The Influence of the Preheating Temperature of the (−2 0 1) β-Ga₂O₃ Substrates on c-Plane GaN Epitaxial Growth

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Abstract: In this paper, we demonstrate the direct epitaxial growth of c-plane GaN on a preheated (−2 0 1) β-Ga₂O₃ single-crystal substrate with no interlayer or pre-patterning processes by using the atmospheric pressure metalorganic chemical vapor deposition method. The results show that high-temperature preheating (>500 °C) can modify the surface morphology of the substrate so that the crystalline quality of the grown GaN layer can be improved. With higher preheated temperatures, the grown GaN layer reveals smaller FWHM (full width at half-maximum) of the X-ray rocking curve. In addition, we find that the photoluminescence spectra of the GaN layers reveal their narrowest linewidth at a preheated temperature of 800 °C. These results support improvements of crystalline quality and provide optimization of a c-GaN grown epitaxially on the preheated (−2 0 1) β-Ga₂O₃ substrates for further device fabrication.

Keywords: β-Ga₂O₃; heterogeneous epitaxy; thermal annealing; GaN; epilayer; APMOCVD (atmospheric pressure metalorganic chemical vapor deposition)

1. Introduction

The group-III-nitride material gallium nitride (GaN), due to its potential optoelectronic properties, plays an important role in a number of commercial products, including high-frequency electronic devices [1], power devices [1,2], light-emitting diodes (LEDs) [3–5], and laser diodes [4,5]. For the performance of GaN-based devices, finding an appropriate lattice-matched substrate is a significant issue. The homoepitaxial growth of GaN on GaN substrate can permit a precise matching of the lattice and the thermal expansion coefficient; however, this approach is expensive, and limited to relatively small substrates. Currently, heteroepitaxial growth of GaN on foreign substrates—such as silicon carbide [2,6,7], silicon [6–8], and sapphire [9–20]—is a common technique for commercially available devices. Problems associated with the substrate, such as significant lattice mismatch and different thermal expansion coefficients, have often resulted in structural defects in the epitaxial layers [21]. Large efforts to reduce the defect densities and to optimize the quality of the GaN epitaxial film—such as substrate etching, nitridation, and slight misorientation from the (0 0 0 1) crystal plane [21], patterned sapphire substrate (PSS) [12–20], or coated AlN on sapphire [22,23]—have been successfully made to improve the quality of GaN epilayers. However, it is noteworthy that these methods will increase the complexity of device fabrication, as well as the cost. On this basis, the direct growth of GaN layers on substrates with less lattice mismatch is preferable.

During the past decade, Ga₂O₃ has attracted a tremendous amount of attention in various fields due to its unique properties. Its energy band gap at the Γ point is about 4.7 eV at room temperature, which means that it is highly transparent in the spectral range from deep ultraviolet to infrared [24]. A large, low-cost, single-crystal β-Ga₂O₃ wafer can be mass-produced either with floating zone growth or the edge-defined film-fed growth method [25,26]. The lattice mismatch between β-Ga₂O₃ and GaN was found to be less than 2.7% for the in-plane epitaxial relationship (1 0 −1 0) GaN || (0 1 1) β-Ga₂O₃ [27], and
4.7% for \((0 0 0 2) \text{GaN} \parallel (-2 0 1) \beta-\text{Ga}_2\text{O}_3\) \cite{28}. Therefore, a \(\beta-\text{Ga}_2\text{O}_3\) wafer becomes a potential candidate as a substrate for GaN-based devices. To date, various efforts have been made to improve the quality of GaN epilayers on \(\beta-\text{Ga}_2\text{O}_3\), such as growing AlN (aluminium nitride) as a buffer layer \cite{29,30}, adapting SiN\(_x\) patterns on the substrates to reduce threading dislocations \cite{31}, growing a thin GaN or AlGaN as a nucleation layer for following GaN epilayer growth \cite{32–34}, or adjusting the NH\(_3\) gas flow rate to control the thickness of the GaN epilayer \cite{35,36}. The last two investigations show the potential to directly grow epitaxial GaN layers on \(\beta-\text{Ga}_2\text{O}_3\) substrates without additional interlayer layers or pre-patterning processes, which can further simplify device fabrication processing. In addition, it is well known that thermal annealing is an efficient method to terrace the surface morphology of the wafers. Thus, we can optimize the epitaxial growth of GaN by preheating the \(\beta-\text{Ga}_2\text{O}_3\) substrate.

Therefore, in this paper, we firstly describe our designed recipe, using the atmospheric pressure metalorganic chemical vapor deposition (APMOCVD) method to directly grow the GaN layer on the \((-2 0 1) \beta-\text{Ga}_2\text{O}_3\) substrate through preheating the substrates, followed by the formation of a GaN nucleation layer, and finally a GaN epilayer. Subsequently, we discuss the influence of the preheating temperature of the substrates on the crystalline quality of the GaN epitaxial layers. Using high-resolution X-ray diffraction (HRXRD) and power-dependent photoluminescence (PL) measurements, we investigate the crystalline qualities of the GaN films. Finally, we compare the crystalline quality of the 1-\(\mu\)m-thick GaN epilayers grown on preheated substrates at 800 °C and 1100 °C, as well as 2-\(\mu\)m-thick GaN epilayers grown on preheated substrates at 500 °C. These results provide useful information to optimize GaN epilayers grown on the preheated \((-2 0 1) \beta-\text{Ga}_2\text{O}_3\) substrate for further device fabrications.

2. Materials and Methods

2.1. Growth Sequence of the GaN Epilayer

The \((-2 0 1) \beta-\text{Ga}_2\text{O}_3\) substrates used in our experiments were commercial 2-inch \((-2 0 1) \beta-\text{Ga}_2\text{O}_3\) wafers (TAMURA, Saitama, Japan), made with the edge-defined film-fed growth method with intentional Sn doping. We cut the wafers into 10-mm \(\times\) 10-mm pieces, then subjected them to a two-stage cleaning procedure. The first step involved organic solvent cleaning, alternately using acetone and methanol for several cycles in an ultrasonic oven, before rinsing them with deionized water (DIW). The second step involved acid cleaning, using a sulfuric acid – hydrogen peroxide mixture (DIW 30%; H\(_2\)O\(_2\) 96%; H\(_2\)SO\(_4\), = 1:1:4) for 5 min, before rinsing again with DIW. After cleaning, the wafers were placed in the APMOCVD chamber (TAIYO NIPPON SANSO, Shinagawa-ku, Japan). The growth sequence of the GaN epilayer was divided into three steps, as shown in Figure 1.

2.1.1. Substrate Preheating

The temperature of the substrates was increased to higher than 500 °C and thermally annealed for 10 min in ambient N\(_2\). This thermal treatment is a common technique for removing contaminants from the substrates, repairing the residual polishing damage, and terracing the surface morphology of the substrate \cite{34,35}. With the change in surface morphology, an effect similar to a patterned substrate occurs, so that the threading dislocations are significantly suppressed by epitaxial lateral overgrowth (ELOG) \cite{36}.

In order to investigate the effects of preheating, five samples were thermally annealed at temperatures of 500 °C, 600 °C, 800 °C, 950 °C, and 1100 °C; then, the surface morphology of the wafers after the thermal treatment was inspected via atomic force microscopy (AFM). In addition, to study the influence of the preheating temperature on the GaN epilayers, during the complete growth cycle, we chose three preheating temperatures at 500 °C, 800 °C, and 1100 °C as three paths of A, B, and C, respectively, as shown in Figure 1.
2.1.2. GaN Nucleation Layer Growth

After the substrate was preheated for 10 min, a 25-nm-thick GaN buffer layer was deposited on the substrate thermally treated at 500 °C for 82 s in a mixed (N₂ + NH₃) gas atmosphere. At the same time, trimethylgallium (TMGa) was carried into the chamber by N₂ gas. Afterwards, the temperature of the sample was raised from 500 °C to 1180 °C in 6.5 min, and the temperature was maintained at 1180 °C for 5 s in a mixed (N₂ + NH₃) gas atmosphere, and then the samples were naturally cooled to room temperature, then heated to 950 °C for the next step.

Here, we should mention that during the 82-s epitaxial process, TMGa and NH₃ were employed as the reactant source materials for Ga and N, respectively. Unlike how hydrogen was used as carrier gas in most previous attempts at GaN growth [9–20], nitrogen was used here, because β-Ga₂O₃ wafers would be etched by hydrogen [28]. Therefore, using N₂ as a carrier gas is necessary for the growth of III-nitrides in order to protect Ga₂O₃ from decomposition. Thus, this 25-nm GaN buffer layer was used not only for the nucleation layer, but also for preventing layers of the substrate from growing the following GaN epilayer in ambient hydrogen. Again, to investigate the effects of preheating, scanning electron microscope (SEM) images of the nucleation layers grown at different preheating temperatures were taken and evaluated.

2.1.3. Growth of the Undoped GaN Layer

In this step, when the temperature of the substrate reached the growth temperature of 950 °C, the carrier gas was changed to H₂ in order to grow better quality GaN films. At the same time, TMGa and NH₃ were again used as reactant source materials for Ga and N, respectively, to the undoped GaN (u-GaN) epilayer at 950 °C for 20 min. At this point, the u-GaN layer was about 1 µm thick. Finally, the sample was naturally cooled to room temperature in a pure N₂ gas atmosphere and moved out from the APMOCVD chamber.

2.2. Measurements

The crystalline qualities of the GaN films were investigated by performing high-resolution X-ray diffraction (HRXRD).

An optical microscope and SEM were used to examine the surface morphology and thickness of the GaN films.
The emission spectra of the GaN films were measured by a power-dependent photoluminescence (PL) measuring system; this was a 355-nm passive Q-switch laser passed through a neutral density (ND) filter and then focused on the samples using an objective lens with a numerical aperture (NA) of 0.25. The ND filter was used to adjust the focusing laser’s power. The fluorescence of the samples passed the same objective lens, reflected by a mirror through a high-pass filter. The high-pass filter filtered the wavelength below 360 nm in order to exclude the excitation light source from the optical spectrum analyzer.

3. Results and Discussions

3.1. Surface Morphology of the Substrate Versus Preheating Temperature

Figure 2a is an image showing the (−2 0 1) β-Ga2O3 wafers preheated at 500 °C (sample R), 600 °C (sample 1), 800 °C (sample 2), 950 °C (sample 3), and 1100 °C (sample 4). All samples show a mirror-like surface, suggesting a sufficient nitridation process. The surface roughness of each sample was measured using an atomic force microscope (AFM, Bruker, Germany). As shown in Figure 2b, the root-mean-square roughness of the β-Ga2O3 substrates increases with preheating temperature, with 0.383, 0.415, 0.593, 0.987, and 1.838 nm at temperatures of 500 °C, 600 °C, 800 °C, 950 °C, and 1100 °C, respectively, as shown in the summarized table in Figure 2c. These results indicate that the surface morphology of the (−2 0 1) β-Ga2O3 wafers is strongly affected by the preheating temperature. The β-Ga2O3 substrate preheated at 1100 °C had the roughest surface; we suppose that the crystalline quality of GaN film grown on this substrate should be the best.

![Figure 2](image_url)

**Figure 2.** (a) The photos of (−2 0 1) β-Ga2O3 wafers preheated at different temperatures. (b) The surface roughness of the (−2 0 1) β-Ga2O3 wafers after preheating was measured using an AFM; the results were 0.383, 0.415, 0.593, 0.987, and 1.838 nm at 500, 600, 800, 950, and 1100 °C, respectively. The detail information is summarized in (c).

<table>
<thead>
<tr>
<th>Samples</th>
<th>R</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<tr>
<td>Temperature (°C)</td>
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<td>600</td>
<td>800</td>
<td>950</td>
<td>1100</td>
</tr>
<tr>
<td>RMS of the surface (nm)</td>
<td>0.383</td>
<td>0.415</td>
<td>0.593</td>
<td>0.987</td>
<td>1.838</td>
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3.2. GaN Nuclear Layer Versus Preheating Temperature

25-nm-thick GaN buffer layers were created on the preheated β-Ga2O3 substrates at the different temperatures of 500, 800, and 1100 °C. The samples were labeled PH-500, PH-800, and PH-1100, corresponding to the preheating temperature. The GaN nuclear deposition of sample PH-500 was the same as its preheating temperature. Figure 3a,b shows 5000 and 50,000× magnification plan-view SEM images of the GaN buffer layers on these preheated substrates. In Figure 3a, cluster islands of the GaN can be observed on the surface of sample PH-500; in contrast, a layer of GaN film appears on the surface of samples
PH-800 and PH-1100. The magnified images (50,000×)—as shown in Figure 3b—provide the detailed morphology of the GaN nucleation layer. Both samples PH-800 and PH-1100 showed more GaN layer than the PH-500. The results show that the rougher the surface of the heat-treated substrate, the better the growth of the nucleation layer for further GaN growth.

3.3. Crystalline Quality of the GaN Film

Figure 4 presents symmetric X-ray rocking curves (XRCs) of the 1-μm (0 0 2) GaN film on these preheated substrates. The full widths at half maximum (FWHM) of the XRC of 1-μm-thick c-GaN layers on PH-500, PH-800, and PH-1100 are 2025, 1367, and 779 arcsec, respectively. It can be seen that the value decreases with preheating temperature. The FWHM of the XRC curve of sample PH-1100 is almost half of that of sample PH-800; this indicates that the crystalline quality of the GaN films is significantly improved. Therefore, the results of XRCs reveal that the crystalline quality of the directly grown GaN film can be improved by using substrates preheated at high temperatures.

We can furtherly verify the improvement by observing the surface morphology of the GaN film. The plan view of bright—(Figure 5a–c) and-dark field (Figure 5d–f) optical microscope (OM) images are shown in Figure 5. As shown in Figure 5b,c,e,f,i both bright-and dark-field OM images, the hexagonal structure of the GaN appears clearly on the surface of both samples PH-800 and PH-1100. In contrast, for sample PH-500, only cluster islands appear, as shown by the OM image in Figure 5a,d. These observations indicate a better crystalline quality of GaN via the substrate preheating method.
3.3. Crystalline Quality of the GaN Film

Figure 4 presents symmetric X-ray rocking curves (XRCs) of the 1-\(\mu\)m (0 0 2) GaN film on these preheated substrates. The full widths at half maximum (FWHM) of the XRC of 1-\(\mu\)m-thick c-GaN layers on PH-500, PH-800, and PH-1100 are 2025, 1367, and 779 arcsec, respectively. It can be seen that the value decreases with preheating temperature. The FWHM of the XRC curve of sample PH-1100 is almost half of that of sample PH-800; this indicates that the crystalline quality of the GaN films is significantly improved. Therefore, the results of XRCs reveal that the crystalline quality of the directly grown GaN film can be improved by using substrates preheated at high temperatures.

Figure 5. Optical microscopic images with 100× magnification of the 1-\(\mu\)m GaN film fabricated on the PH-500, PH-800, and PH-1100 substrates: (a–c) bright- and (d–f) dark-field OM images.

Figure 6 shows SEM (with 500× and 15,000× magnification) images of the GaN films on both samples PH-800 and PH-1100, providing further detail. As shown in Figure 6a,c, SEM images with 500× magnification of samples PH-800 and PH-1100 show the hexagonal structure and parallel stripes on the surface of the GaN films. In addition, from the plan-view SEM images with 15,000× magnification—as shown in Figure 6b—a clear hexagonal GaN structure on the surface of sample PH-800 is observed. In contrast, Figure 6d shows the formation of GaN islands on the surface of sample PH-1100, revealing a single crystal orientation. Thus, the results are consistent with the measurements of the XRCs. The crys-
talline quality of GaN on sample PH-1100 is better than that on sample PH-800. However, it should be noted that the high-density stripes observed on the surface of sample PH-1100 indicate that this film contains a lot of threading dislocation defects, which may affect further device fabrication applications.

Figure 6. Plan-view SEM images of the GaN films on PH-800 with (a) 500× and (b) 15,000× magnification, and on PH-1100 with (c) 500× and (d) 15,000× magnification.

3.4. Power-Dependent Photoluminescence

Figure 7 shows the power-dependent photoluminescence (PL) of the GaN films. The peak wavelength of the GaN film on PH-500 was from 364.68 nm to 365.16 nm, with the excitation intensity increasing from 0.8 W/cm² to 200 W/cm². The peak wavelength of the GaN film on PH-800 was from 364.645 nm to 365.74 nm, with the exciting intensity increasing from 0.8 W/cm² to 200 W/cm². The peak emission wavelength was slightly redshifted, with the exciting power increasing due to the thermally induced bandgap reduction. With the exciting intensity increasing from 0.8 W/cm² to 200 W/cm², the peak wavelength of the GaN film on PH-1100 was almost maintained at 364.19 nm. This result reveals that the GaN film on PH-1100 was thermally stable. The peak wavelength was consistent with the bandgap of GaN (Eg = 3.4 eV at 300 K) [37]. The luminescence spectrum of the GaN film was affected by the film quality and defects [38,39]. The bandgap and defect luminescence depended on the incident light intensity linearly and nonlinearly, respectively [40]. Higher intensity and shorter linewidth of the PL spectra proved the better quality and fewer defects of the grown film. The PL intensity of PH-800 and PH-1100 was similar, and higher than that of PH-500. Therefore, the quality of the GaN films on PH-800 and PH-1100 was better than that of the GaN film on PH-500. The linewidths of the GaN films on PH-500, PH-800, and PH-1100 at an exciting intensity of 200 W/cm² were 14.516 nm, 13.064 nm, and 15.968 nm, respectively. According to the PL linewidth,
the GaN film on PH-800 has fewer defects. Although PH-1100 has the best crystal quality, the surface defects may cause the spectrum to broaden.

![Figure 7. The power-dependent photoluminescence (PL) of the GaN films on PH-500, PH-800, and PH-1100.](image-url)
3.5. 2-μm-Thick GaN Film Growth on Substrate without Preheating

It is well known that the crystal quality of the GaN film on the substrate can be improved by growing thicker films. Therefore, we used the fabricated sequence of sample PH-500 to grow a 2-μm GaN layer on a β-Ga2O3 substrate. Figure 8 shows the results of the 2-μm u-GaN layer on the (−2 0 1) β-Ga2O3 substrate. Figure 8a shows an image of the 2-μm u-GaN film on the (−2 0 1) β-Ga2O3 substrate, which resembles a flat mirror. The OM images show the flat surface morphology of the GaN film with 10× and 100× magnification, as shown in Figure 8b. Figure 8c is a plan-view SEM image showing the surface of the GaN epilayers with 500×, 5000×, and 10,000× magnification. The defects in this type of GaN growth are inverted hexagonal pyramids, or “V-type” pits [41], which can be seen in the SEM images. The FWHM of the XRC of the 2-μm-thick c-GaN layers was 1028 arcsec—as shown in Figure 8d—which is almost comparable with that of the 1-μm-thick c-GaN layers on sample PH-800. This indicates that, indeed, preheating (−2 0 1) β-Ga2O3 substrate is an efficient method of improving the crystal quality of GaN films, providing better grounds for further device fabrication applications.

4. Conclusions

We have successfully demonstrated a simple way to obtain a better crystalline quality in a thinner GaN film grown on preheated (−2 0 1) β-Ga2O3 substrate. The XRC FWHM
of the 1-μm-thick c-GaN layer on the preheated substrate at 800 °C and 1100 °C was 1367 arcsec and 779 arcsec, respectively. The 1-μm-thick and 2-μm-thick c-plane GaN layers grown on the substrate at 500 °C showed an XRC FWHM from 2025 to 1025 arcsec. The FWHM of the XRC of the 2-μm-thick c-GaN layers was almost comparable with that of the 1-μm-thick c-GaN layers on sample PH-800. This indicates that preheating (~2 0 1) β-Ga2O3 substrate is an efficient method of improving the crystalline quality of GaN films. The power-dependent PL showed relatively fewer defects on sample PH-800 due to high intensity and short linewidth. For this reason, the high-temperature preheated substrates obtain better crystalline quality in a thinner GaN film, which is an important and simple way to improve GaN-based devices fabricated on β-Ga2O3 wafers.

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**References**


