Faceted sidewall etching of n-GaN on sapphire by photoelectrochemical wet processing

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A wet etch process that produces smooth sidewalls aligned with the m-plane ($\{1\bar{1}00\}$) crystal facets of Ga-polar GaN grown on sapphire is demonstrated by combining photo-electrochemical (PEC) treatment with a postprocessing wet etch step. This novel process results in faceted and extremely smooth vertical etched sidewalls. This two-step process consists of a PEC treatment to define the geometry by converting the region to be removed to an oxide, followed by selective wet-chemical removal of the oxide in buffered HF and post-etch immersion in KOH (0.5 M) at 150 °C to smooth the surface and reveal the crystal planes. The dependence of the PEC treatment parameters (optical intensity, solution composition, direct current bias) on the resulting etch rates and morphology has been investigated. © 2014 American Vacuum Society. [http://dx.doi.org/10.1116/1.4896592]

I. INTRODUCTION

GaN is widely used for high power and high frequency electronic devices,[1–3] as well as light emitting diodes.[4] Due to its high chemical stability, it is difficult to wet etch GaN compared with other III–V semiconductors,[5] and thus etching of GaN for device fabrication is dominated by dry etching.[6] However, it is difficult to achieve well-controlled features with vertical sidewalls such as mesa structures or waveguide facets in GaN by dry etching alone, due to the limited anisotropy typically obtained with dry etch processes on GaN. Furthermore, the performance of dry etched devices can be degraded due to ion bombardment damage that can lead to leakage current and interface states, as well as surface roughness caused by dry etch processing. To address these challenges, a low-damage wet etch for GaN that produces smooth etched surfaces has been developed.

Several chemical solutions have been previously demonstrated for wet etching of GaN, including KOH, H_3PO_4, and tetramethylammonium hydroxide (TMAH),[7–9] although in general these etches require elevated temperatures and high concentrations in order to produce useful etch rates, and the resulting surface morphology and etch performance is often poor for device applications. Photoelectrochemical (PEC) etching offers significant advantages; the use of optical illumination to generate electron-hole pairs near the surface during the etch process allows for additional flexibility such as dopant- and bandgap-selective etching.[10–13] When immersed in KOH or other electrolytic solutions and illuminated with above-bandgap optical excitation, the photogenerated holes at the surface assist the oxidation and dissolution of the n-type GaN into the electrolyte (e.g., KOH). The significant potential advantages of wet-etch processing for III-N materials have led to recent efforts in this area. For example, Hardy *et al.* demonstrated m-plane GaN-based blue superluminescent diodes using selective chemical wet etching,[14] and Jung *et al.* investigated PEC wet etching of both N-polar and Ga-polar GaN films grown on sapphire substrates.[15] Kodama *et al.* demonstrated the formation of smooth surfaces on GaN aligned to the nonpolar crystal planes by wet etch using TMAH,[16] and Murata *et al.* reported atomically smooth GaN surfaces by chemical etching with a platinum (Pt) catalyst.[17] For some device applications, however, the ability to create vertical facets—which to the best of the authors' knowledge has not been reported—would be beneficial.

In this paper, we demonstrate a wet etch process that produces smooth sidewalls aligned with the crystal facets of GaN by combining PEC treatment with a postprocessing wet etch step. This novel process results in faceted and extremely smooth vertical etched sidewalls. This two-step process consists of PEC treatment to define the geometry by converting the region to be removed to an oxide, followed by removal of this oxide in buffered hydrofluoric acid (BHF) (10:1) and post-etch immersion in KOH (0.5 M) at 150 °C to smooth the surface and reveal the crystal planes. The dependence of the PEC treatment parameters [optical intensity, solution composition, and direct current (DC) bias] on etch rates and morphology has also been investigated. The results indicate that structures with very smooth sidewalls can be obtained using this novel PEC-based wet etch process. This is promising for the fabrication of novel electrical and optoelectronic GaN-based devices.

II. EXPERIMENT

n-type GaN grown by metalorganic chemical vapor deposition with c-plane crystal orientation on sapphire substrates was used for the PEC-enabled process reported here. The process starts with the deposition and liftoff of an etch mask consisting of 150 nm of titanium (Ti) by electron beam evaporation. This Ti layer serves as both the PEC mask as well as an electrical contact to the n-GaN to complete the electrochemical cell.[13] Figure 1 shows a schematic diagram of the experimental configuration. The GaN sample was placed on a Teflon holder and immersed in the KOH solution. A

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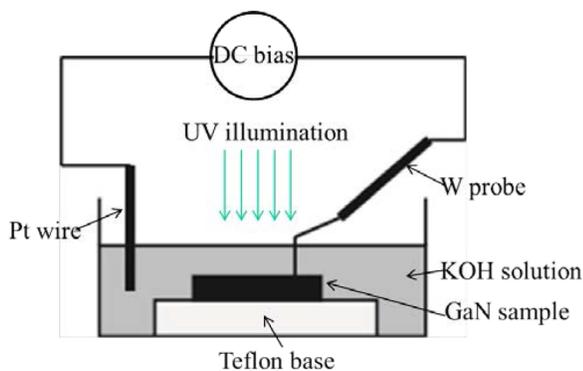
FIG. 1. (Color online) Schematic of the experimental configuration.

tungsten (W) probe was used to contact the Ti mask on the GaN sample. A Pt wire was inserted in the KOH solution as the cathode to form the electrochemical current loop. Both the tungsten probe and the platinum wire were connected to a Keithley Model 2400 Sourcemeter to simultaneously provide DC bias to the electrochemical cell as well as monitor the current flow during the PEC treatment. A 1000 W mercury–xenon lamp was used to provide the ultraviolet (UV) illumination during the PEC treatment. As will be discussed in more detail in Sec. III, the intensity of the UV light during the PEC treatment is an important process parameter. In the work reported here, intensities ranging from 800 to 3000 mW/cm^2 were evaluated. A broadband Si power meter was used to measure the intensity of the UV light. After the PEC treatment, the sample was immersed in BHF (10:1) for 30 min to completely remove both the Ti mask as well as the surface oxide formed during the PEC treatment. This was then followed by immersion in KOH (0.5 M) at 150 °C for 30 min to form the smooth sidewalls. The GaN sample was examined by scanning electron microscope (SEM) after each step to monitor the evolution of the surface and sidewall morphology.

III. RESULTS AND DISCUSSION

The evolution of the sidewall formation is shown in Fig. 2. After the PEC treatment step, surfaces such as those shown in Figs. 2(a) and 2(b) were obtained. For this example, the n-GaN sample was illuminated at a UV light intensity of 3000 mW/cm^2 and an applied DC bias of 0.6 V, while immersed in a KOH concentration of 2 mM at 60 °C. As can be seen in the inset of Fig. 2(a), the mask pattern consisted of a series of parallel rectangles oriented in two orthogonal directions. The surface after PEC treatment results in a raised surface (i.e., the exposed surface after PEC treatment is above, rather than below, the masked surface) as shown in the oblique-incidence SEM shown in Fig. 2(b). As can be seen, this raised surface exhibits significant cracking, but the cracks are confined to the regions of the surface that were exposed to the PEC treatment; they do not propagate into the areas that were masked with Ti during the treatment. To evaluate the composition of the apparently expanded material formed during PEC treatment, energy-dispersive x-ray spectroscopy (EDS) was performed. As
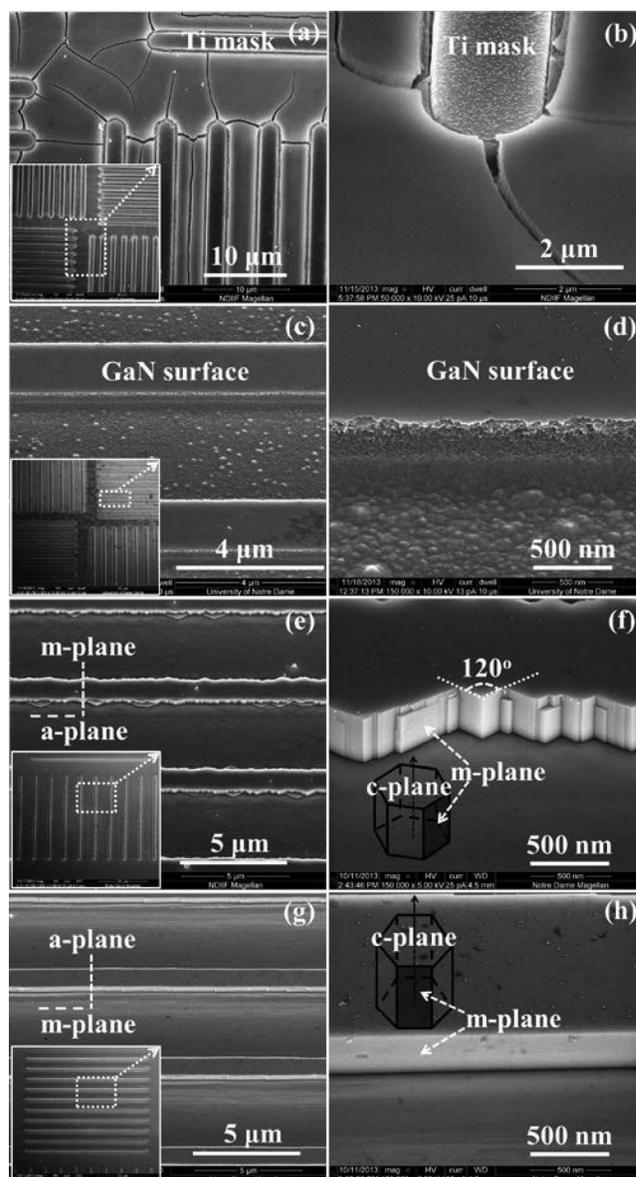
FIG. 2. SEM micrographs: (a) and (b) after PEC treatment of n-GaN with UV light intensity of 3000 mW/cm^2, DC bias of 0.6 V in KOH (2 mM) at 60 °C, showing growth and expansion of oxide film during treatment; (c) and (d) images after immersion in BHF (10:1) for 30 min to remove the Ti mask and the oxide film formed during PEC treatment; and (e)–(h) two facet sidewalls of GaN after immersion in KOH (0.5 M) at 150 °C.

shown in Fig. 3(a), Ga and O peaks were detected using the EDS in the PEC-treated area, indicating that the PEC process results in the formation of GaO$_x$ in the exposed area. This is consistent with the observed cracking in Figs. 2(a) and 2(b), since GaO$_x$ is known to expand anisotropically as it grows.[18] Under similar process conditions, Rotter *et al*. reported photoassisted wet chemical formation of thin oxide films on n-GaN layers in KOH (2 mM), and found that growth of a 250 nm-thick oxide on c-plane GaN consumed 45 nm of the underlying GaN, indicating that the Pilling–Bedworth ratio for c-plane oxide growth is >5.[19] However, Peng *et al*. found that the photoenhanced oxidation rate of nonpolar m-plane GaN is one order of magnitude slower than that on

FIG. 3. (Color online) EDS spectroscopy: (a) after PEC treatment of n-GaN and (b) after the immersion of n-GaN in BHF (10:1).

should be mentioned that the sidewalls in both perpendicular directions of the mask features appear essentially the same, with no clear crystallographic preference. The sample was then immersed in KOH (0.5 M) for 30 min at 150 °C. After this treatment, the sidewalls of the GaN features take on a strongly crystallographic character, as shown in Figs. 2(e)–2(h). For the sidewalls aligned in the direction shown in Figs. 2(e) and 2(f), the sidewalls form m-plane facets ($\{1\bar{1}00\}$) with an angle of 120° between them. Features in the perpendicular direction to this are shown in Figs. 2(g) and 2(h). In this case, the facet sidewalls are smooth, vertical, and extremely flat. As can be seen in Figs. 2(g)–2(h), smooth sidewalls extending for more than 2 μm have be achieved. Since the etched surfaces are crystallographic planes, the length over which a flat surface is achieved is limited primarily by the alignment accuracy between the mask pattern and the underlying crystal planes, though defects in the mask edge can also lead to local defects in the etched surface. It has previously been reported that KOH (0.5 M) treatment at 150 °C can effectively remove the grasslike oxide features remaining after conventional PEC etching and produce a smooth surface. However, to the best of our knowledge, the formation of smooth sidewalls after a PEC treatment (that is not an etch, since under the conditions used here the PEC treatment strictly grows the oxide, with the etching taking place in a subsequent process step) has not previously been reported.

In order to both explore the process window for formation of smooth sidewalls as well as to gain additional insight into the kinetics of the underlying processes, the impact of several process parameters on etch rate and morphology has been assessed. Figure 4 shows an example of the impact of UV illumination intensity on sidewall morphology. These images are taken along each of the perpendicular directions associated with the mask features, and were obtained from the polar c-plane.[18] This combination of expansion during oxide growth and strong directional growth rate anisotropy leads to the cracked surface morphology shown in Figs. 2(a) and 2(b). The strongly anisotropic oxide growth rates between polar (c-plane) and nonpolar (m-plane) surfaces have been attributed to surface band bending in the GaN caused by the surface states and discontinuity of spontaneous polarization.[20] For c-plane orientations, these effects result in large internal electric fields, and thus enhance the photo-oxidation process, whereas along the nonpolar m-plane directions in GaN such field action is minimized.[18,21]

To complete the etch, this GaO$_x$ film was etched away by the immersion in BHF (10:1), leaving a moderately rough surface as shown in Fig. 2(c). After the BHF (10:1) etch, EDS spectroscopy showed clear Ga and N peaks and a much-reduced O peak in the etched area, as shown in Fig. 3(b). The strong Ga and N peaks are attributed to the exposed GaN surface, while the much weaker O peak indicates that the GaO$_x$ layer has been removed. A rather rough, possibly porous, sidewall morphology was observed for the GaN after BHF (10:1) etching, as shown in Fig. 2(d). It

FIG. 4. SEM micrographs of two facet sidewalls of GaN using different intensity of UV light (a) and (b) 800 mW/cm^2 and (c) and (d) 1500 mW/cm^2.

samples in which the PEC illumination intensity was 800 and 1500 mW/cm^2. The other key parameters were held constant; a DC bias of 0.6 V and KOH concentration of 2 mM at 60 °C were used for both. At the relatively low UV intensity of 800 mW/cm^2, a clear undercut can be seen along the sidewall, as shown in Figs. 4(a) and 4(b), as well as the formation of "inverted pyramids" similar to previous reports.[22] However, for a UV intensity of 1500 mW/cm^2, the two facet sidewalls become smooth and take on a strongly crystallographic character, as shown in Figs. 4(c) and 4(d); this is essentially identical to the results shown in Fig. 2 with an even higher UV intensity of 3000 mW/cm^2. These results indicate that the crystallographic character of the GaN sidewalls appear for UV intensities above a threshold value, in this case between 800 and 1500 mW/cm^2. This process dependence on UV intensity suggests the key physical mechanism underlying this new process: under low-intensity illumination ($\leq$800 mW/cm^2), the rate of oxide formation and oxide removal in the KOH (2 mM) solution are more closely balanced, leading to a conventional PEC etching mode, and the same morphology as has been previously observed.[22] In this conventional PEC etching mode, the different density of broken bonds between Ga-face and N-face surfaces leads to different etch behaviors, and the formation of the inverted pyramids structures on the N-face surfaces.[22,23] However, at high UV light intensities, the rate of GaO$_x$ formation can greatly exceed the rate of chemical dissolution, resulting in the formation of the thick GaO$_x$ layer. Thus in the process reported here, the physical processes that normally compete in conventional PEC-based etching are separated into discrete process steps (oxide formation in the PEC treatment, oxide dissolution in the subsequent BHF and KOH treatments).

The dependence of sidewall morphology on PEC treatment KOH concentration was also evaluated. At a lower concentration of KOH (1 mM) [shown in Figs. 5(a) and 5(b)], the resulting sidewalls are essentially identical to the results obtained for 2 mM concentrations in Figs. 2(h) and 2(f), but the effective etch rate (of the overall oxidation/etch process) was reduced by approximately 25%, due primarily to reduced PEC-enhanced oxidation rate. At a much higher PEC treatment KOH concentration of 0.01 M, the effective etch rate increases dramatically, by approximately 16 times, and the facet sidewall morphology changes significantly, as shown in Figs. 5(c) and 5(d). The facet that had previously been smooth takes on square- and irregularly shaped features, while the hexagonal face facet takes on a much more rapid variation, with each plane being typically smaller. This can also be understood using the basic kinetic model postulated previously; higher KOH concentrations during the PEC treatment result in increased dissolution of the oxide during formation, roughening the surface.

The dependence of etch rate and surface morphology on the externally applied voltage bias was also evaluated. A DC bias is applied between the W probe contact with the Ti mask (anode) and the Pt wire (cathode) in the KOH PEC treatment solution. While the UV illumination is responsible for the excess minority carriers that facilitate the oxidation of the exposed surface, the process can be "tuned" through
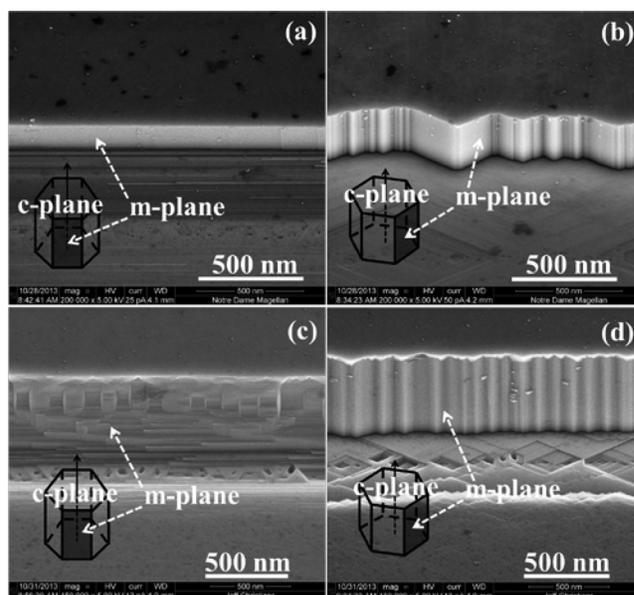
FIG. 5. SEM micrographs of two facet sidewalls of GaN using different concentration of KOH (a) and (b) 1 mM KOH and (c) and (d) 0.01 M KOH.

the externally applied bias. For the forward-bias conditions shown here—which were previously identified as favorable for forming smooth sidewalls in conventional PEC etching[13]—the positive bias applied to the Ti mask acts to
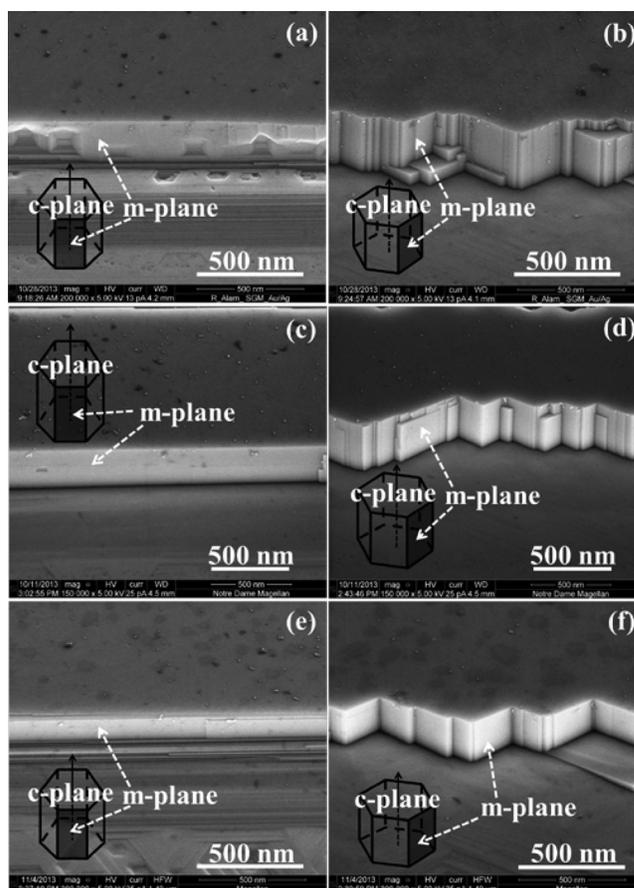
FIG. 6. SEM micrographs of two facet sidewalls of GaN using different DC bias (a) and (b) 0 V, (c) and (d) 0.6 V, and (e) and (f) 2 V.

improve the extraction efficiency of electrons from the UV-exposed surface and allowing photogenerated holes to more efficiently promote oxide formation at the exposed surface. This previously reported "photopotential" effect results from the open-circuit potential shifting to a more negative value for n-type semiconductors under illumination.[24,25] As a result, an increasing positive potential between the W probe and Pt cathode promotes electron-hole separation, decreases the recombination probability and enhances the etch rate. As can be seen in Figs. 6(a) and 6(b), at 0 DC bias, a morphology quite similar to that obtained with higher-concentration KOH solutions (formation of square and rectangular features on one facet, short-period hexagonal facets on the other) is obtained. For larger biases [0.6 and 2 V shown in Figs. 6(c)–6(f)], however, the smooth side-walls appear, as expected, since with these bias conditions the efficiency of the oxidation is increased, while without applied bias (or with negative bias, not shown) the oxidation efficiency is suppressed and the dissolution of the GaN in the KOH solution becomes significant, resulting in conventional PEC-etching like morphologies. This is also consistent with the observation that the etch rate increases with applied bias; the etch rate is approximately 3.8 times higher for 2 V bias than for the unbiased case.

IV. SUMMARY AND CONCLUSIONS

A PEC-based process for forming smooth, vertical, crystallographic m-plane facets in n-GaN on sapphire is reported. Unlike conventional PEC etching, in this process the oxide formation and oxide dissolution steps are separated into distinct process steps, which enables unique etch morphologies to be obtained. The facet sidewall morphology has been investigated as a function of UV illumination intensity, PEC treatment solution concentration, and applied bias voltage, and the results are consistent with a process dominated by oxidation (in the PEC treatment step) and oxide dissolution (in the post-treatment wet etch steps). This process may offer advantages for the formation of vertical facets in optoelectronic devices such as edge-emitting lasers and wave-guide sidewalls, as well as the fabrication of low-damage sidewalls for electrical devices due to the absence of ion-bombardment damage (endemic in conventional dry-etch processing for nitrides) in wet etch processing.

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