Realization of Ga-polarity GaN films in radio-frequency plasma-assisted molecular beam epitaxy

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Abstract

GaN heteroepitaxial growth on sapphire (0001) substrates was carried out by radio-frequency (RF) plasma-assisted molecular beam epitaxy. The lattice polarity of RF-MBE-grown GaN films on sapphire (0001) substrates was investigated as a function of buffer layer process. GaN films with Ga-face lattice polarity were fabricated using an AlN high-temperature buffer layer before GaN growth. Direct measurements by coaxial impact collision ion scattering spectroscopy, as well as reflection high-energy electron diffraction, scanning electron microscope observations of surface morphologies and chemical etching, confirmed the polarity assignment. Realization of Ga-polarity films on sapphire substrates by RF-MBE is a promising result and is expected to lead to a breakthrough in fabricating high-quality MBE-grown III-nitride films for device applications. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, lattice polarity in III-nitride films becomes a hot topic due to its great influence on the optical and electrical properties [1]. Several techniques have been applied to characterize the film polarity, such as convergent beam electron diffraction (CBED) [2,3], hemi-spherically scanned X-ray photoelectron diffraction (HSXPD)[4], Rutherford backscattering ion channeling [5], chemical wet etching [6] and surface reconstruction as observed by reflection high-energy electron diffraction (RHEED) [7], etc. Based on these results, Ga-polarity films are believed to be typical of metalorganic chemical vapor deposition (MOCVD), which is known to be the most suitable technique for III-nitride growth at present. Contrary to the case of MOCVD, the lattice orientation of conventional molecular beam epitaxial (MBE)-grown samples are assumed to be predominately N-polarity [1]. It
is well known that MBE is one of the most successful techniques for III–V semiconductor growth. However, for the case of III-nitride materials, the quality of MBE-grown films is usually poor compared with those grown by MOCVD with electrical properties suffering the most. Many efforts have been made to improve the quality of MBE-grown film using a variety of techniques, for example, using MOCVD-grown GaN templates as substrates [8], In-doping [9–11], and NH3 as a nitrogen source [12,13]. Several groups have reported high electron mobilities [8,13]. However, the essential reason behind the quality improvements observed is not clear. Recently, we have shown that GaN growth carried out under Ga-polarity conditions results in high film quality in MBE [14]. Therefore, the realization of growth using Ga-face polarity in MBE has become an important subject. In addition, it is well known that Ga-face GaN films have additional advantages compared to N-face samples, such as smoother surface morphology, stable chemical and thermal properties, enhanced two-dimensional electron density, etc. [1]. However, it is still uncertain how to obtain Ga-polarity GaN films on sapphire substrates by MBE at present.

In this study, we investigated the film polarities of MBE-grown GaN epilayers concentrating on the use of different buffer layer processes during the initial stages of growth by radio-frequency plasma-assisted MBE (RF-MBE). The buffer layer formation of GaN or AlN was performed in both the low- (LT) and high-temperature (HT) regions in the initial growth stage, and GaN layers subsequently grown on them were compared. RHEED, surface morphology observations, wet chemical etching and direct clarification of surface polarity by coaxial impact collision ion scattering spectroscopy (CAICISS) were applied to identify the lattice polarity of the as-grown GaN films.

2. Experimental procedure

The GaN films were grown on sapphire (0001) substrates by RF-MBE. LT, HT GaN and AlN buffer layers were deposited during the initial growth stage, respectively. The LT buffer layer process here means buffer layer growth at about 500°C, where an amorphous layer was first formed before recrystallization. The HT buffer layer process here is defined as when the buffer layer was grown at 700°C, where a crystallized layer was directly grown on the substrate. The thickness of both the LT and HT buffer layers was 20 nm before the main GaN growth. Except for the use of different buffer layer processes, other growth conditions were kept the same for the main GaN growth. The growth processes and conditions are as follows. Before depositing buffer layers, the substrate was exposed to a N2-plasma flux at 700°C for 5 min to induce nitridation. After this step, the different buffer layer growth procedures as described above were applied. A GaN film was then subsequently grown on the buffer layer. During the growth of the GaN film, the N2-plasma power was kept at 350 W and the N2 flow rate was 5 sccm. The growth temperature was fixed at 700°C and the growth rate was 0.6 μm/h. The total thickness of the GaN film was about 1.2 μm.

Wet chemical etching of GaN films was carried out using a NaOH solution (1.8 mol NaOH solution [10] or a NaOH:H2O2:H2O = 5 g:20 cm3:5 cm3) about 20 min at room temperature. The CAICISS technique was used to clarify the lattice polarity directly. In the CAICISS measurements, a He+ ion beam was employed as an incident beam.

3. Experimental results and discussions

3.1. In situ RHEED observations of GaN surface

Table 1 gives the results of RHEED observations taken during and after the growth. As a reference, the results of RHEED by Smith et al. [7] are also shown. RHEED showed (1 × 1) streak patterns during the growth of GaN, regardless of the buffer layers. However, various RHEED patterns with different reconstructions were observed when the substrate temperature was decreased after growth. For the case of the LT GaN or AlN, and HT GaN buffer layers, a (3 × 3) reconstruction (and sometimes a (1 × 3) pattern) was usually observed. According to Smith et al. [15], these types of reconstruction typically reflect the presence of a N-polarity GaN surface. On the other hand, other types of
Table 1  
Surface reconstruction of GaN epilayers grown on different kinds of buffer layers  

<table>
<thead>
<tr>
<th></th>
<th>During the growth at $T_g = 700 \degree C$</th>
<th>After the growth during lowering down the $T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LT GaN buffer</td>
<td>$1 \times 1$</td>
<td>$3 \times 3, 1 \times 3$</td>
</tr>
<tr>
<td>HT GaN buffer</td>
<td>$1 \times 1$</td>
<td>$2 \times 2, 1 \times 2, 5 \times 5$</td>
</tr>
<tr>
<td>LT AlN buffer</td>
<td>$1 \times 1$</td>
<td>$3 \times 3, 6 \times 6, c(6 \times 12)$</td>
</tr>
<tr>
<td>HT AlN buffer</td>
<td>$1 \times 1$</td>
<td>$2 \times 2, 1 \times 2, 5 \times 5, 6 \times 4$</td>
</tr>
<tr>
<td>Conventional MBE-grown GaN on sapphire $^b$</td>
<td>$1 \times 1$</td>
<td>$3 \times 3, 6 \times 6, c(6 \times 12)$</td>
</tr>
<tr>
<td>MBE-grown GaN on a MOCVD template $^c$</td>
<td>$1 \times 1$</td>
<td>$2 \times 2, 1 \times 2, 5 \times 5, 6 \times 4$</td>
</tr>
</tbody>
</table>

$^a$LT: low temperature, HT: high temperature, $T_g$: growth temperature.  
$^b$Assumed to be N-polarity [15].  
$^c$Assumed to be Ga-polarity by Smith et al. [15].

reconstructions ((2 × 2), (1 × 2) and (5 × 5)) was observed with the use of HT AlN buffer layers, depending on the growth conditions. When growth was carried out under Ga-rich (Ga-droplets present on the surface) conditions, a (5 × 5) reconstruction was always visible. When growth was done near stoichiometric growth conditions, a (2 × 2) or (1 × 2) reconstruction were observed. These trends agree well with the observations of RHEED reconstructions of the Ga-polarity films grown on MOCVD-grown GaN substrates [7]. Therefore, it is suggested that GaN film with Ga-polarity can be achieved by using HT AlN buffer layer process, while other buffer layers result in N-polarity films.

3.2. Wet chemical etching of the GaN surface

Surface morphologies of GaN films with different buffer layer processes were also characterized by secondary electron microscopy (SEM) observations and wet chemical etching. Fig. 1 shows typical surface images of 1.2 μm-thick GaN films with a GaN HT buffer layer (Fig. 1(a)) and an AlN HT buffer layer (Fig. 1(c)), for which RHEED (3 × 3) and (1 × 2) patterns were observed after growth, respectively. It is clear that the film with a HT GaN buffer layer consists of hexagonal domains, while the film with an AlN HT buffer layer shows a very uniform and flat morphology. Surface morphologies after wet chemical etching by a NaOH solution are shown in Figs. 1(b) and (d), respectively. It is obvious that the film with a HT GaN buffer layer can be etched rapidly and the surface becomes very rough (Fig. 1(b)). On the other hand, the film with an AlN HT buffer layer shows much less etching and has a flat morphology even after etching (Fig. 1(d)). This result agrees well with the conclusion from MOCVD-grown films that films with hexagonal pyramidal morphology grown on sapphire are N-face and smooth films are usually Ga-face [1]. GaN films with LT buffer layers also show the similar behavior as that shown in Figs. 1(a) and (b). Based on the above results, the correlation between RHEED reconstruction and surface morphology has been used to confirm the lattice polarity of GaN films. This result also implies that it is possible to obtain Ga-polarity films by growing a HT AlN buffer layer in MBE.

3.3. Direct characterization of lattice polarity by CAICISS

Recently, the CAICISS technique has been shown to be a direct way to characterize the lattice polarity of GaN films [16,17]. We applied this technique to our GaN films to directly characterize the lattice polarity. Fig. 2 shows CAICISS results for two kinds of GaN samples with HT AlN and GaN buffer layers. The figure shows the polar angle (the beam incident angle of He$^+$ with respect to the normal to the (0001) surface) dependence of the Ga signal intensity. It is clear that two large peaks around 20° and 40° were observed from the film.
Fig. 1. Surface morphologies observed by secondary electron microscopy: (a) a GaN film with a HT GaN buffer layer, (b) the same GaN film shown in (a) after etching in a NaOH solution, (c) a GaN film with a HT AlN buffer layer, (d) the same GaN film shown in (c) after etching in a NaOH solution.

3.4. Discussions

The experimental results described above clearly show that the Ga-polarity GaN film can be realized even in RF-MBE growth by the use of a HT AlN buffer layer, while other kinds of buffer layers result in N-polarity films. During the growth of HT and LT AlN buffer layers on sapphire substrates, we observed different growth behavior by in situ RHEED observations. In the growth of the HT AlN buffer layer, the RHEED pattern became a little dark in the very early stages of growth (~4 nm growth). Subsequently, the RHEED
Fig. 2. Polar angle (beam incident angle of He$^+$ with respect to the normal to the (000 1) surface) dependence of Ga signal intensity of GaN films grown using a HT AlN buffer layer (upper curve) and a HT GaN buffer layer (lower curve), by CAICISS measurements.

pattern of AlN became streaky and bright indicating that the AlN growth was two-dimensional under near-stoichiometric conditions. On the other hand, the LT AlN buffer layer was amorphous as initially deposited. The crystallization process under a nitrogen-plasma flux exposure resulted in a spotty RHEED pattern. The above growth behaviors indicate that the growth processes of HT and LT AlN buffer layers are different, where surface conditions (such as the III/V ratio and crystallization process, etc.) are presumably different. Recent theoretical calculations [18] considering surface energy stability suggested that the lattice polarity of AlN on sapphire substrates is determined by the surface conditions. Therefore, our experimental results concerning the lattice polarity obtained when using HT and LT AlN buffer layers may be explained by differing surface conditions. It is still unknown why GaN buffer layers result in a N-face polarity in RF-MBE, regardless of the formation temperature. RHEED pattern of the HT GaN buffer layers growth did not darken at very early stage as HT AlN buffer did, while the RHEED pattern of LT GaN buffer layer growth showed the same behavior as that of LT AlN buffer one. We hypothesize that the mechanisms for GaN buffer layers resulting in N-polarity may also be related to the surface energy. GaN buffer layers may prefer to form N-polarity than Ga-polarity in RF-MBE growth conditions. To completely understand the mechanism of the lattice-polarity formation with buffer layers, more detailed investigations, such as high-resolution cross-sectional transmission electron microscopy (HRTEM) and theoretical studies, are necessary.

It is necessary to point out that the buffer layer effects on the lattice polarity described in this study are available using the RF-MBE growth technique. However, the details may be different from those of other growth techniques, such as MOCVD. The differences in the source materials, growth environments (temperature, pressure, etc.) and the surface reaction process between growth techniques most likely lead to different results. However, the realization of a Ga-polarity film is essential because it is expected to lead to a dramatic improvement in the film quality [14].

4. Summary

The lattice polarity of RF-MBE-grown GaN films on sapphire (0001) substrates was investigated using different buffer layer processes. We succeeded in obtaining Ga-polarity GaN films by using an AlN HT buffer layer process, while other kinds of buffer layer processes resulted in N-polarity films. In situ RHEED, SEM observations of surface morphology before and after wet chemical etching, and direct measurements by CAICISS confirmed the lattice polarity assignment. Realization of Ga-polarity films on sapphire substrates by RF-MBE is a promising result and is expected to lead to a breakthrough in obtaining high-quality MBE-grown III-nitride films for device applications.

Acknowledgements

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References