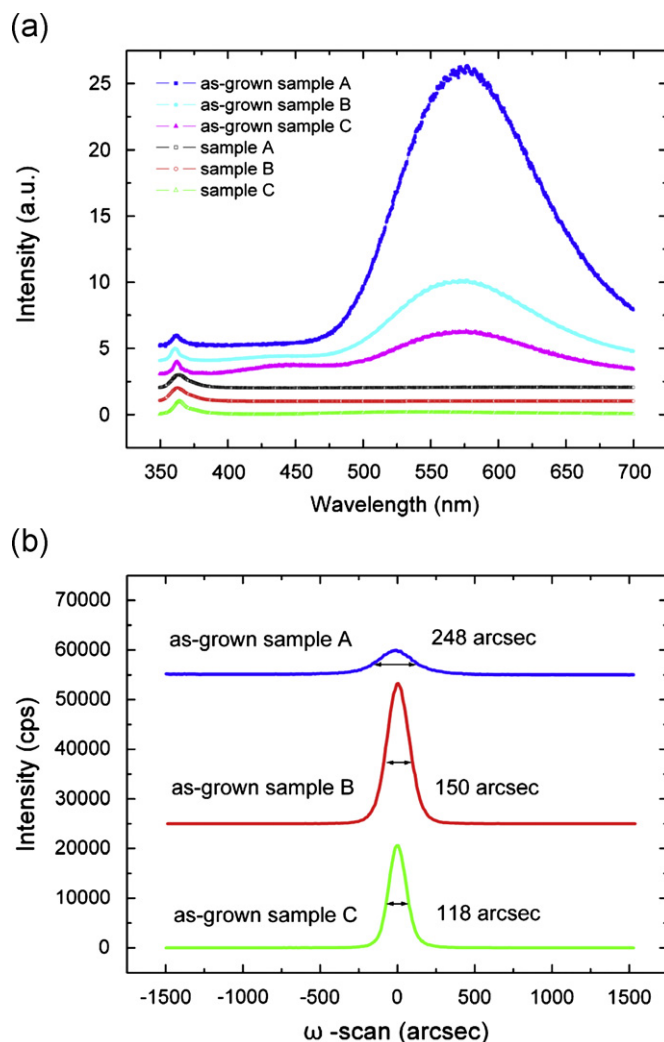


Fig. 7. (a) Room-temperature PL measurement at the Ga-polar face of the GaN substrates and as-grown MOVPE GaN epilayers. (b) HRXRD ω -scan in (002) reflection at the Ga-polar face of MOVPE overgrown GaN epilayers on GaN substrates.

in the (002) reflection of HRXRD measurements of as-grown samples A, B, and C were 248, 150, and 118 arcsec, respectively.

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