Microstructures of GaN Thin Films Grown on Graphene Layers

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The growth of high-quality gallium nitride (GaN) thin films on graphene layers has paved the way for a new field of transferable optoelectronics and electronics.[1] High-quality films are grown on graphene layers using ZnO nanowalls and a low-temperature GaN (LT-GaN) buffer layer grown at 600 °C as intermediate layers. Due to the layered structure of graphene, the GaN films can be easily transferred to foreign substrates, enabling the fabrication of transferable light-emitting diodes (LEDs). To further exploit GaN films in more sophisticated devices, such as transferable lasers or high-electron mobility transistors, films should be prepared with a low density of threading dislocations, which are reported to be critically deleterious to device performance.[2,3] Thus, threading dislocation characteristics in GaN films need to be investigated. Other microstructural properties, including crystalline orientation and grain boundaries in the films, should also be thoroughly investigated. However, the microstructural properties of GaN thin films grown on graphene layers have rarely been studied.[4] In this letter, we report the microstructural properties of GaN thin films and the interface between GaN and ZnO nanowalls on graphene layers.

The microstructural properties of GaN thin films on graphene layers were investigated by plan-view dark field (DF) images and selected area electron diffraction (SAED) (Figure 1a and b). Although threading dislocations were observed in the two-beam DF image in Figure 1a, the SAED in the inset of Figure 1a shows clear six-fold symmetry, representing single crystalline hexagonal structure in this region. However, many of the two-beam DF images taken from other regions show low-angle grain boundaries composed of dislocation cores in a curved line. The representative feature of the low-angle grain boundary and the SAED from the relevant region are shown in Figure 1b and the inset of Figure 1b, respectively. The misorientation angles measured from two diffraction patterns of adjacent grains were less than 3°. Low-angle grain boundaries in GaN thin films are believed to be formed from both grain boundaries of the graphene layers and coalescence of the adjacent nuclei in the early stage of the GaN growth. Even though most of the misorientations occurred due to the high interface energy between GaN nuclei and the growth template, the misorientation angle was less than 3° presumably because it is based on epitaxial growth on single crystalline substrates. The lateral grain size related to those low angle grain boundaries, measured from plan-view DF images, was in the range of 0.3–4 μm. Large-angle grain boundaries were not observed in the region available for electron diffraction analysis, which was about 60 μm in our plan-view specimen. Furthermore, we investigated the crystallinity of the GaN films on a much larger scale by X-ray diffraction (XRD) since the probe size of the XRD measurement is as large as a few millimeters. The typical 0–2θ XRD measurement in the previous report verified highly c-axis oriented crystal structure of the GaN films.[5] In addition, azimuthal Φ-scans exhibited six distinct peaks separated by 60° which indicate six-fold symmetry of the GaN films (not shown here).

The two-beam DF images shown in Figure 1a and b were taken with g = [1120] and a specimen tilt of about 18° from the [0001] zone axis, which allowed total threading dislocation densities to be properly assessed.[6] The threading dislocations were identified as pairs of spots, the small length of a line, and a mixture of spots and lines, depending on the dislocation type.[6] To calculate the total threading dislocation density in GaN films, 15 different DF images were taken at random positions on a scale of 2 μm, and the number of the threading dislocations were counted excluding dislocation cores localized at low-angle grain boundaries. The estimated total threading dislocation density ranged from 1.2 × 10^9 to 2.4 × 10^9 cm⁻², comparable to that of GaN grown on Si (111) substrates using an AlN buffer layer (1.1 × 10^9 to 5.8 × 10^9 cm⁻²) and slightly higher than that of GaN grown on sapphire substrates (7.6 × 10^9 to 7.45 × 10^9 cm⁻²).[7,8] Threading dislocation types in the GaN thin films were determined by applying the g ⋅ b criterion to the two-beam DF images of cross-sectional TEM specimen, which were recorded near the [1100] zone axis with g = [1120] and [0002] in Figure 2a and b, respectively.[9] The perfect dislocations that often occur in hexagonal GaN have three types of Burgers vectors: i) a = 1/3 <2110>, ii) c = <0001>, and iii) a + c = 1/3 <2113>.[10] The dislocations with the a-component are visible in the g = [1120] two-beam images, and those with the c-component are visible in the g = [0002] two-beam images. Because the threading dislocations have a dislocation line vector parallel to the c-axis, the dislocations only shown in the g = [1120] two-beam image are pure edge a-dislocations, and those only shown in the
longer growth time for obtaining LT-GaN buffer layer on ZnO compared to that in the GaN on sapphire. It is likely that much may be attributed to higher density of screw-type dislocations.

Figure 2a and b. Specific grains that were not activated appeared as a black region, although the adjacent grain was activated, because the tilting angle for the two-beam condition differed with respect to grain orientation. However, this phenomenon did not occur in the $g = [0002]$ two-beam DF image in Figure 2a, indicating that those grains had the same $c$-axis orientation. Thus, lines between those grains marked with arrows in Figure 2b are low-angle grain boundaries, which we investigated using TEM plan-view analysis earlier, and they had only in-plane misorientations. As shown in Figure 2a and b, those grain boundaries and the many threading dislocations started from the LT-GaN buffer layer which has columnar structures.

We also investigated the microstructural properties of the LT-GaN buffer layer grown on the ZnO nanowall intermediate layer. For this analysis, only an LT-GaN buffer layer was grown on ZnO nanowalls; it was not exposed to high-temperature growth conditions because of potential changes in the structures of the intermediate layers. The bright field (BF) image in Figure 3a shows that ZnO nanowalls were formed on the graphene layers with a thickness of 160 nm which was also confirmed clearly in energy dispersive X-ray spectroscopy mapping analysis (not shown here). The LT-GaN buffer layer with columnar structures was grown on the ZnO nanowalls with a thickness of 400 nm.

As shown in Figures 3b and c, SAED patterns were also taken from the upper part of the LT-GaN buffer layer and the LT-GaN/ZnO interface, respectively. The SAED pattern shown in Figure 3b indicates that LT-GaN has a cubic structure with a high density of stacking faults, similar to the crystal structure of LT-GaN on sapphire substrates. Additional diffraction spots relevant to the hexagonal ZnO nanowall intermediate layer are also shown in Figure 3c, indicating that hexagonal (h) ZnO nanowalls and cubic (c) GaN had the orientation relationship of GaN $\{11\bar{1}0\}$ $\{\bar{2}1\bar{1}0\}$ and GaN $\{110\}$ $\{\bar{2}1\bar{1}0\}$, and GaN $\{11\bar{1}0\}$ $\{\bar{2}1\bar{1}0\}$. The overall orientation relationships of HT-GaN/LT-GaN/ZnO nanowalls/graphene layers are also represented in Table 1.

According to the TEM analysis, the LT-GaN buffer layer has a cubic rather than hexagonal structure, even though it was grown on hexagonal ZnO nanowalls. This indicates that the effect of thermodynamic growth conditions, such as temperature, was stronger than the effect of the type of substrate or template layers for determining the crystal structure of the GaN.

g = [0002] two-beam image are pure screw $c$-dislocations. Moreover, the dislocations shown in both the $g = [11\bar{2}0]$ and $g = [0002]$ two-beam images are mixed $a$–$c$ dislocations. Most of the dislocations shown in the $g = [11\bar{2}0]$ two-beam image are also shown in the $g = [0002]$ two-beam image, indicating that predominant dislocations in GaN thin films grown on ZnO-coated graphene layers were mixed-type dislocations. Limited numbers of edge- and screw-type dislocations were present and are marked in Figure 2a and b. The predominance of the mixed-type dislocations for GaN films grown on graphene layers differed from previous reports that the dominant threading dislocation types in GaN grown on sapphires substrates are pure edge-type dislocations. Mixed-type dislocations in GaN films are usually a result of reactions between edge-type and screw-type dislocations. Accordingly, predominance of mixed-type dislocations may be attributed to higher density of screw-type dislocations compared to that in the GaN on sapphire. It is likely that much longer growth time for obtaining LT-GaN buffer layer on ZnO coated graphene layers causes larger out-of-plane distortions on the surface, resulting in increase in the number of screw-type dislocations.

The grain boundaries between grains with different in-plane orientations are also shown in the two-beam DF image with $g = [11\bar{2}0]$ in Figure 2b. Specific grains that were not activated appeared as a black region, although the adjacent grain was activated, because the tilting angle for the two-beam condition differed with respect to grain orientation. However, this phenomenon did not occur in the $g = [0002]$ two-beam DF image in Figure 2a, indicating that those grains had the same $c$-axis orientation. Thus, lines between those grains marked with arrows in Figure 2b are low-angle grain boundaries, which we investigated using TEM plan-view analysis earlier, and they had only in-plane misorientations. As shown in Figure 2a and b, those grain boundaries and the many threading dislocations started from the LT-GaN buffer layer which has columnar structures.
films, which is consistent with the previous study of GaN on sapphire substrates.\(^\text{[15,16]}\) This suggests that the LT-GaN buffer layer grown on ZnO-coated graphene layers was similar to the LT-GaN buffer layer grown on sapphire substrates in terms of the structural properties. Nevertheless, the LT-GaN buffer layer on ZnO-coated graphene layers was much thicker than the LT-GaN buffer layer on sapphire substrates in order to protect the ZnO nanowall intermediate layer which is otherwise destroyed in HT-GaN growth step, as discussed in the Experimental section. However, the thickness of the LT-GaN buffer layer was reported to be crucial in determining the crystallinity of the HT-GaN films.\(^\text{[18–20]}\) Thus, the thickness of the LT-GaN buffer layer needs to be optimized so that it is thick enough to protect the ZnO nanowall intermediate layers and thin enough to prevent deterioration of optical properties.

The microstructures of epitaxial GaN thin films grown on graphene layers using ZnO nanowalls and LT-GaN buffer layers were investigated using TEM. The predominant dislocations in the GaN thin films grown on ZnO-coated graphene layers were mixed-type dislocations. The typical threading dislocation density in the films was determined to range from \(1.2 \times 10^9\) to \(2.4 \times 10^9\) cm\(^{-2}\), which is comparable to that of GaN on Si substrates and slightly higher than that of GaN on sapphire substrates.

Moreover, GaN films that were grown at high temperatures showed highly \(c\)-axis-oriented crystal structures, and the in-plane misorientation angle between the grains was less than 3°. Because the growth parameters, including LT-GaN buffer layer thickness, have yet to be optimized, there is still room to improve the crystalline quality of the GaN thin films for a promising future in transferable optoelectronics applications.

**Experimental Section**

**Preparation of Graphene Layers:** Graphene layers were mechanically exfoliated from single crystalline graphite flakes using Scotch tape and transferred onto SiO\(_2\)/Si wafer. Oxygen-plasma treatment was performed at an oxygen partial pressure of 100 mTorr and an applied current of 30 mA. The reactor pressure and temperature during growth were maintained at 3 Torr and 600 °C, respectively. As previously reported, high-density ZnO nanowalls play an important role in the heteroepitaxial growth of GaN on graphene layers.\(^\text{[21]}\) Similarly, it was reported that a very small lattice mismatch with the same crystal structure enables the epitaxial growth of GaN on ZnO, fabricating GaN/ZnO heterostructures in the form of films or coaxial nanostructures.\(^\text{[21,22]}\) However, the ZnO is vulnerable to H\(_2\) ambient gas and high temperatures, necessary conditions for growing high-quality GaN films. Accordingly, an LT-GaN buffer layer was grown on the ZnO nanowall intermediate layer with sufficient thickness to protect the ZnO nanowalls during HT-GaN growth.\(^\text{[12,23]}\) The reactor pressure and temperature during the LT-GaN buffer layer growth were kept at 200 Torr and 600 °C, respectively, and hydrogen was used as a carrier gas in a H\(_2\) atmosphere. The typical thickness of the GaN thin films grown for 1 h was 5 μm.

**MOCVD Growth of GaN Thin Films:** After LT-GaN buffer layer growth, high-quality GaN thin films were grown at 1130 °C. During high-temperature growth, the reactor pressure was maintained at 100 Torr, and hydrogen was used as a carrier gas in a H\(_2\) atmosphere. The typical thickness of the GaN thin films grown for 1 h was 5 μm.

**TEM Analysis of GaN Thin Films on ZnO-Coated Graphene Layers:** To sample plan-view TEM specimens of the GaN thin films, several steps were required to obtain only the GaN thin films. The GaN films grown on ZnO-coated graphene layers were readily exfoliated from the SiO\(_2\)/Si substrate by attaching it to a slide glass with crystal wax. The graphene layers were exfoliated mechanically using Scotch tape to separate the graphene layers from GaN films. Using acetone, the remaining GaN films on the ZnO layers were exfoliated from the slide glass and attached to a TEM hole grid using M-Bond. Finally, ion milling was performed to thin the GaN films. TEM cross-section specimens of the GaN films and LT-GaN buffer layers were prepared using a focused ion beam (FIB) etching technique. A 200 kV field-emission TEM instrument (Tecnai F20) was used for SAED, BF imaging, and DF imaging.

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