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Characteristics of free-standing hydride-vapor-phase-epitaxy-grown GaN with very low defect concentration

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A free-standing 300-μm-thick GaN template grown by hydride vapor phase epitaxy has been characterized for its structural and optical properties using x-ray diffraction, defect delineation etch followed by imaging with atomic force microscopy, and variable temperature photoluminescence. The Ga face and the N face of the c-plane GaN exhibited a wide variation in terms of the defect density. The defect concentrations on Ga and N faces were about $5\times10^5\ \mathrm{cm}^{-2}$ for the former and about $1\times10^7\ \mathrm{cm}^{-2}$ for the latter. The full width at half maximum of the symmetric (0002) x-ray diffraction peak was 69 and 160 arc sec for the Ga and N faces, respectively. That for the asymmetric (10–14) peak was 103 and 140 arc sec for Ga and N faces, respectively. The donor bound exciton linewidth as measured on the Ga and N faces (after a chemical etching to remove the damage) is about 1 meV each at 10 K. Instead of the commonly observed yellow band, this sample displayed a green band, which is centered at about 2.44 eV. © *2000 American Institute of Physics.* [S0003-6951(00)04649-0]

Semiconductor nitrides such as aluminum nitride (AlN), gallium nitride (GaN), and indium nitride (InN) are very promising materials for optoelectronic (both emitters and detectors) and high power/temperature electronic devices.[1–3] Nitride semiconductors have been deposited by hydride vapor phase epitaxy (HVPE),[4,5] organometallic vapor phase epitaxy (OMVPE),[6,7] and by molecular beam epitaxy (MBE).[8]

GaN and its alloys have been grown on many substrates due to lack of large area native substrates. Among them are sapphire, SiC, ZnO, $MgAl_2O_4$, Si, GaAs, MgO, NaCl, W, Hf, and TiO_2.[9] The heretofore preference for sapphire is ascribed to its wide availability, hexagonal symmetry, and its ease of handling and pregrowth cleaning. SiC with its good thermal conductivity and closer structural match to nitrides is 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 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[10–13] 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 letter, we present characteristics of a representative free-standing HVPE-grown GaN with extended defect density in the mid $10^5\ \mathrm{cm}^{-2}$ which represents several orders of magnitude reduction over typical figures.

The samples were grown by HVPE on sapphire substrate to a thickness of 300 μm. In order to obtain a free standing GaN substrate, the thick GaN layer was separated from the sapphire by laser induced lift-off.[14] The GaN wafers were then mechanically polished and dry etched on the Ga face to obtain a smooth epiready surface, whereas the N face was only mechanically polished. Both the Ga and N faces were independently etched in hot phosphoric acid (H_3PO_4) to reveal the defects as examined by atomic force microscopy (AFM) imaging. X-ray diffraction (XRD) investigation was carried out in 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 the damaged surface layer in wet chemistry.

Before the defect revealing process, as received surfaces of GaN were examined by AFM imaging. The morphology of the Ga face is shown in the AFM image of Fig. 1(a). Here, the scratches from the mechanical polishing are visible across the surface. The indicated scratch is 2 nm in depth and

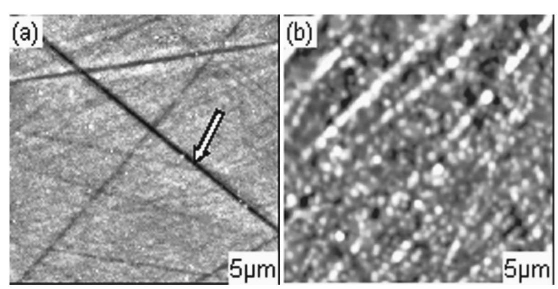

FIG. 1. AFM images of the mechanically polished and dry etched Ga face (a), and the mechanically polished N face (b) of the GaN substrate. The lines visible in (a) result from the mechanical polishing of the Ga face. Less distinct lines can also be seen on the N face (b).

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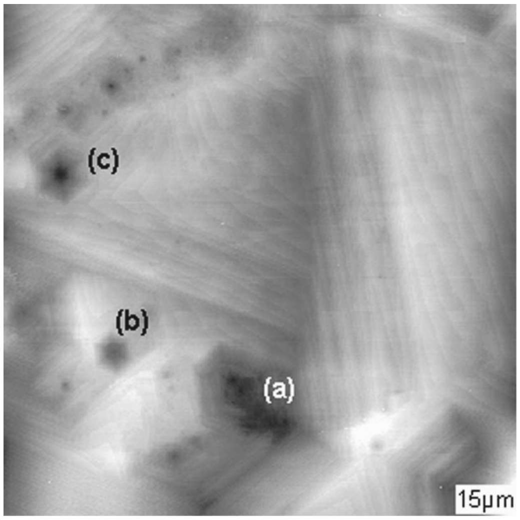

FIG. 2. AFM image of the N face of the substrate after etching in H_3PO_4 for 15 s at 160 °C. The surface has been significantly etched at defect sites; so much that valleys, ridges and terraces have been formed on the surface. The deep etch pits on the surface marked (a), (b), and (c) are 2.1, 1.2, and 1.5 μm wide by 6, 4.7, and 8 nm deep respectively.

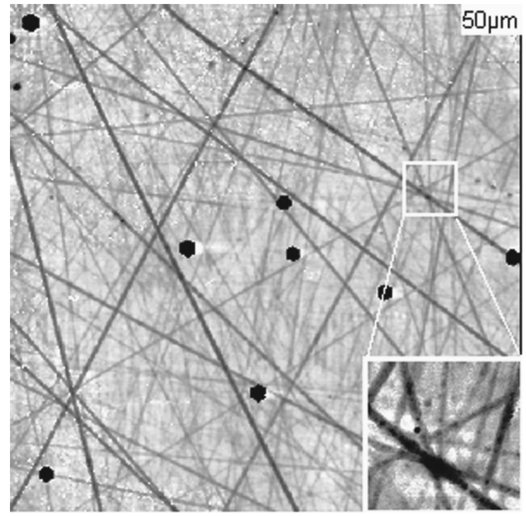

FIG. 3. AFM image of the Ga face etched for 50 min at 160 °C in H_3PO_4. The lines from the mechanical polishing are still visible on the surface, indicating that the nondefective GaN has not been significantly etched. The point defect sites on the surface have been etched by the acid. There are three discreet sizes of defects found on the surface. The large defects are roughly 1.5 μm wide, the medium sized defects (upper left corner of image) are generally 800 nm wide, and the small defects are approximately 200 nm wide. A small defect can be seen in the inset, which is a zoom into the boxed region.

150 nm wide. The root mean square (rms) roughness of the surface is 0.44 nm. Figure 1(b) shows an AFM image of the mechanically polished N face of the GaN substrate. Because the N face was not dry etched, the rms roughness (6.1 nm) is much higher than that of the Ga face. Again, lines from the mechanical polishing are still visible on the surface, though to a lesser degree than on the Ga surface.

It has been reported that hot H_3PO_4 etches defect sites on the surface of GaN, producing etch pits that reveal the location, and therefore density, of extended defects that form in GaN.[15,16] With this in mind, the two faces of the sample were etched in H_3PO_4 at 160 °C until the defects on the surface were clearly revealed. The N face was etched in H_3PO_4 for 15 s at 160 °C, and the etched surface is shown in the AFM image of Fig. 2. After the etching, the rough and disordered surface found in Fig. 1(b) has been smoothed (rms roughness=1.9 nm), and the defect sites have been etched, revealing hexagonal pits. By counting the etch pits on several images, we ascertain that the density on the N face is about $1\times10^{7}\,\mathrm{cm}^{-2}$. The deep etch pits on the surface marked (a), (b), and (c) are 2.1, 1.2, and 1.5 μm wide by 6, 4.7, and 8 nm deep, respectively. Also visible on the surface are terraces that have formed, many of which terminate at dislocation sites.

It is well known that H_3PO_4 strongly attacks the N face of GaN, and that the etch rate for the Ga face is considerably lower. This creates a problem when etching the Ga face in that it is possible to etch through the sample from the N face while trying to form etch pits on the Ga face. This is especially a problem when the sample is of high quality, as it will often take considerable time to etch defect sites on the Ga side to a point where they are visible with AFM imaging. To solve this problem we used the surface tension of the acid to float the sample with the Ga face down, minimizing the effects of the acid on the N face. Note, however, that even this method has limits, as the vapor of the acid will slowly etch the N face. The morphology of the Ga face etched with this method for 50 min is depicted in Fig. 3. Still visible on the surface are the scratch lines that resulted from the mechanical polishing process, indicating that the nondefective c-plane GaN has not been significantly etched by hot H_3PO_4 acid. The inset of the figure is a zoom into the region indicated by the white box and shows that the black dot barely visible in the larger image is in fact a small hexagonal etch pit that has formed on the surface. We found three distinct sizes of etch pits. These pits, termed (for simplicity) small, medium, and large can all be seen in Fig. 3. The small pit, visible in the inset, has a width of 215 nm and a depth of 10 nm. The medium etch pit can be seen in the upper left corner of the image and is 800 nm wide by 13 nm deep. The large etch pits are $\sim$1.5 μm in width and $\sim$300 nm deep. The total density of etch pits on the Ga face is $\sim5\times10^{5}\,\mathrm{cm}^{-2}$, a value that is more than one order of magnitude lower than that found on the N face. Future studies will attempt to explain the dependence of the size of pits to the type of defects.

High resolution x-ray rocking curves (omega scan) were measured by a Philips X'Pert MRD system equipped with four-crystal Ge monochrometer. The instrument resolution is verified to be better than 10 arc sec under this diffraction geometry where Cu $K\alpha_1$ line of x-ray source is used.

The full width at half maximum (FWHM) of the symmetric (0002) peak was 69 arc sec for the Ga face and 160 arc sec for the N face. The FWHM of the asymmetric (10–14) peak was 103 arc sec for Ga face and 140 arc sec for the N face. These figures are indicative of very good quality and can be compared with published FWHM of 5–7 arc min for (0002) and 10–12 arc min for (10–12) axis obtained in thinner HVPE films.[17] The difference in the XRD measurement of the two types of polarities, mainly the (0002) peak, suggests different defect structure and surface preparation. It is believed that the width of the (0002) peak reflects lattice distortion from dislocations with a screw component, while that of the (10–14), or (10–12), is associated with lattice distortion from edge dislocations.[18]

Variable temperature (10–300 K) photoluminescence (PL) was used to assess the optical quality of the GaN template. PL from the as-prepared Ga face and after hot H_3PO_4-based etching was taken. The Ga face PL was similar before and after the chemical etching and demonstrated very sharp lines in the excitonic region. The peaks observed at 3.4710 and 3.4778 eV are attributed to exciton bound to a neutral shallow donor (BDE) and free exciton (FE), respectively. The FWHM of these peaks at 10 K are 1.1 and about 2.5 meV, respectively. A small peak between BDE and FE peaks (at 3.4748 eV) is not identified. Instead of the typical exciton bound to a shallow acceptor peak occurring at 3.465–3.466 eV,[19] we have observed a set of sharp peaks in the range 3.440–3.455 eV with the largest peak being at 3.4465 eV. We attribute this peak to exciton bound to some deep acceptor. In the range 3.0–3.4 eV one can find peaks related to exciton transitions involving one to three longitudinal optical (LO) phonons, as well as weak peaks due to shallow donor-acceptor transitions (the main peak at 3.257 eV is followed by few LO phonon replicas). Instead the commonly observed yellow luminescence centered at about 2.2–2.3 eV in our OMVPE and MBE grown samples, a broad green band with the maximum at 2.44 eV and FWHM about 370 meV was observed from the Ga face.

Low-temperature PL from the N face, which was originally only mechanically polished and cleaned, essentially revealed broadened exciton peak with the maximum at about 3.47 eV and FWHM of about 20 meV. Contrary to the Ga face, a yellow luminescence band centered at about 2.3 eV has been observed. After a chemical etching, the PL spectrum from the N face became nearly identical to that of the original Ga face. The FWHM of the main exciton peak at 3.471 eV decreased down to about 1.0 meV. The transformation of the spectrum is most likely due to the removal of the surface damage. More detailed investigations as to the identity of several peaks which have not heretofore been reported in the literature are underway.

In conclusion, we have investigated the structural and optical characteristics of a freestanding GaN template grown by HVPE. The defect concentrations on Ga and N faces were about 5×10^5 and 1×10^7 cm^{-2} respectively, as revealed by a hot H_3PO_4 etching. The FWHM of the symmetric (0002) x-ray diffraction peak was 69 and 160 arc sec for the Ga and N faces, respectively. That for the asymmetric (10–14) peak was 103 and 140 arc sec for Ga and N faces, respectively. After chemically etching the N face to remove the damage caused by the mechanical polishing procedure, the PL spectra from the Ga and N faces were similar, with the N face being slightly stronger, and exhibited donor bound exciton linewidths of about 1 meV.

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