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Dislocation density in GaN determined by photoelectrochemical and hot-wet etching

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Defects in GaN layers grown by hydride vapor-phase epitaxy have been investigated by photoelectrochemical (PEC) etching, and by wet etching in hot H_3PO_4 acid and molten potassium hydroxide (KOH). Threading vertical wires (i.e., whiskers) and hexagonal-shaped etch pits are formed on the etched sample surfaces by PEC and wet etching, respectively. Using atomic-force microscopy, we find the density of ''whisker-like'' features to be $2\times10^{9}\ \mathrm{cm}^{-2}$, the same value found for the etch-pit density on samples etched with both H_3PO_4 and molten KOH. This value is comparable to the dislocation density obtained in similar samples with tunneling electron microscopy, and is also consistent with the results of Youtsey and co-workers [Appl. Phys. Lett. **73**, 797 (1998); **74**, 3537 (1999)]. © *2000 American Institute of Physics.* [S0003-6951(00)05348-1]

Successful fabrication of gallium nitride (GaN) -based devices depends on the ability to grow epitaxial films on substrates such as sapphire or silicon carbide, with a low density of defects.[1,2] The poor match in both lattice parameter and thermal expansion coefficient, results in a high density ($10^{8}-10^{10}\ \mathrm{cm}^{-2}$) of threading dislocations embedded in the nitride film.[3–5] It is known that these defects affect both the electrical and optical properties of the material.[6,7] Therefore, the availability of reliable and quick methods to investigate the defects and dislocations in GaN is of great interest.

Wet-chemical etching is a commonly used technique for surface defect investigation. Hot phosphoric acid (H_3PO_4), mixed H_3PO_4/H_2SO_4 solution, and molten potassium hydroxide (KOH) have been shown to etch pits at defect sites on the *c* plane of GaN.[8–13] Kozawa *et al.*[8] found etch pits tentatively ascribed to dislocations using molten KOH to etch metalorganic chemical-vapor deposition (MOCVD) GaN samples. However, the etch-pit density (EPD) was $2\times10^{7}\ \mathrm{cm}^{-2}$, while the dislocation density found by transmission electron microscopy (TEM) was $2\times10^{8}\ \mathrm{cm}^{-2}$. Hong and co-workers[9,10] related the hexagonal-shaped etch pits formed by H_3PO_4 etching on MOCVD GaN samples to nanopipes (open-core screw dislocations). No etch pits were reported to have formed at both screw and edge dislocations. Shiojima[11] investigated etch pits formed on MOCVD GaN samples by molten KOH etching. By atomic-force microscopy (AFM) and TEM analyses, they attributed the origin of etch pits to mixed dislocations. Admittedly, the origin of etch pits is still controversial and the obtained EPD (in the range $4\times10^{5}-1\times10^{8}\ \mathrm{cm}^{-2}$) is lower than the dislocation density ($10^{8}-10^{10}\ \mathrm{cm}^{-2}$) found by TEM.

Recently, Youtsey and co-workers[14,15] demonstrated photoenhanced electrical chemical (PEC) etching to be suitable for dislocation-density estimation in *n*-type GaN films. Nanometer-scale ''whisker-like'' features on etched surfaces were obtained by etching crystalline GaN material between dislocation sites in a KOH-based electrochemical cell. Moreover, with cross-sectional TEM analysis, propagation of both pure-edge and mixed pure-screw dislocations from the unetched GaN into the whiskers was shown.

In each of the above studies, one or more, but not all, methods were used to study the GaN defects, with inconsistencies observed between etch techniques, when compared. The purpose of this letter is to investigate defect decoration of GaN by the PEC method and chemical etching using both H_3PO_4 and molten KOH solutions, and to determine how these methods can all be brought to bear for a better estimation of the defect density and a greater understanding of defects. An additional aim is to determine whether, and under what conditions, these various techniques are consistent. Using atomic-force microscopy of PEC-etched Si-doped GaN samples, the density of whisker-like features is determined to be $2\times10^{9}\ \mathrm{cm}^{-2}$, the same value found for the EPD on samples etched with H_3PO_4 and molten KOH.

The samples investigated here consisted of intentionally Si-doped *n*-type ($n\sim2\times10^{18}\ \mathrm{cm}^{-3}$) GaN layers grown by hydride vapor-phase epitaxy (HVPE) (Refs. 16 and 17) on sapphire. The thickness of the nitride films is about 9 μm. A tapping-mode Digital Instruments AFM was used to investigate the as-grown and etched-surface morphology of the GaN samples. The AFM image of the as-grown GaN surface reveals few point defects (pits) positioned at surface step terminations (Fig. 1). These pits correspond to the surface termination of pure-screw or mixed dislocations.[18,19] The average step height is 0.8 nm and the root-mean-square (rms) roughness is 0.4 nm. Often, AFM is used to estimate defect

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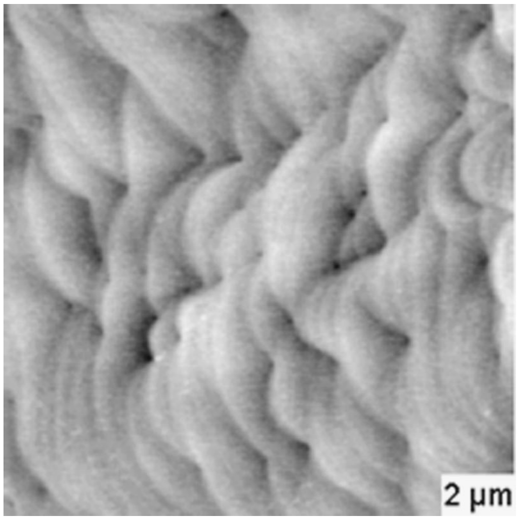

FIG. 1. AFM image ($2\times 2\ \mu m^2$) of as-grown GaN. Some point defects (pits) positioned at surface step terminations are visible. The average step height is 0.8 nm and the root-mean-square (rms) roughness is 0.4 nm. The vertical scale ranges from 0 to 10 nm.

density on the surface of as-grown films. However, this method can only be implemented when the surface is atomically smooth. By wet etching, this requirement is circumvented.

The PEC etching of GaN samples was carried out in a standard electrochemical cell at room temperature using an unstirred 0.02 molar KOH solution and a He–Cd laser (325 nm) as a source of the UV illumination. A 100-nm-thick Ti mask was patterned around the periphery of the sample with a standard lift-off process. The Ti contact served to assist photocurrent conduction. No additional bias was applied between the sample and the cathode during etching. Moderate illumination density ($10–100\ mW/cm^2$) was used to etch crystalline GaN material selectively, leaving threading vertical wires on the surface. At higher excitation densities, the PEC etching process left a smooth surface with no freestanding wires. This is due to the surface reaction being limited by

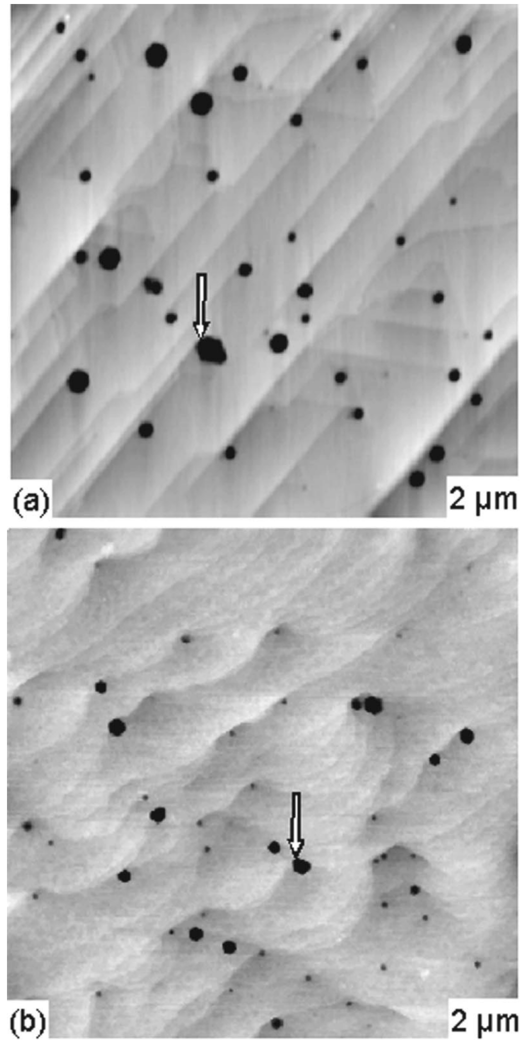

FIG. 3. AFM images ($2\times 2\ \mu m^2$) of the GaN samples etched by wet etching. (a) Surface morphology of the GaN sample after etching by molten KOH for 2 min at 210 °C. Etch pits are revealed on the surface with a density of $1\times 10^9\ cm^{-2}$. (b) Surface morphology of the GaN sample after etching by H_3PO_4 for 6 min at 160 °C. The EPD is the same found for the KOH-etched sample. The vertical scale ranges from 0 to 10 nm.

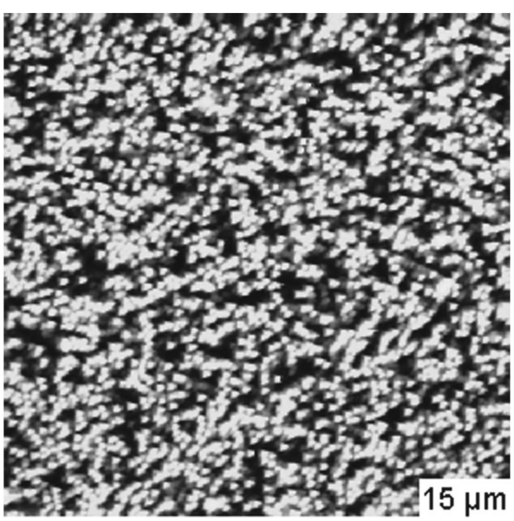

FIG. 2. AFM image ($15\times 15\ \mu m^2$) of the GaN sample etched by the PEC process. ''Whisker-like'' features revealed by etching are present on the surface. We estimate the height of the features to be about 700 nm and the lateral size of the order of 100 nm. The density is approximately $2\times 10^9\ cm^{-2}$. The vertical scale ranges from 0 to 1200 nm.

reactants in the solution rather than holes. The abundance of holes on the surface leads to etching of GaN in the dislocation sites as well.

Figure 2 illustrates an AFM image of the etched-surface morphology produced by the PEC process after 60 min of etching. We have estimated the height of the whisker-like features to be about 700 nm and the lateral size of the order of 100 nm. The density is approximately $2\times 10^9\ cm^{-2}$ and, according to the TEM analysis,[16] this value is quite close to the effective density of dislocations and is consistent with the results of Youtsey and co-workers[14,15] obtained on a similar sample.

In order to clarify further the relation between EPD and dislocation density in GaN and look for any consistency among the various chemical etches, we have used H_3PO_4 and molten KOH as defect etchants in GaN, which produce hexagonal-shaped etch pits. By varying the time and temperature, we were able to optimize the etching process to produce a pitted surface that clearly reveals the size and density of the pits.

The AFM image of the GaN sample etched by molten

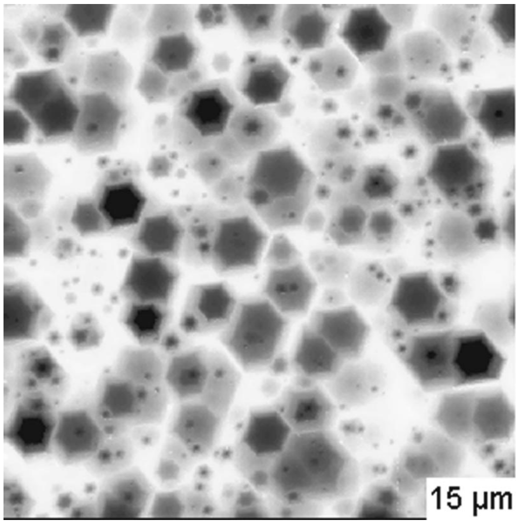

FIG. 4. AFM image ($15\times15\ \mu m^2$) of the GaN sample etched for 10 min at 200 °C using H_3PO_4. Two different types of etch pits with different sizes are revealed on the etched surface. Altogether, we estimated the EPD to be $1\times10^8\ cm^{-2}$. The vertical scale ranges from 0 to 450 nm.

KOH for 2 min at 210 °C is shown in Fig. 3(a). The etch pits, with a density of about $1\times10^9\ cm^{-2}$, are of hexagonal shape and their size ranges from 40 to 100 nm in diameter and from 10 to 30 nm in depth. Most etch pits terminated surface steps, which is consistent with the high concentration of pure-screw- or mixed-screw-edge dislocations found in HVPE GaN samples by the TEM study.[16]

Figure 3(b) shows the surface morphology of the GaN sample etched in H_3PO_4 for 6 min at 160 °C. The EPD is the same as that found for the KOH-etched sample, $1\times10^9\ cm^{-2}$. The size of the etch pits ranges from 25 to 70 nm in diameter and from 8 to 20 nm in depth.

By careful adjustment of the etching parameters, we obtain similarly pitted surface morphologies with the same value of EPD using both molten KOH and H_3PO_4 etching. During the etching process, a careful balance must be struck to ensure that every defect is etched to a point where it can be distinguished, but not overetched to the point where they begin to merge together. When the latter occurs, the density of defects is underestimated. To elucidate this further, we show in Fig. 4 a $15\times15\ \mu m^2$ AFM scan of a GaN surface etched for 10 min at 200 °C in H_3PO_4. Two different types of etch pits with different sizes are revealed on the etched surface. Larger pits have diameters of more than 1 μm and a depth of $\sim$450 nm (lower limit), whereas smaller pits are $\sim$250 nm in diameter and around 70 nm (lower limit) in depth. Altogether, we estimate the EPD to be $1\times10^8\ cm^{-2}$, an order of magnitude less than the correct value obtained earlier due to overetching.

In conclusion, PEC and both H_3PO_4 and molten KOH chemical etching were carried out on HVPE GaN samples to investigate the density of defects. Employing atomic-force microscopy, we have found that the density ($2\times10^9\ cm^{-2}$) of the whisker-like features on PEC-etched samples is very close to the EPD (as high as $1\times10^9\ cm^{-2}$) obtained on samples etched with both H_3PO_4 and molten KOH. Future studies will include plane-view and cross-sectional TEM analysis on etched samples to relate in detail the etch pits to the nature of dislocations in the GaN material.

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