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Dislocation- and crystallographic-dependent photoelectrochemical wet etching of gallium nitride

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Polarity and dislocation dependence study of photoelectrochemical wet etching on GaN was carried out on lateral epitaxial overgrown nonpolar $(11\bar{2}0)a$-GaN/$(1\bar{1}02)r$-plane sapphire substrate. This LEO nonpolar GaN sample has low dislocation density Ga- and N-faces exposed horizontally in opposite directions, which can be exposed to identical etching conditions for both polarity and dislocation dependence study. It is observed that N-face GaN is essentially much chemically active than Ga-face GaN, which shows the hexagonal pyramids with $\{10\bar{1}\bar{1}\}$ facets on the etched N face. No obvious etching was observed on Ga face in the same etch condition. As for dislocation dependence, the ''wing'' (low dislocation density) region was etched faster than the ''window'' (high dislocation density) region. Smooth etched surfaces were formed with the $(\bar{1}\bar{1}22)$ facet as an etch stop plane both on Ga and N-wing region. © *2004 American Institute of Physics.*

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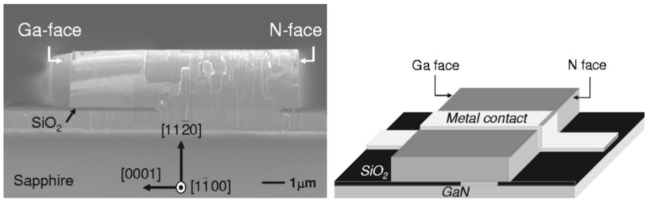
Photoenhancement of a wet chemical etch has proven to be a useful tool in the fabrication and analysis of group III-nitride materials. Above band-gap illumination of III-nitrides immersed in electrolytes such as KOH has resulted in substantial augmentation of etch rates in both the vertical and lateral directions,[1] allowing the formation of electronic,[2] optical,[3] and mechanical devices.[4] In general, photoenhanced wet etching of semiconductors depends on the wavelength and intensity of the illumination source, the nature of the electrolyte, and the doping and band gap of the semiconductor. In the case of III-nitride materials, the high density of threading dislocations of the material also exercises a critical influence on the etch rate and morphology of the etch process. In fact, PEC etching has been used to delineate the density of threading dislocations in GaN due to the behavior of dislocation-trapping holes.[5,6] This latter fact has limited the smoothness of the etched surface obtainable, even with the incorporation of an etch-stop layer. Such etch-stops layers include GaN, when selectively etching the lower band-gap InGaN (Refs. 3 and 4) and p-GaN when selectively etching n-GaN.[7,8] In order to better understand and apply the PEC etching to GaN device fabrication, it is important to understand the relative influence exercised by the photo-driven component compared to the chemically reactive component, and to better understand the influence of the defects and dislocations in the material. In addition, it is also interesting to explore the dramatically different chemical reactivities of the Ga and N face.[9,10]

This work helps to elucidate such issues through etching of substrate materials formed by lateral epitaxial overgrowth (LEO) of nonpolar $(11\bar{2}0)a$-GaN grown on an $(1\bar{1}02)r$-plane sapphire substrate. The films used in these studies have two principal distinguishing features: (1) they were formed by metalorganic chemical vapor deposition (MOCVD) growth on a $(1\bar{1}02)r$-plane sapphire substrate, producing a planar $(11\bar{2}0)a$-GaN film and (2) essentially low dislocation density material was produced by lateral epitaxial overgrowth. The resulting material appeared as shown in Fig. 1(a), with the nonpolar a-plane of GaN along the growth direction, and the polar Ga and N faces exposed as shown. These substrates allowed us to determine the etch rate and morphology of dislocation-dependent etching (low defect density versus high defect density) and crystallographic-dependent etching (Ga-face vs N-face GaN) carried out under the same etch conditions.

The conventional lateral overgrowth technique shown here includes an intermediate processing step between two growth steps. Initially, a planar $(11\bar{2}0)a$-GaN film was heteroepitaxially grown on $(1\bar{1}02)r$-plane sapphire substrate in a vertical MOCVD reactor using a two-step technique.[11] The as-grown nonpolar GaN film was coated with 200 nm SiO_2, which was subsequently patterned with parallel 5 μm wide mask openings (windows) spaced 15 μm apart and crystallographically aligned to $[\bar{1}100]_{GaN}$, perpendicular to the c axis. The sample was subjected to MOCVD regrowth using the same condition as planar growth.[12] During selective epitaxial regrowth, the GaN grew vertically through the window and laterally over the mask. The regrowth time was kept short, forming an uncoalesced stripe morphology. This pro-



(a) (b)

FIG. 1. (a) Cross-section SEM image of as-grown lateral epitaxial overgrown (LEO) nonpolar $(11\bar{2}0)a$-GaN/$(1\bar{1}02)r$-plane sapphire, with Ga- and N face exposed horizontally, (b) schematic illustration of patterned LEO stripe. Ti/Au/Pt is patterned perpendicular to the LEO stripe as a metal contact for PEC etching.

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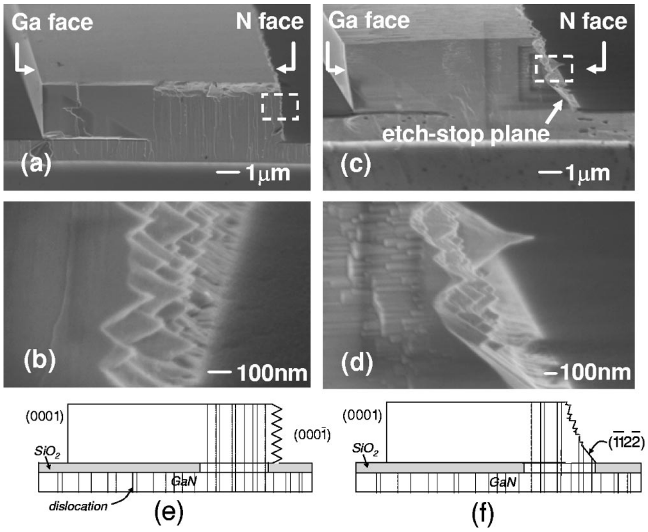

FIG. 2. Cross-section SEM image of etched LEO stripe: (a) after 10 min etch in 0.004 M KOH; (b) magnified view of the etched N face defined by the dashed box on part (a) shows hexagonal pyramids with {1011} facets; (c) after 10 min etch in 0.55 M KOH; (d) magnified view of the etched N face defined by the dashed box on part (c) shows etched cones with variable sizes and shapes than in (a). An etch-stop plane appears at the bottom of the N face; (e) schematic illustration of etch morphology of the low dislocation density N-face wing; (f) schematic illustration of surface morphology as the etch proceeds into the highly dislocated window region.

vided regrowth ''wings'' formed under the same growth conditions, with the Ga- and N-face exposed. The polarity of each side has been verified by convergent beam electron diffraction (CBED) analysis.[13] The wing with the Ga-face exposed grows at a rate almost one order of magnitude faster than the wing with N-face exposed.

Metal contact stripes with Ti/Au/Pt (30/50/50 nm) were patterned perpendicular to the LEO stripes (which are along the $[\bar{1}100]_{\mathrm{GaN}}$ direction). Figure 1(b) shows a schematic illustration of the patterned LEO stripe, which was then subject to photoelectrochemical wet etching. Note that the GaN LEO stripe has three regions: (1) a narrow, low dislocation density region (called the ''wing'') terminated by the N face, (2) a wider low dislocation density wing terminated by the Ga face, and (3) a high dislocation ''window'' region.[8] KOH electrolyte was used (0.004–2.2 M) and the illumination source is a 1000 W Xe lamp. The detailed PEC etch setup has been described elsewhere.[1] Front-side illumination was used for all experiments in this article. The etching morphology was observed using a JEOL 6340F field emission scanning electron microscope (FE-SEM) operated at 2 kV with an emission current of 12 μA.

Figures 2(a) and 2(b) show the lateral etching morphology after 10 min etch in 0.004 M KOH. The exposed N face on the shorter wing shows clear evidence of etching, with the development of cones of similar size and shape. Under higher magnification, the cones were observed to be formed of hexagonal pyramids, defined by the {1011} planes. The angle between the {1011} and (0001) planes is ~62°. The hexagonal pyramid shape is consistent with other chemical etching studies of *c*-plane N-face GaN.[10] Indeed, the hexagonal inverted pyramid structure was observed as the V-defect structure observed in InGaN/GaN QW growth by MOCVD.[14] In contrast, no measurable etching was observed on the Ga face by comparison to the as-grown Ga face shown in Fig. 1(a). This result is consistent with previous polarity dependent studies. In chemical mechanical polishing (CMP) studies of GaN, the N-face polishing rate can be as fast as 1.1 μm per hour, while no obvious polishing was observed on the as-grown Ga face.[15] Lithographic patterning and MBE regrowth was used to define different lateral regions of Ga- and N-terminated GaN.[10] These regions also exhibited large difference in etch rate in a KOH solution. Further studies should be done to determine the reasons underlying the difference in etch rates between the Ga-face and N-face GaN.

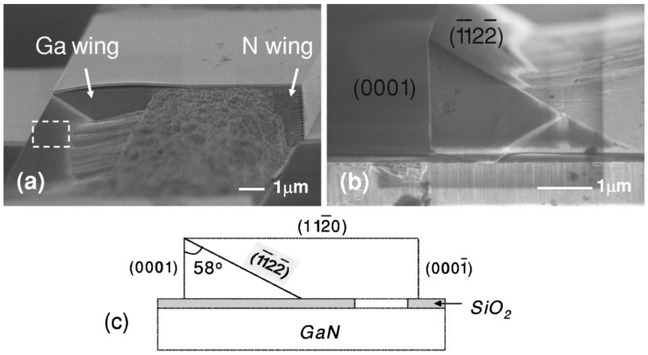

FIG. 3. Etching morphology after 60 min etch in 0.004 M KOH: (a) the window (highly dislocated) region was etched more slowly than the wing (low dislocation density) region; (b) SEM shows the smooth (1122) etched surface in the Ga-wing region; (c) schematic illustration shows (1122) plane, at an angle of 58° with (0001) Ga face.

As the etching proceeded into the highly dislocated window region, the cones on the N-face showed a greater variability of shape and size. This can be seen in Figs. 2(c) and 2(d), which shows the etch morphology after a 10 min etch in higher (0.55 M) KOH concentration. The higher KOH concentration resulted in a chemical greater reactivity. Within 10 min, the etch extends into the high dislocation region. We believe that the change in the uniformity of the cone structures arises as the etch proceeds from a kinetically controlled crystallographic etching of the low dislocation density N-face material to a dislocation-mediated etch process. Dislocations can serve as hole traps, and thus slow the etch rate of a PEC process. In the immediate vicinity of the dislocations, this mechanism in turn modifies the etch morphology, as suggested in Figs. 2(e) and 2(f). In all cases discussed, no measurable etching was observed on the chemically stable Ga face.

As the etching from the N-face progressed, an etch-stop plane gradually developed, as can be seen in Fig. 2(c). This stable crystallographic plane is believed to be the (1122) plane, and is also observed in the etching of the Ga wing. Although no etching was observed on the Ga face, the top of the Ga wing region was etched, with a slow-etching plane that also corresponds to the (1122) plane, shown in Figs. 3(a) and 3(b). The sample shown was etched for 60 min in 0.004 M KOH. Figure 3(c) illustrates that the (1122) plane forms an angle of 58° with the (0001) Ga face. Note the smoothness of the etched surface in the low dislocation density wing material. Figure 3(a) also shows the clear difference in etch morphologies between the low dislocation density (''wing'' region) and highly dislocated regions (''window'' region). The low dislocation density material has

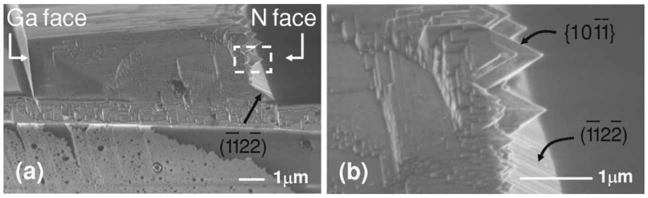

FIG. 4. Etch morphology under chemical etching without illumination in 2.2 M KOH for 24 h (a) large hexagonal structure is shown on the N face; (b) $(\overline{11}2\bar{2})$ plane is shown as smooth etch-stop plane.

clearly been etched more rapidly than the highly dislocated window region. The morphology on the Ga-face wing near the smooth etched plane, showing an undulating surface, may indicate the mixture of both the *a* plane $\{11\bar{2}0\}$ and *m* plane $\{10\bar{1}0\}$ from a geometric standpoint. This crystallographic etch morphology in the Ga wing region indicates that with the achievement of high quality, low-dislocation material in the future, we may similarly be able to find smooth, crystallographic chemical etching processes for GaN.

To further understand the role of illumination on the polarity dependence and dislocation dependence etching of GaN, we also subjected this material to simple etching in KOH without illumination. Figures 4(a) and 4(b) show the etching after 24 h in 2.2 M KOH without illumination. Since no illumination was applied, the dislocations do not affect the etch process by trapping photogenerated holes. Thus no dramatic difference between low dislocation areas (wing) and high dislocation (window) regions is observed. No obvious etching was observed on the top of the Ga wing and Ga face under this etching condition. As for the N-face GaN without illumination, etching still takes place, but at an etch rate more than two orders of magnitude lower than obtained in the presence of illumination. The etching morphology on the N face still displays the hexagonal pyramids, similar in shape to those shown in Figs. 2(a) and 2(b). Purely chemical wet etching also shows the $(\overline{11}2\bar{2})$ etch-stop plane on the N face.

In conclusion, we have explored photoelectrochemical wet etching on nonpolar, *a*-plane GaN formed by lateral epitaxial overgrowth. The different etch behavior in the high dislocation ‘‘window’’ region compared to the low dislocation ‘‘wing’’ region, clearly showed the effect of threading dislocations on etch rate and etch morphology. Crystallographic etching was observed in the low dislocation density GaN material. N-face etching shows a cone-like etching morphology bounded by hexagonal pyramids, which are believed to be $\{10\overline{11}\}$ facets. A very smooth etched surface $(\overline{11}2\bar{2})$ was observed in the low dislocation density Ga-wing region. However, no obvious etching was observed on the Ga face under our etching conditions. These preliminary observations indicate that the Ga face may be the most chemically inert plane. It should be noted that this has also been the predominant GaN face utilized in etch studies to date.

The observation of crystallographic etching of the N face in the low dislocation density material provides a straightforward means of surface texturing that might be important for applications such as enhanced light extraction in GaN-based LEDs.[16] The observation of the atomically smooth $(\overline{11}2\bar{2})$ chemically etched surface may provide an important regrown surface on the etched high quality GaN in LEO *a*-plane GaN wing region, which is observed as the stacking fault free materials.[12] All these studies are currently under exploration.

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