Characterization of free-standing HVPE GaN

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Abstract

A free-standing GaN template grown to a thickness of 300 μm by hydride vapor phase epitaxy (HVPE) has been characterized for its structural properties by transmission electron microscopy (TEM). The TEM investigation was augmented by X-ray diffraction, defect delineation etching process followed by imaging with atomic force microscopy (AFM), and variable temperature photoluminescence (PL). Convergent Beam Electron Diffraction (CBED) was employed to determine the polarity of the free surface and the side juxtaposed to substrate before separation. The substrates side was confirmed to the N-face indicating a growth in the [0001] direction from Ga to N. The density of dislocations near the N-face was determined to be, in order, $3 \pm 1 \times 10^7$, $4 \pm 1 \times 10^7$, and about 1×10^7 cm^{-2} as determined by cross-sectional TEM, plan-view TEM and a defect revealing etch, respectively. Identical observations on the Ga-face revealed the defect concentration to be, in order, less than 1×10^7 cm^{-2} by plan-view TEM, 5×10^5 cm^{-2} by cross-sectional TEM, and 5×10^5 cm^{-2} by defect revealing hot H_3PO_4 acid, respectively. The full width at half maximum (FWHM) of the symmetric (0002) X-ray diffraction peak was 69 and 160 arcsec for the Ga and N-faces, respectively. That for the asymmetric ($10\underline{1}4$) peak was 103 and 140 arcsec for Ga- and N-faces, respectively. The donor bound exciton linewidth as measured on the Ga and N-face (after the removal of the damage) is about 1 meV each at 10K. Instead of the commonly observed yellow band, this sample displayed a green band, which is centered at about 2.44 eV.

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INTRODUCTION

Semiconductor binary and ternary nitrides and their heterostructures are very promising materials for optical emitters and detectors, and high power/temperature electronic devices[1,2,3]. Nitride semiconductors have been deposited by hydride vapor phase epitaxy (HVPE)[4,5], and organometallic vapor phase epitaxy (OMVPE)[6,7], and by molecular beam epitaxy (MBE).[8]

These wide bandgap semiconductor structures have been grown on many substrates, such as sapphire, SiC, ZnO, $MgAl_2O_4$, Si, GaAs, MgO, NaCl, W, Hf and TiO_2 due to the lack of large area native substrates.[9] The predilection for sapphire has been ascribed to its wide availability, hexagonal symmetry, and its ease of handling and pre-growth cleaning. SiC with its good thermal conductivity and closer structural match to nitrides has been making inroads. Despite progress, nitride semiconductors contain many structural and point defects which are undoubtedly caused, to a large extent, by lattice mismatched substrates. Due to the high N overpressure on GaN and very small solubility of N in a Ga melt, production of large area GaN has not yet been realized. Consequently, the attention has turned to the growth of very thick GaN films[10,11,12,13] on sapphire or other substrates, such as GaAs by HVPE. Due to deposition on sapphire, the large extended defect density is of great concern. In this paper, we present TEM data, both cross-sectional and plan view, on the structural characteristics of a free standing HVPE grown GaN with electron mobilities of 1100 $cm^2/V{\cdot}s$ (300K) and 6800 $cm^2/V{\cdot}s$ (50K), and 300 K donor and acceptor concentrations of $2.10x10^{16}$ cm^{-3} and $4.9x10^{15}$ cm^{-3}, respectively.[14]

EXPERIMENTAL PROCEDURE

The samples were grown by HVPE on sapphire substrate to a thickness of 300 μm and separated from the sapphire by laser induced lift off.[15] The GaN layer was then mechanically polished, and dry etched on the Ga-face to obtain a smooth epi-ready surface, whereas the N-face was only mechano-chemically polished. In this work we performed a defect analysis of this free-standing GaN template by use of transmission electron microscopy (TEM) technique.

Three specimens were prepared for TEM studies: one cross-sectional and two plan-view (from both template sides) samples. The cross-sectional specimen was prepared in such a way that [1$\underline{1}$00] zone axis would be later accessible during TEM observation. In order to prepare this sample a strip of the template was glued between two "dummy" silicon strips. This structure was then thinned down to electron transparency by a standard method of mechanical pre-thinning followed by Ar-ion milling. When electron transparent areas appeared in the sub-surface regions on both GaN template sides the ion milling was terminated. A similar method of mechanical thinning and Ar-ion milling was applied to prepare both, plan-view specimens. All three samples were investigated using a TOPCON 002B microscope, operated at 200 kV acceleration voltage.

Conventional TEM techniques were used to analyze defects present in these sample. Bright field images, recorded under multi-beam conditions (in order to image dislocations with different Burgers vectors), were used to estimate the density of dislocations.

In order to determine the polarity on the two sides of the GaN template the well-established method of convergent beam electron diffraction (CBED) was applied. Since GaN is non-centrosymetric, the difference in the intensity distribution within (0002) and (000$\underline{2}$) diffraction discs in the CBED pattern can be attributed to Ga and N distributions within the unit cell. However, this intensity distribution depends on sample thickness. Therefore, in order to use this method correctly one needs to compare the experimental CBED patterns with patterns simulated for the thickness indicated by the pattern in the central, (0000) disc. To apply this method for our studies, we recorded several (for different thicknesses) [1$\underline{1}$00] zone axis CBED patterns on each side of the cross-sectional specimen and then compared them with simulated patterns.

For a more complete analysis, the TEM data were supplemented by X-Ray, PL and defect revealing etching methods. The X-ray diffraction investigation was carried out using a Philips MRD high-resolution system. Variable temperature photoluminescence measurements were carried out in the range of 10 - 300 K on both the Ga and N-faces before and after the removal of what was presumably a damaged surface layer in wet chemistry. Both the Ga and N-faces were independently etched in hot H_3PO_4 to reveal the defects as examined by AFM imaging.

EXPERIMENTAL RESULTS

TEM study of cross-sectional specimen revealed that the surface of the side, which was juxtaposed to the substrate was of relatively poor quality as expected from the application of mechanical polishing only and representing interfacial region between the GaN epitaxial layer and the sapphire substrate (see Fig.1a). The roughness of this surface was about 0.1 μm. Besides, the sub-surface layer of about 0.2-0.3 μm was severely damaged containing many defects.

The analysis of Convergent Beam Electron Diffraction (CBED) patterns obtained on the side previously next to the substrate indicates that it is of [000$\underline{1}$], N-polarity which means that a long bond along the c-axis is from N to Ga (see Fig.1). The polarity determination by CBED is consistent with chemical etching experiments in which the N-face etched very rapidly in hot phosphoric acid (H_3PO_4). In addition, Schottky barriers fabricated on this surface exhibited a much reduced Schottky barrier height (0.75 eV vs. 1.27 eV on the Ga-face), only after some 30-40 μm of the material was removed by mechanical polishing followed by chemical etching to remove the damage caused by the first mechanical polish[16].

First investigation of a plan-view specimen prepared for the N-face side revealed the presence of a very damaged surface, covered by a nearly amorphous layer. It is most

likely that the surface was damaged during mechanical polishing as observed in cross-section (Fig.1a). An additional very short ion milling was performed in order to remove this highly defective sub-surface layer. Only after such a procedure, was the sample adequate for studying the defect distribution within the layer. A bright field image of this sample is shown in Fig.2a. Some dislocations (indicated by arrows) threading across the layer into the surface are visible edge-on. The density of these dislocations determined from the plan-view sample was estimated to be about $4 \pm 1 \times 10^7$ cm^{-2}. These treading dislocations were observed also in cross-section. Few of them are clearly visible in bright field images as shown in Fig.3. The density of these dislocations determined from cross-section was found to be about $3 \pm 1 \times 10^7$ cm^{-2}. This value is in good agreement, within experimental error, with the value obtained from the plan-view sample. For comparison, a density of about 1×10^7 cm^{-2} was obtained by etching the N-face in H_3PO_4 for 15 seconds at 160°C followed by counting the etch pits on several Atomic Force Microscopy (AFM) images. The agreement between these two very different techniques lends confidence concerning the densities reported here.

Our study suggests that most of these threading dislocations are of mixed Burger's vector because they are visible on bright field images with g-vector parallel and perpendicular to the c-axis (see Fig.3). However, one needs to be careful with such a conclusion because of the very low statistics (very few dislocations observed within the electron transparent area).

In contrast to the N-polarity side, which was previously attached to the substrate, the opposite surface was very flat (Fig.1). There were only some defects visible close to the sample surface, but since in the neighboring "dummy" silicon we observed severe damage, these defects might be an artifact of TEM sample preparation. The majority of these defects appear in cross-section configuration on the c-plane and therefore they should be visible in plan-view as loops or half-loops. However, this was not observed supporting the notion that these defects were due to sample preparation.

The intensity distribution within the CBED pattern measured on this face of the template indicates that it is of [0001] orientation which implies a Ga polarity and means a long bond along the c-axis is from Ga to N direction (see Fig.1). This is in agreement with wet chemical etching experiments in that the etch rate in hot H_3PO_4 was negligible. Additional confirmation was obtained from Schottky barriers formed on this surface with barrier heights of about 1.27 eV, as opposed to about 0.75 eV on the etched N-face.

TEM studies of a plan-view specimen prepared for the Ga-face side revealed a nearly defect-free surface. Very few dislocations were found on this surface. Two such dislocations marked by arrows are shown in Fig.2b. Based on the plan-view study, the density of these dislocations was estimated to be less than 1×10^7 cm^{-2}, however due to the very low statistics there is a relatively large uncertainty for this estimation. In cross-sectional study we could not find any threading dislocation within the electron transparent area and based on this information we estimated that density of these dislocations is less than about 0.5×10^6 cm^{-2}.

The very low defect concentrations on the Ga-face of the sample necessitate application of another method for a more accurate determination of the dislocation count. To this end, we employed several defect revealing etches, such as hot H_3PO_4 acid. Several AFM images, after etching, with large area scans, up to 50 μm x 50 μm, indicated a dislocation count of about 5×10^5 cm^{-2}. It is remarkable that the cross-sectional TEM and hot H_3PO_4 acid methods are in such good agreement.

In conclusion, a free-standing wafer of HVPE GaN was studied by various TEM methods. The standard method, based on analysis of the CBED pattern, was applied to determine layer polarity. It was found that the original, flat surface of the layer is Ga-terminated, whereas the rough surface (due to mechanical polishing), which was originally next to the interface with the substrate is N-terminated. This is consistent with other HVPE GaN layers. Threading dislocations (mainly of mixed Burger's vectors) were found below the N-terminated surface. Their density determined from both plan-view and cross-sectional studies was about $3 \div 4 \times 10^7$ cm^{-2}, which compares well with the value of about 1×10^7 cm^{-2} obtained from defect revealing etches. Only occasional dislocations were found in the plan-view sample on the Ga-terminated surface. The density of the threading dislocations below this surface, estimated from cross-sectional studies, was less than 5×10^6 cm^{-2}. Defect revealing chemical etches indicated a density of about 5×10^5 cm^{-2}, which is in remarkable agreement with the figure estimated from cross-sectional TEM data considering the small statistical base in TEM. The significantly lower density of dislocations on the G-face side with respect to that near the N-face was probably due to dislocation interaction within the layer.

All our results showed a very low density (of the order of 10^7 cm^{-2}) of threading dislocations in the present sample compared to values measured in standard HVPE GaN layers[17,18] indicating a very high structural quality of the free-standing GaN template under investigation.

X-Ray diffraction measurements indicated a full width at half maximum (FWHM) of the symmetric (0002) peak of 69 and 160 arcsec near the Ga and N-faces, respectively. That for the asymmetric (10-14) peak was 103 and 140 arcsec for Ga- and N-faces, respectively. The donor bound exciton linewidth as measured on the Ga and N-face (after the removal of the damage) is about 1 meV each at 10K. The observed yellow band gave way to a green band, which is centered at about 2.44 eV, in this sample.

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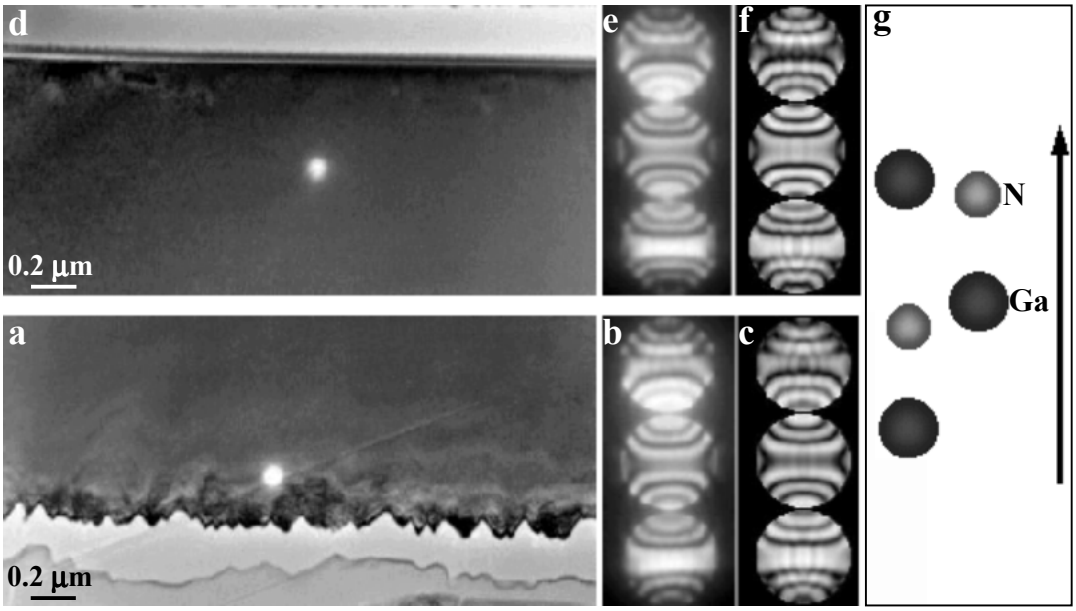
Figure Captions

Fig.1. TEM micrographs taken near surfaces (a) previously attached to the substrate and (d) top surface of the template. Experimental [1$\underline{1}$00] CBED patterns (b and e) taken from marked areas shown in images a and d, respectively. Simulated (for 185 nm and 200 nm, respectively) CBED patterns (c and f). Distribution of N and Ga atoms along the c-axis (g). Growth direction is shown by arrow.

Fig.2. Bright-field TEM micrograph of a plan-view sample prepared for the N-face (a) and Ga-face (b), respectively. Visible edge-on dislocations are marked with arrows.

Fig.3. Bright field TEM micrographs of a cross-section sample near the N-face side for the g-vectors perpendicular (a) and parallel (b) to the c-axis. Note that both dislocations are visible in both images.



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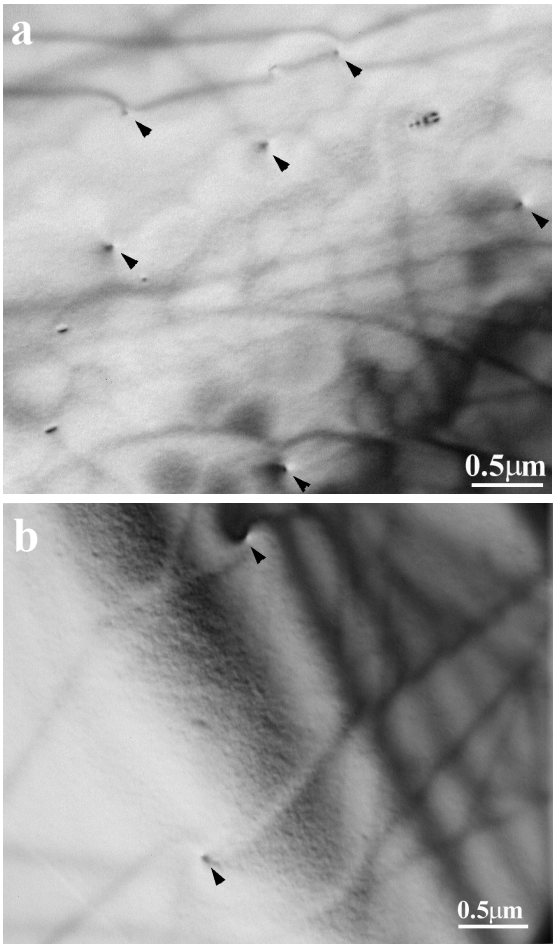

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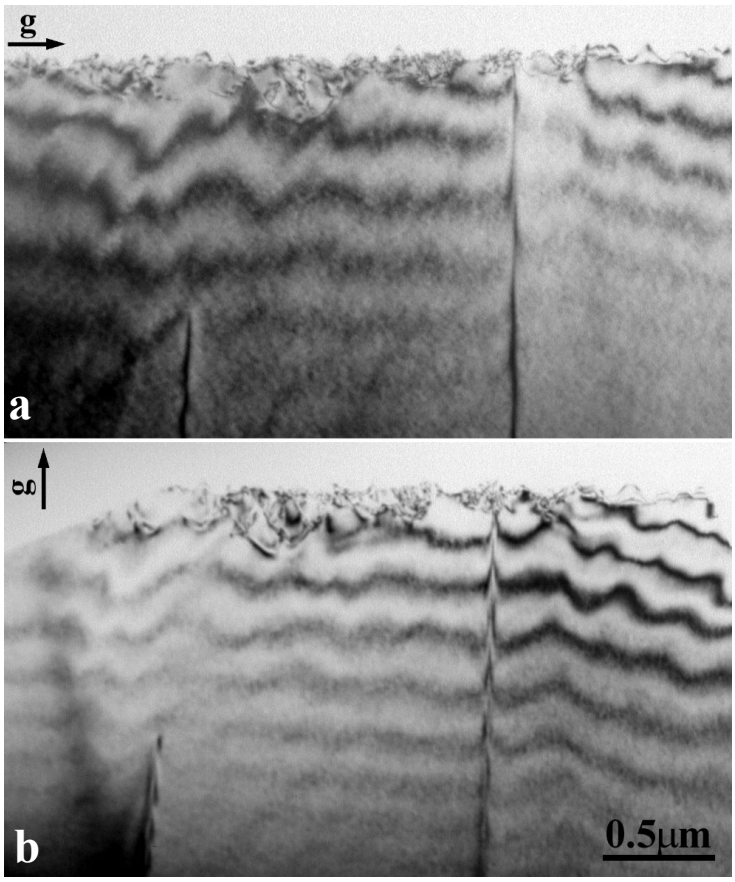

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