X-ray diffraction characterization of epitaxial zinc-blende GaN films on a miscut GaAs(0 0 1) substrates using the hydride vapor-phase epitaxy method

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Abstract

In this study, cubic GaN epitaxial films are grown on a $2^\circ$ miscut GaAs(0 0 1) substrate by hydride vapor-phase epitaxy reactor with a low-temperature GaN buffer layer before the growth of the GaN epitaxy film. X-ray diffraction spectra reveal that the epitaxial film contains most of the zinc-blende GaN with a few percent of wurtzite GaN also embedded in the film. The crystalline coherence length of the zinc-blende GaN is 30 nm and the rocking curve width is 4.8\textdegree. In addition, two small peaks in two-fold symmetry which did not correspond to the substrate orientation relation of GaN(0 0 1)$\parallel$GaAs(0 0 1) and GaN(0 1 0)$\parallel$GaAs(0 1 0). These two small peaks were grown along the miscut direction of the substrate. Photoluminescence spectra confirm that a cubic GaN edge emission peak appears at 388 nm as well as a strong yellow emission at 500 nm region.

Keywords: Cubic GaN; X-ray; Hydride vapor-phase epitaxy

1. Introduction

Gallium nitride (GaN) is a promising wide-band gap material for light emitting devices in the blue region. The band gap energy is $E_g = 3 \times 18$ and 3.39 eV for cubic (zinc-blende structure) and hexagonal (wurtzite structure) symmetry at room temperature, respectively [1]. Growing a cubic GaN is a priority concern. For instance, fabricating a laser diode by cleaving the wafer to form the facet faces requires an epitaxial GaN film with cubic symmetry instead of hexagonal symmetry. Furthermore, before Nakamura et al. [2] successfully obtained p-type GaN by N$_2$-ambient thermal annealing, Pankove [3] reported that the cubic form of GaN may be more amenable to p-type doping than hexagonal GaN. However, the hexagonal symmetry appears to be more stable than the cubic symmetry. Therefore, preparing a GaN film with zinc-blende type is quite difficult [4,5]. Especially, the lattice mismatch is as large as 19.9\% between...
the GaN and GaAs. In addition, hydride vaporphase epitaxy (HVPE) is a viable alternative owing to its faster growth rate than MOCVD methods [6,7]. Nevertheless, by HVPE method, Tsuchiya et al. [8,9] successfully grew zinc-blende and wurtzite structure on the thin MBE-GaN/GaAs(0 0 1) and thin MBE-GaN/GaAs(1 1 1) substrate, respectively. However, to prepare an MBE-GaN buffer layer is no light work. Direct HVPE on miscut substrate might be possible to grow cubic phase in a particular direction. It should be born in mind that a miscut of the substrate is essential in ensuring the epitaxial growth by step flow process. For instance, the substrate with a miscut along the GaAs[1 1 0] was used for the growth of AlGaInP [10]. According to the work of Yamaguchi et al. [11], a pure wurtzite GaN structure can be grown on a miscut GaAs substrate. Growth of a pure cubic GaN film might also be possible on a substrate with an appropriate miscut direction and miscut angle. In this study, we report on HVPE-grown cubic GaN films with a miscut GaAs substrate. A low-temperature HVPE-grown buffer layer was prepared before the growth of the cubic epitaxial GaN film. In addition, we adopt $\phi$-scan (or $hk$-circle scan) to further verify the in-plane epitaxy relation on the miscut substrate.

2. Experimental procedure

The samples were deposited by HVPE with a GaCl and NH$_3$ as Ga and N sources at atmospheric pressure. As Fig. 1 depicts, the apparatus is a vertical quartz reactor system. The GaCl compound was prepared by reacting the HCl gas with Ga solid at 700°C in region I of Fig. 1. The wafer holder was tilted 15° relative to the gaseous stream direction in an attempt to reduce undesirable reactions between GaCl compounds and NH$_3$ gas, as well as to improve the uniformity of the grown GaN film on a 2" diameter substrate. A significant amount of H$_2$ acting as a carrier gas was fed through a delivery tube to the slanted substrate at a high flow rate of around 13.5 l/min. The HCl and NH$_3$ flow rates were 80 and 2400 cc/min, respectively. The molar ratio of NH$_3$ to GaCl was around 30, i.e. lower than that in the growth process of MOCVD (exceeding 1000). This difference in molar ratio may be due to the fact that the HVPE is a hot wall system that decomposes the NH$_3$ into active N atoms more effectively. The GaAs substrates used in this study were cut with 2° misorientation along the [1 0 0] direction. The substrate was pretreated with HCl gas for 2 min at 700°C in the reactor. Before growth of GaN, a GaN buffer layer was initially deposited and then the substrate temperature was raised to the growth temperature for about 60 min in the flow of hydrogen and ammonia. The GaN growth rate is approximately 0.1 µm/min. Two samples, 401 and 411, were deposited with the buffer layer grown at temperatures of 545 and 525°C. Finally, the GaN films were grown at higher temperatures of 780 and 750°C, respectively.

The GaN film thickness and surface morphology were measured by optical microscopy (OM). X-ray diffraction was performed to analyze the crystallization of thin films. The measurement was taken using a high-resolution setup of X-ray diffractometer, which consists of an 18 kW rotating anode X-ray generator (Cu target), and a Huber 5042 large diffractometer. In this experiment, a Ge(1 1 1) monochromator and 200 µm precision slits were
used to filter out the Cu Kα2 and Kβ; only Kα1 line was used. Five different X-ray diffraction methods were employed: (1) the conventional 0/20 scan normal to the epitaxial plane, (2) grazing incidence X-ray diffraction and (3) φ-scan (or hk-circle scan) around the GaN[0 0 1] or GaAs[0 0 1] axis to probe the in-plane epitaxial relation. The scan geometry on the sample are shown in Fig. 2. The hk-circle scan is shown as dash line in the figure. The scattering vector is kept as constant, while the sample is rotated azimuthally. (4) X-ray radial scans across reciprocal lattice along different directions, such as GaN[0 0 2], GaN[2 0 0] and GaN[0 2 2], in order to measure the anisotropic strain field. During the radial scan, the reciprocal lattice vectors of the samples to be measured were adjusted by the φ-circle and X-circle of the Eulerian cradle of a standard four circle diffractometer, so that the reciprocal lattice vectors were aligned to the scattering plane and 0/20 scans followed. (5) Rocking curve measurements with fixed scattering vectors were also performed to measure the spread of crystalline orientations. In addition, luminescence was studied by photoluminescence (PL) at room temperature. Furthermore, the Hall effect was used to measure the electrical properties at room temperature.

3. Results and discussion

3.1. X-ray diffraction measurement

Both samples 401 and 411 were measured with X-rays. The results indicate that the structures of these two samples grown at different temperatures are very similar to each other within our measurement accuracy. Both epitaxial films are predominant in zinc-blende structures with the lattice parameters close to 0.4526 nm. The epitaxial relations to the substrates are as follows: GaN(0 0 1)||GaAs(0 0 1), GaN(0 1 0)||GaAs(0 1 0) and GaN(1 0 0)||GaAs(1 0 0). Fig. 3 shows the 0/20 scan along the plane normal direction, in which, two zinc-blende GaN peaks of (0 0 2) and (0 0 4) appear at 2θ equal to 39.8 and 86.6°, respectively. In contrast to the results of Miura et al. [12], some wurtzite inclusions were still found in the films grown by us. For instance, wurtzite GaN peaks, e.g. (0 0 0 2) and (1 0 1 0), also appeared. The coexistence of zinc-blende and wurtzite structures are quite common in the HVPE growth process [13,14]. Tsuchiya et al. [15] observed that a pure zinc-blende structure could only be grown at a narrow temperature range around 900°C. However, the sample prepared by Tsuchiya et al. is only measured by X-ray 0/20 scan which reveals only the plane normal epitaxial relation. In this work, the hk-circle scan shows the in-plane epitaxial relation.

![Fig. 2. The scan geometry of φ-scan (or hk-circle scan) rotated about the GaN[0 0 1] or GaAs[0 0 1] axis with the scattering vector fixed at GaN[0 2 2]. The dash line indicates the scan direction. Two small extra peak marks as "S" were found.](image1)

![Fig. 3. The X-ray diffraction reveals the 0/20 scan along the plane normal direction.](image2)
with additional detailed information about the samples. In addition, the 2θ breadth of the wurtzite GaN(0 0 2) peak is much narrower than that of the zinc-blende peaks, implying that large wurtzite crystals were formed. No other wurtzite GaN peak with different orientations can be found in the θ/2θ scan, implying that the wurtzite structure is in a preferred orientation somewhat aligned with the zinc-blende structure. Presumably, the coexistence and alignment between wurtzite and zinc-blende structures may be attributed to the close lattice match among three lattice spacings GaN(1 1 2 0) and one lattice spacing of the wurtzite GaN(1 0 0). Further study is necessary to clarify the mechanism of the growth of wurtzite structure and how to eliminate them in the growth process.

The lattice misfit is $-19.9\%$ between zinc-blende type GaN and GaAs along the epitaxial direction. To form a good epitaxial layer, the GaN film can be arranged in 5 GaN(1 0 0) (or GaN(0 1 0)) lattice spacings in coinciding with 4 GaAs(1 0 0) (or GaAs(0 1 0)) lattice spacings. The subsequent lattice misfit is only $-0.06\%$ with a superlattice spacing of 2.26 nm. This small misfit in a superlattice structure may be the source of stabilizing the zinc-blende GaN(0 0 1) epitaxial films on GaAs(0 0 1) substrates. Table 1 lists the strains measured by the radial scan of X-rays along different directions with respect to a lattice parameter of 0.4526 nm. The strain of in-plane peaks ($-0.43 \pm 0.1\%$) exceeds the misfit ($-0.06\%$) of superlattice misfit between GaN(1 0 0) and GaAs(1 0 0). These results suggest a compressive stress on the GaN films in the interface plane. This larger compressive stress may be attributed to the inclusions of wurtzite structures embedded in the zinc-blende structure.

As Fig. 4 depicts, the line shape of GaN(0 0 2) diffraction peak is a Lorentzian one instead of a Voigt shape typically found in the powder diffraction. This result suggests that the level of disorder of GaN structure is high with a position correlation decaying in an exponential fashion. The lattice coherence length, or crystallite size, $D$, of the zinc-blende structure in vertical direction can be calculated from the Scherrer formula $D = \frac{0.94\lambda}{\beta \cos \theta}$ where $\beta$ denotes the breadth of 2θ determined from the measured breadth in the θ/2θ scan after deconvoluting the instrumental breadth and correcting the breadth broadening due to the microstrain. From the $\beta$ values of GaN(0 0 2) and GaN(0 0 4) peaks, we assume that the 2θ breadth broadens since the finite $D$ remains constant for both GaN(0 0 2) and GaN(0 0 4) peaks. Therefore, we can infer that the coherence length of the GaN

### Table 1
The X-ray crystallographic results of zinc-blende GaN on GaAs assuming that the lattice constant is 0.4526 nm [5]. The strain determination has an error about ±0.1%.

<table>
<thead>
<tr>
<th>Peak (FWHM)</th>
<th>$d$-spacing (nm) (strain)</th>
<th>Rocking curve width (FWHM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN(0 0 2) plane-normal</td>
<td>0.2263 (0%)</td>
<td>4.8°</td>
</tr>
<tr>
<td>GaN(0 0 4) plane-normal</td>
<td>0.1123 (-0.7%)</td>
<td>—</td>
</tr>
<tr>
<td>GaN(0 2 2) or GaN(2 0 2)</td>
<td>0.1594 (-0.37%)</td>
<td>4.5°</td>
</tr>
<tr>
<td>GaN(0 2 2) (miscut)</td>
<td>0.1592 (-0.49%)</td>
<td>3.1°</td>
</tr>
<tr>
<td>GaN(2 2 0) in-plane</td>
<td>0.1593 (-0.43%)</td>
<td>4.8°</td>
</tr>
</tbody>
</table>
film is about 30 nm with a microstrain of about 0.9%. This large microstrain indicates the presence of the wurtzite inclusions in the zinc-blende matrix. The width of the rocking curve in the in-plane direction is approximately the same as that in a plane-normal direction which indicates an isotropic distribution of dislocations or defects along these different directions. This observation markedly differs from the MOCVD-grown wurtzite GaN(0 0 1) on Al₂O₃(0 0 1) where a columnar-like structure was found [16,17]. The rocking curves of wurtzite structure GaN(0 0 2) and GaN(1 0 1 0) were also measured and are shown in Fig. 4. Although the orientation of GaN(0 0 2) more closely resembles a powder, the orientation distribution is not uniform. The GaN(1 0 1 0) is preferable along the plane-normal direction. However, its rocking curve width (about 7° FWHM) markedly exceeds the width of zinc-blende GaN(0 0 2) (about 4.8° FWHM). This result indicates that the wurtzite crystals embedded in the films are not well aligned.

Fig. 5 summarizes typical results of the \( \phi \)-scan (or \( hh \)-circle scan) around the GaN[0 0 1] or GaAs[0 0 1] axis with the scattering wave vector fixed at GaN{0 2 2}. This figure clearly indicates that four GaN{0 2 2} diffraction peaks (in four-fold symmetry) appeared by rotating the \( \phi \) angle in every 90° azimuthally, which corresponds to four GaAs{0 2 2} peaks. Interestingly, another two small peaks appeared at \( \phi = 143 \) and 323° (marked as “S” in Figs. 2 and 5) which did not correspond to the substrate orientation relation of GaN(0 0 1)||GaAs(0 0 1) and GaN(0 1 0)||GaAs(0 1 0). These two small peaks cannot be interpreted as some of the GaN crystalline, that favor an epitaxial growth along the GaAs[1 1 0] direction (miscut direction) owing to the nature of four-fold symmetry if a portion of the GaN(1 0 0) grows along GaAs[1 1 0]. Our experimental results indicated only two-fold symmetry (the peaks located at \( \phi = 53 \) and 233° were missing). A closer examination of the experimental data revealed that the epitaxial directions of these two small peaks follow the steps (miscut) of the substrate. These misoriented GaN structures having grown along the steps are highly elongated so that only two-fold symmetry can be detected. The rocking curve of this peak displays a smaller value (3.1° comparable with those of other \{0 2 2\} peaks) (Table 1). This value could be attributed to a slight constraint by the step of miscut GaAs surface.

![Fig. 5. Typical results of the \( \phi \)-scan rotated about the GaN[0 0 1] or GaAs[0 0 1] axis with a scattering wave vector fixed at GaN{0 2 2}.](image-url)
These two small peaks grown in the direction of steps are quite unique because in typical epitaxial growth, the step-flow is a prominent factor in the growth process. The misorientation of cubic GaN along the step indicates that the step energy is close to the substrate chemical periodical potentials. This misorientation also indicates that during the buffer layer growth, the epitaxy on the terrace prevails during the thin film growth instead of the step-flow model typically found in other epitaxial growth modes. This finding also strongly suggests the following scenario: to grow a high quality cubic GaN film, the best miscut direction for the GaAs(0 0 1) substrate should be along GaAs[1 0 0] or GaAs[0 1 0].

3.2. Photoluminescence and Hall measurements

The PL was measured at room temperature on two samples (samples 410 and 411) using an 8 mW He–Cd laser (λ = 325 nm). Figs. 6a and b depict the room temperature PL spectrum for these two samples. Both samples emitted PL at a wavelength of 388 nm (peak-1) which is due to the near band-edge emission, i.e. the characteristic spectrum of a zinc-blende GaN as reported by Edgar [18]. In comparison with the results of these two samples, we can find that the sample 401 has stronger intensity than the sample 411 in the peak-1, and the sample 411 consists of two distinct peaks between the wavelengths of 450 and 550 nm (peak-2), as shown in Fig. 6. In this work, although the two samples were grown at different temperatures, their structures, studied by X-ray, are almost identical and, the features of yellow peaks are quite distinguishable. The difference in the feature of yellow peaks may be attributed to lower concentration defects such as N vacancies or carbon contamination [19] that cannot be detected by X-ray diffraction.

In addition, the electron mobility and carrier concentration was measured by Hall measurement. According to these results, the room temperature mobility is 13 cm²/V s and the background carrier concentration is $3.8 \times 10^{18}$ cm⁻³. The low mobility is attributed to the large lattice mismatch (19.9%) between the GaN and GaAs and thus lead to a poor quality of GaN epitaxial layer. In comparison with Tsuchiya et al. [15], who grew the cubic GaN by HVPE on GaAs(1 0 0) substrate, although the mobility is lower in our sample, the carrier

![Fig. 6. The PL spectrum: (a) pre-deposited buffer layer at 575°C and, then, grew the cubic GaN at 780°C; (b) pre-deposited buffer layer at 550°C, finally growing the cubic GaN at 750°C.](image-url)
concentration is markedly lower than their sample. Thus, p-type cubic GaN film may be easier to obtain. This structural imperfection might also deteriorate the thin film’s mobility.

4. Summary

In this study, a zinc-blende epitaxial GaN film was grown on GaAs substrates using the HVPE reactor with low-temperature HVPE grown buffer layer. Although the 4.8° FWHM of rocking curve is still quite inferior to most of the wurtzite GaN films (0.1°) grown on sapphire, the films are continuous and reflective. Also, the zinc-blende GaN successfully grows following the GaAs registry, except for a small portion of misorientated GaN structure grown following the steps of the substrate surfaces. This type of growth suggests that the thin film growing at steps on the miscut GaAs surface might give a comparable energy to the island growth following the terrace registry potential. Some wurtzite inclusions are still preferred to grow at defect sites of zinc-blende matrix at these growth temperatures, ultimately causing a large strain and low electron mobility on the thin film.

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