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Chemical Etch Characteristics of N-Face and Ga-Face GaN by Phosphoric Acid and Potassium Hydroxide Solutions

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We report the chemical etching characteristics of Ga-face and N-face GaN using phosphoric acid (H_3PO_4) or potassium hydroxide (KOH) solutions. Hexagonal pyramids, which consisted of the {10-1-1} planes, were present on the N-face after KOH (2M, 100°C) etching. By contrast, using the H_3PO_4 (85 wt.%, 100°C) solutions, the nitrogen surface of GaN showed dodecagonal pyramids. Dodecagonal and hexagonal pyramids repeatedly appear on the etched surface when using the H_3PO_4 or KOH solutions, respectively. A low concentration of H_3PO_4 (H_3PO_4 : deionized water = 1:32, 1:64) produced a roughened surface with coexistence of dodecagonal and hexagonal pyramids. The photoluminescence (PL) intensity of the etched surfaces significantly increased due to multiple scattering events compared to the non-etched surface. Thus, the etching techniques developed in this study were shown to improve the light extraction efficiency of light emitting diodes (LEDs), avoiding the damage to the GaN typically created by plasma etching methods.
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Group-III nitride materials are widely used in high-power optoelectronic and electronic devices. GaN LEDs have a very small critical angle (∼23.6°) due to the difference in the refractive index between GaN (n = 2.5) and air (n = 1) according to Snell's law.[1] When the interface between GaN and air is very flat and wide, it has been reported that only 4% of the generated photons can escape the surface.[2] Many methods have been developed to address this issue, including the use of a photonic crystal structure,[3] graded-refractive-index layer[4] and pattered sapphire substrate.[5] Among these approaches, wet chemical etching has been commonly used for the surface texturing of group-III nitride material systems due to its characteristics such as simple equipment set-up and absence of lattice damage, scalability and good selectivity.[6] Photo-enhanced chemical (PEC) wet etching has been demonstrated at room temperature, but it has issues with scalability.[7] In addition, PEC etching is an effective technique for anisotropic and bandgap-selective etching.[6–8] A variety of methods for surface texturing through wet etching are currently employed to increase the light extraction efficiency in group-III nitride-based LEDs.[2,11–14] Hexagonal pyramid structures, which can be formed on N-face surface by KOH etching, assist in the escape of photons which are caught inside due to total internal reflection. These hexagonal pyramids have commonly been observed on KOH etched N-face GaN. In a previous study, we examined the etching behavior Ga- and N-face GaN using KOH solutions.[15,16] In addition, Jung et al. enhanced the light extraction efficiency of non-polar a-plane GaN LEDs by etching the sidewall and the n-type GaN surface via KOH etching.[12] A mixed solution of H_2SO_4 and H_3PO_4 was also used to produce the hexagonal pyramids on the surface of c-plane GaN.[17] Hot H_3PO_4 and KOH etching on the N-face GaN, which was grown using a molecular beam epitaxy system, was also performed by Visconti et al.[18] In previous studies, hot H_3PO_4 etching of the N-face GaN films was shown to very quickly result in drastic changes in the surface morphology. Qi et al.[19] fabricated roughened surfaces containing dodecagonal pyramids by hot H_3PO_4 etching of N-face GaN prepared by laser lift-off process. However, it has been rarely reported the effects of the various solutions and concentrations on both Ga- and N-face GaN. In this paper, we investigated the different etching behavior and mechanism of H_3PO_4 and KOH solutions in Ga- and N-face GaN.

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Experimental

Commercial Ga-face and N-face GaN samples were used in our experiments. GaN samples contained in a Teflon holder were etched in H_3PO_4 solution (Sigma Aldrich, 85 wt.% in H_2O). The H_3PO_4 etched sample was etched in 2M KOH solution, followed by a rinsing in deionized (DI) water. The sample was then dried under a flow of nitrogen. Several pieces cut from the same GaN were etched in the H_3PO_4 solution at different concentrations (H_3PO_4 (85 wt.%): Deionized water = 1:0, 1:16, 1:32 and 1:64) to determine the relationship between surface morphology and the concentrations of solutions. The temperature of the solutions was maintained at 100°C and the stirring rate was 200 rpm in all cases. The duration of the etching was 20 minutes. A scanning electron microscope (SEM, Hitach S-4700) was used to characterize the surface morphologies. The optical properties of the non-etched and etched samples were measured using a micro-PL equipments (325nm He-Cd laser, KIMMON Koha Co., Ltd.).

Results and Discussion

In order to determine the relationship between surface morphology and etchant type, H_3PO_4 or KOH solutions were used to etch the same GaN samples. The N-face GaN already exhibited a rough surface before wet etching (Fig. 1a). It is generally known that the surface of N-face GaN is rougher than that of Ga-face GaN.[20] SEM images of the surface morphology of the samples after being etched by H_3PO_4 (85 wt.%) for 20 minute at 100°C are shown in Fig. 1b. Dodecagonal pyramids were formed on the surface of the N-face GaN after H_3PO_4 etching, which is consistent with the previous report.[19] By comparing Fig. 1b and Fig. 1c, it can be clearly seen that KOH etching changed the surface morphology from dodecagonal pyramids to hexagonal pyramids. It has been reported that the N-face GaN is more chemically active than the Ga-face GaN, where the hexagonal pyramids exposed after KOH-based chemical etching consist of six {10-1-1} facets.[15,20,21] Ga-face GaN has been shown to be chemically stable and no obvious etching was observed in the KOH solution. The number of dangling bonds on the surface is believed to control the etching behavior of the Ga-face and N-face GaN.[20,21] On the Ga-face,

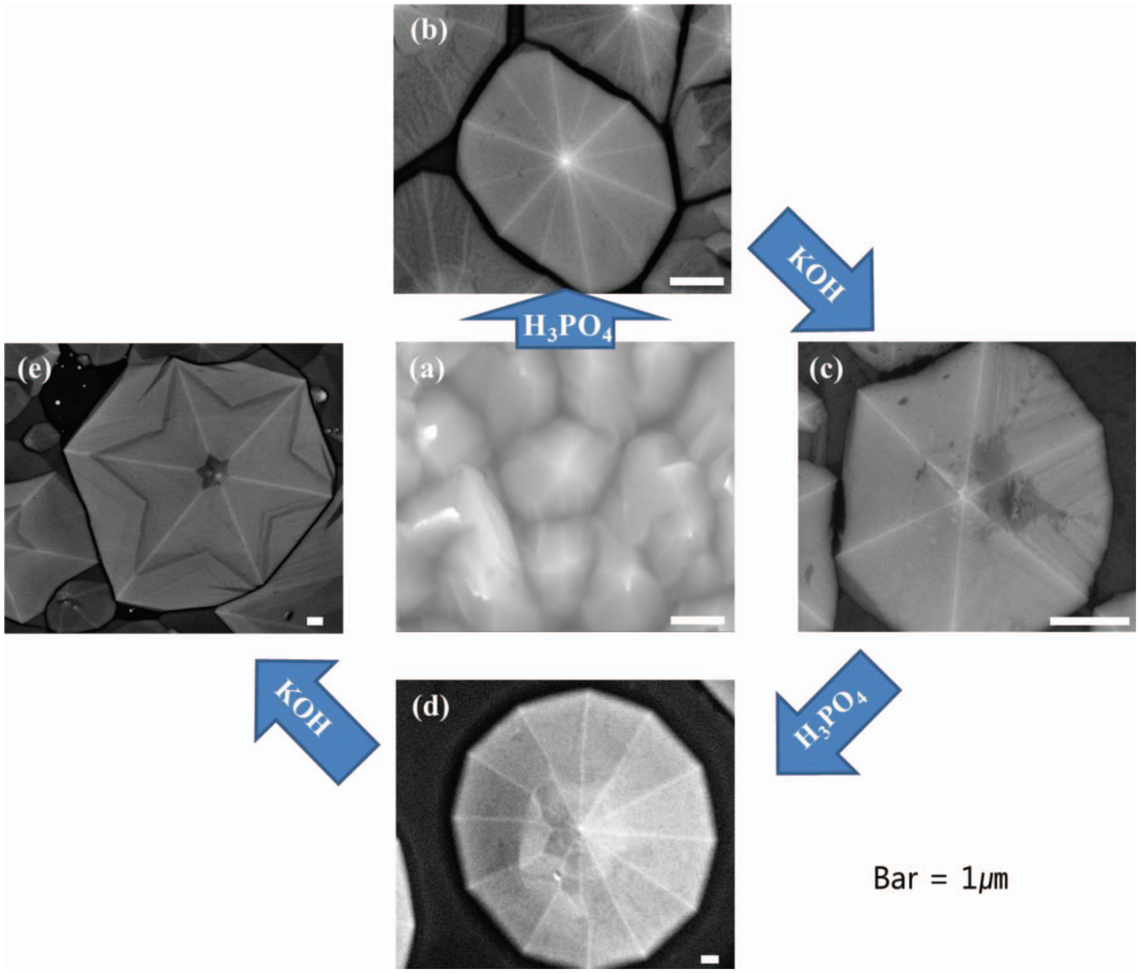

Figure 1. SEM images of N-face GaN (a) before etching, (b) after H_3PO_4 etching, (c) after KOH etching, (d) after H_3PO_4 etching, (e) after KOH etching.

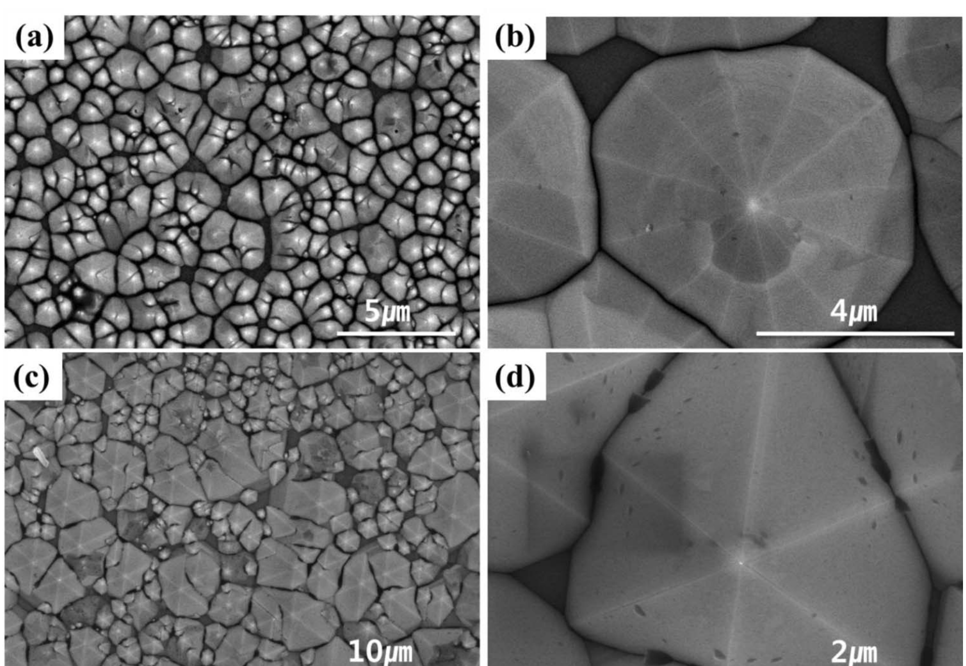

Figure 2. SEM images after (a, b) 85 wt.% H_3PO_4 etch and (c, d) 2M KOH etch at 100°C.

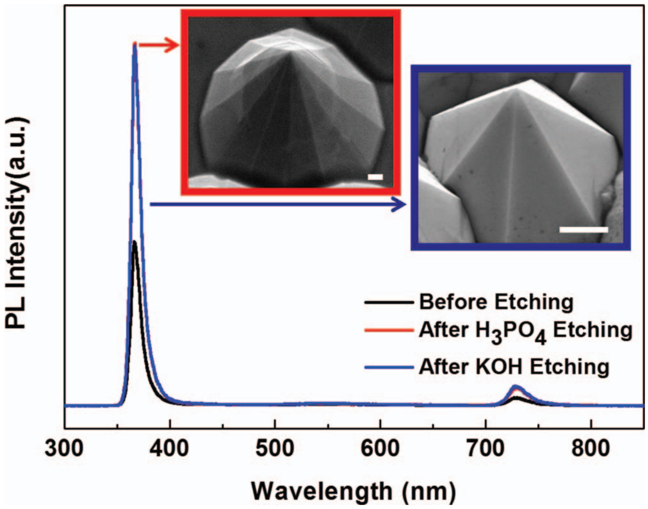

Figure 3. PL spectra of non-etched (black line), KOH-etched (blue line) and H_3PO_4 etched (red line) N-face GaN. Inset shows feature of the pyramid under each conditions (scale bar = 1μm).

each nitrogen atom, which exists on the surface after removing the first Ga-layer by OH^- ions, has three dangling bonds. Consequently, wet etching cannot continue due to the repulsive force between the three dangling bonds and OH^- ions. For this reason, the surface morphology of the Ga-face GaN remained flat (stable) after KOH-based wet etching, which was unlike the N-face GaN. The chemical reaction will be[20,21]

$$2GaN + 3H_2O \rightarrow Ga_2O_3 + 2NH_3$$

By sharp contrast, Ga-atoms under the Nitrogen atoms with only one dangling bond are easily accessible to OH^- ions and the Ga-atoms and OH^- ions can form Ga-O compounds, which are soluble in the KOH solution. The change in surface morphology from hexagonal pyramids to dodecagonal pyramids by etching in the H_3PO_4 solution is shown in Fig. 1d. Once again, dodecagonal pyramids on the GaN surface became hexagonal pyramids after KOH etching using the H_3PO_4 etched sample in Fig. 1e. Through a series of experiments, different pyramid shapes were selectively formed on the surface of the N-face GaN when using the H_3PO_4 or KOH solution at 100°C. The size of the pyramids increased after each treatments, which is in consistent with the previous report.[19] Figure 2 shows the SEM images after KOH (2M) or H_3PO_4 (85 wt.%) etch at 100°C. The dodecagonal (Fig. 2a and 2b) or hexagonal (Fig. 2c and 2d) pyramids were observed from N-face GaN after chemical etch. In addition, these results were highly reproducible.

PL measurements were used to characterize the effects of light extraction efficiency on the etched surfaces. There is a very small critical angle (∼23.6°) between air and GaN as calculated by Snell's law $\left(\theta c = \sin^{-1}(n_2/n_1)\right)$.[1] However, the probability of light extraction can be improved with an increase in the effective surface area, which can be produced by wet etching. Fig. 3 shows that the PL intensity significantly increased after wet etching. Based on these results, we concluded that chemical wet etching changed the surface into a structure that allows photons to escape easily. Also, we did not observe any difference in PL intensity between the different (dodecagonal and hexagonal) features of the pyramids on the GaN surface.

Qi et al. reported that the dodecagonal pyramids were formed on N-face GaN by hot phosphoric acids due to their nature of kinetic-limited process, rather than the thermodynamic one.[19] The kinetic-limited factors of the etch process result in dodecagonal pyramids which consist of twelve facets with {20-2-3} and {22-4-5} facets.[22] We believe that GaN hexagonal crystals with six {10-10} facets are turned into dodecagonal pyramids with {20-2-3} and {22-4-5} facets, which become hexagonal pyramids with {10-1-1} facets under molten KOH solutions. Dodecagonal and hexagonal pyramids reproducibly appear under hot H_3PO_4 solutions and molten KOH solutions, respectively. We believe that N-face GaN wet etching preferentially slows down on {10-1-1} facets of N-face GaN under molten KOH solutions, and {20-2-3}/{22-4-5} facets under hot H_3PO_4 solutions due to their low surface energies. In KOH-based etch, Ga atom reacted with OH- to form Ga_2O_3, which subsequently dissolved in base solution. In H_3PO_4-based etch, it has been reported that the oxidation of GaN took place in aqueous H_3PO_4 solutions.[23,24] Then, the Ga_2O_3 dissolved in acid solution. Therefore, the formation of Ga_2O_3 is critical in both cases. We also examined the changes in surface morphology at different H_3PO_4 concentrations. Fig. 4 shows a SEM image of the N-face GaN surface with a diluted phosphoric acid ((85 wt.% H_3PO_4): H_2O = 1: 32) at 100°C. Using the (1:0) and (1:16) 85 wt.% H_3PO_4 : H_2O, the pyramids that were present on the etched surface of the N-face GaN maintained their dodecagonal features. However, as shown in the Fig. 4b, hexagonal pyramids were partially observed on the etched surface using (1:32) 85% H_3PO_4:H_2O. This phenomenon was also observed at lower concentrations. In the case of (1:64) and (1:128) 85 wt.% H_3PO_4 : H_2O, hexagonal pyramids were also partially observed on the N-face GaN with the dodecagonal pyramids (Fig. 4c, (1:128) is not shown). In this study, we demonstrated partial formation of hexagonal pyramids on the N-face GaN after diluted H_3PO_4 etching.

In GaN-based LED, roughening of the N-face GaN by either base- or acid-based chemical etching holds promise in increasing the light extraction efficiency. In addition, the light extraction efficiency may be further improved by optimizing the H_3PO_4 etching conditions since the surface area of dodecagonal pyramids is larger than that of hexagonal pyramids.

Conclusions

We examined the etching behaviors of Ga- and N- face GaN in hot H_3PO_4 or KOH solutions. Changes of surface morphology between hexagonal and dodecagonal pyramids were found to be dependent on the (KOH or H_3PO_4) etchant and the concentrations. Different distributions of the pyramid shapes were also found to be dependent on the concentrations of H_3PO_4. Both hexagonal and dodecagonal pyramids were present on the N-face GaN after the chemical etch

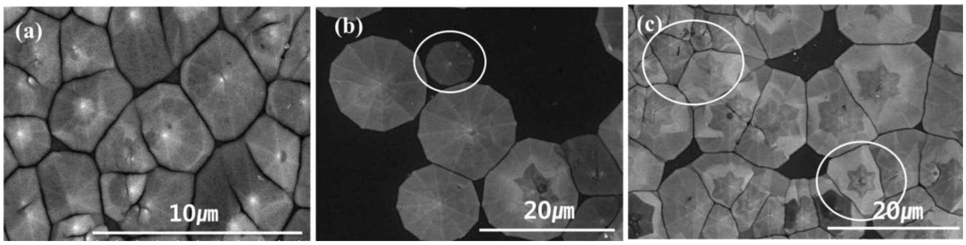

Figure 4. SEM images of the N-face GaN surface etched at low concentrations; (a) 85 wt.% H_3PO_4 (b) (1:32) 85 wt.% H_3PO_4 : H_2O (c) (1:64) 85 wt.% H_3PO_4 : H_2O (Note: the hexagonal pyramids were observed inside the circle).

with lower H_3PO_4 concentrations. These chemical etch methods by acid or base solutions will be helpful to improve the light extraction efficiency in GaN-based LEDs.

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