Journal of The Electrochemical Society, **157** (6) H676-H678 (2010)
0013-4651/2010/157(6)/H676/3/$28.00 © The Electrochemical Society

Effects of Photoelectrochemical Etching of N-Polar and Ga-Polar Gallium Nitride on Sapphire Substrates

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We studied the effects of photo electrochemical (PEC) etching by using various concentrations (1, 2, and 4 M) of KOH solutions on both Ga- and N-face GaN layers on sapphire substrates. The Ga-face was chemically stable for KOH solutions, while by sharp contrast the KOH could etch the N-face, where the 6-fold symmetry was observed after the PEC etching. Surface texturing of GaN-based light emitting diodes and solar cells by KOH-based PEC etch could enhance the efficiency of GaN-based photonic devices by increasing the number of the scattering events and randomly changing the angles of the light.
 [DOI: 10.1149/1.3384713]

Manuscript submitted February 28, 2010; revised manuscript received March 10, 2010. Published April 28, 2010.

The gallium nitride (GaN) material system has been developed for a broad range of applications involving light emitting diodes (LEDs), laser diodes, and high power electronic devices.[1-3] In particular, the exceptional optical properties such as direct bandgap (3.4 eV at room temperature) and the availability of bandgap engineering through alloying with In and Al make the nitride system ideal for emerging optoelectronic applications.[4] Although GaN-based LEDs have been successfully commercialized, there are still issues related to the choice of crystal polarity. Current GaN-based LED structures employ Ga-face growth of GaN and these layers are generally smoother and more stable than N-face GaN.[5,6] Because the availability of large area homoepitaxial GaN substrates is still limited, most GaN-based LEDs have been grown on sapphire, where the thermal conductivity is extremely low (about 42 W/(m K) at room temperature).[7] To efficiently remove the generated heat, LED flip-chip technologies, where the N-face is facing up, have been developed. In this case, GaN is in contact with the heat sink and provides more efficient cooling because the thermal conductivity [160 W/(m K) at room temperature] of GaN is about 4 times higher than that of sapphire.[4]

Low light extraction efficiency is also an issue that hinders further improvement in the light output from LEDs.[4] The escape cone from GaN into air is about 24°, according to Snell's law. Because the bond strength of Ga–N is very high (8.92 eV/atom), GaN is chemically and mechanically very stable. Much effort has focused on developing methods to improve the light extraction efficiency, including the use of photonic crystals, photoelectron-chemical etching, conventional lithography, and nanoimprinting technologies.[8-11] Among these, PEC (photo electrochemical) etching has advantages in terms of the compatibility with conventional semiconductor processing equipment and easy scalability to large wafers as well as the processing cost.

Recently, GaN-based solar cells have also attracted much interest, with demonstrations that the theoretical conversion efficiency can be as high as 40.3% at air mass 1.5.[12,13] Because these solar cells suffer from losses due to the total reflection at the interface between air and solar cells, the minimization of the reflection is critical to optimize the structure of the cells.[4] In the crystalline Si solar cells, a pyramid structure obtained using the wet etching method has been widely employed because the wet etching does not cause any lattice damage to the crystal compared with dry etching methods such as reactive ion etching (RIE) and ion-induced sputtering.[14] GaN with its wurtzite structure can be preferentially wet-etched to form the hexagonal pyramid structure depending on the facets and polarity.[15-19] It is believed that the surface texturing is also important for GaN-based solar cells. In this paper, we directly compared the characteristics of KOH-based PEC etching on both Ga-face and N-face GaN by using atomic force microscopy (AFM), scanning electron microscopy (SEM), and the reflectance measurement at various KOH concentrations.

Experimental

Several pieces of GaN cut from the same sample were used for contactless PEC etching experiments in various KOH concentrations. The nominally undoped ($n \sim 5 \times 10^{16}$ cm^{-3}) 3 μm thick layers were grown by metallorganic chemical vapor deposition, as described elsewhere.[20] To compare the morphologies of both Ga- and N-face GaN after PEC etch treatments, both faces were dipped in the solution for the same time (10 min). We used various concentrations (1, 2, and 4 M) at 50°C under UV illumination with a magnetic stirrer (300 rpm). Figure 1 shows our experimental setup. The GaN samples were contained inside a Teflon holder during the PEC etch process. The surface morphologies and optical properties of both Ga- and N-faces were characterized by AFM (VEECO Multimode), scanning electron microscope (Hitachi S-4700), and reflectivity measurements (Ocean Optics Inc., USB 2000+).

Results and Discussion

Figures 2 and 3 present the SEM and AFM images of Ga-face and N-face GaN after each PEC etch, respectively. As shown in Fig. 2, the Ga-face GaN was initially very flat before PEC etching. The Ga-face GaN became even flatter after PEC etching, which is consistent with the previous reports that Ga-face GaN is very stable and inert.[5,6] Table I shows that the root-mean-square (rms) roughness of Ga-face GaN changed from 27.9 nm (before PEC treatment) to 2.1 nm (4M KOH). The triangular inclusion in Fig. 2B can be explained by the removal of the defects, for example, the inverted domain. By sharp contrast, pristine N-face GaN was rough with rms of 141.3 nm. After PEC etching at 4 M KOH concentrations, the roughness went up to 227.7 nm. As can be seen in the SEM and AFM images, the facets of the hexagonal pyramids became very sharp as a result of the PEC etching process. In addition, the density of the hexagonal pyramids was increased after the PEC treatments. Li et al. reported the etch reaction under similar conditions as

$$2GaN + 3H_2O \xrightarrow{KOH} Ga_2O_3 + 2NH_3$$

where KOH is both a catalyst for the reaction and a solvent for the resulting Ga_2O_3.[17] Because the wet etch process occurs through the negatively charged OH^- ions, Ga-face GaN is more stable than N-face GaN due to the negatively charged triple dangling bonds at the surface of Ga-polar GaN.[17,18] This etch process can be acceler-

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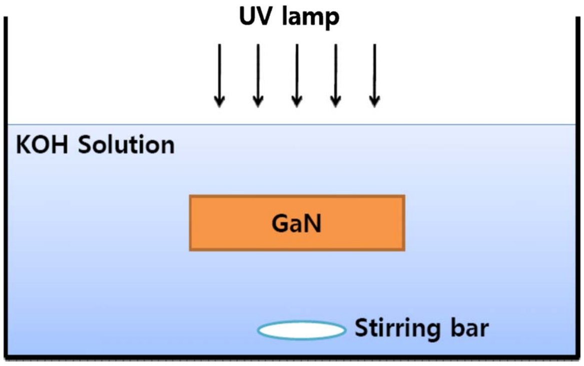

Figure 1. (Color online) Schematic of PEC etch setup used in our experiments. The GaN samples were immersed at various KOH concentrations (1, 2, and 4 M) for 10 min under UV lamp illumination with a stirring speed of 300 rpm.

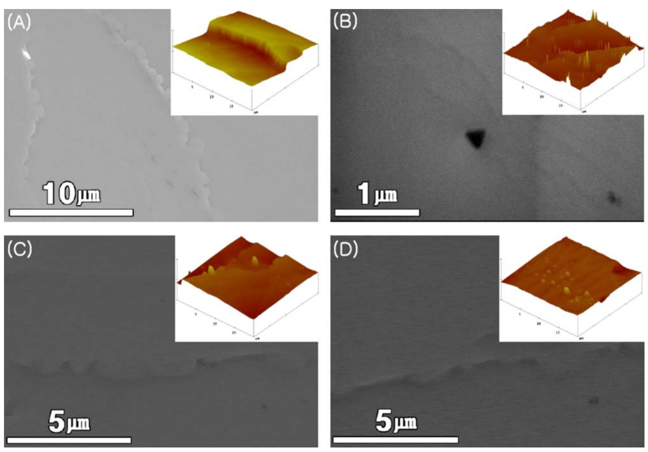

Figure 2. (Color online) Top-view SEM and AFM (inset) images of the surface morphology on Ga-face GaN/sapphire at 50°C for 10 min in various concentrations of KOH solutions (A) before etching, (B) 1 M KOH, (C) 2 M KOH, and (D) 4 M KOH.

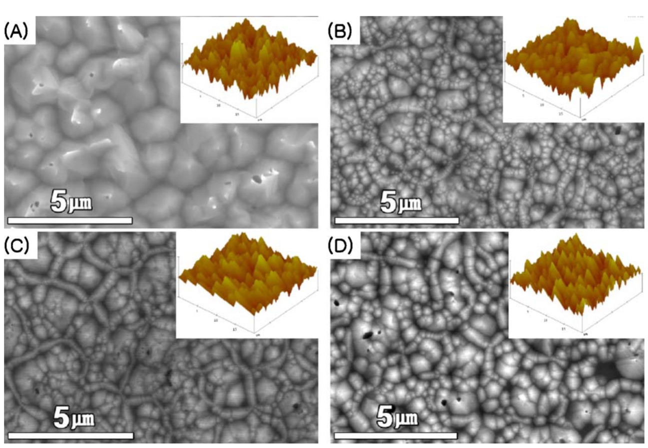

Figure 3. (Color online) Top-view SEM and AFM (inset) images of the surface morphology on N-face GaN/sapphire at 50°C for 10 min in various concentrations of KOH solutions (A) before etching, (B) 1 M KOH, (C) 2 M KOH, and (D) 4 M KOH.

Table I. Summary of rms data of each faces (Ga-, N-) at various PEC etch conditions.

rms	Ref (nm)	1 M-10 min (nm)	2 M-10 min (nm)	4 M-10 min (nm)
Ga-face	27.9	20.7	18	2.1
N-face	141.3	191.9	203.4	227.7

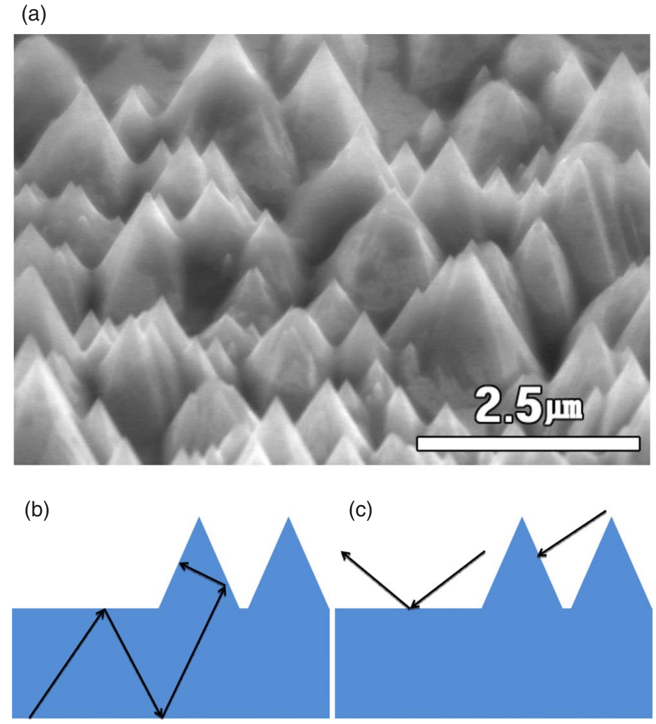

Figure 4. (Color online) (A) SEM image of N-face GaN surface after PEC etching. [(B) and (C)] figures are schematic drawings of the light path to compare the flat surface with the textured surface for applications in (B) LEDs and (C) solar cells.

ated by increasing the KOH concentrations by adding more OH^- ions.

To extract the photons generated within the quantum well in LEDs and to absorb the incoming light into the semiconductor in solar cells, a roughened surface is highly desirable because it can reduce the total reflection by increasing the number of the reflection events and randomizing the angles of the light rays.[21] In contrast to the dry etching process, which involves high energy ions, the KOH-based PEC etching avoids the damage induced by high energy particles. Figure 4A is our optimal surface structure after the PEC etch of N-face GaN, where the surface with dense hexagonal pyramids is ideal for both LEDs (Fig. 4B) and solar cell applications (Fig. 4C). Figure 5 shows the image from N-polar GaN that was PEC-etched

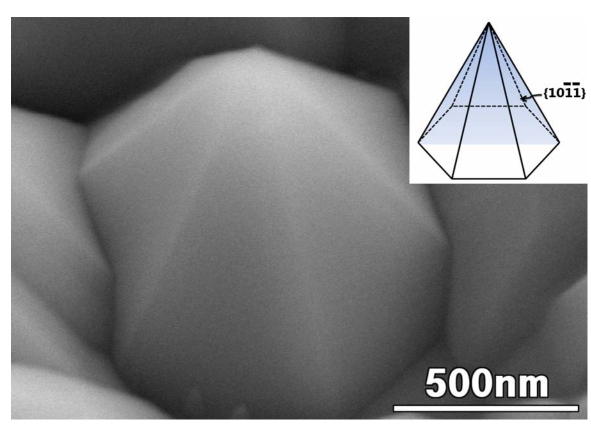

Figure 5. (Color online) High magnification SEM image of hexagonal pyramid on N-face GaN after PEC etch. (Inset: schematic view of the pyramid with six $\{10\bar{1}\bar{1}\}$ facets)

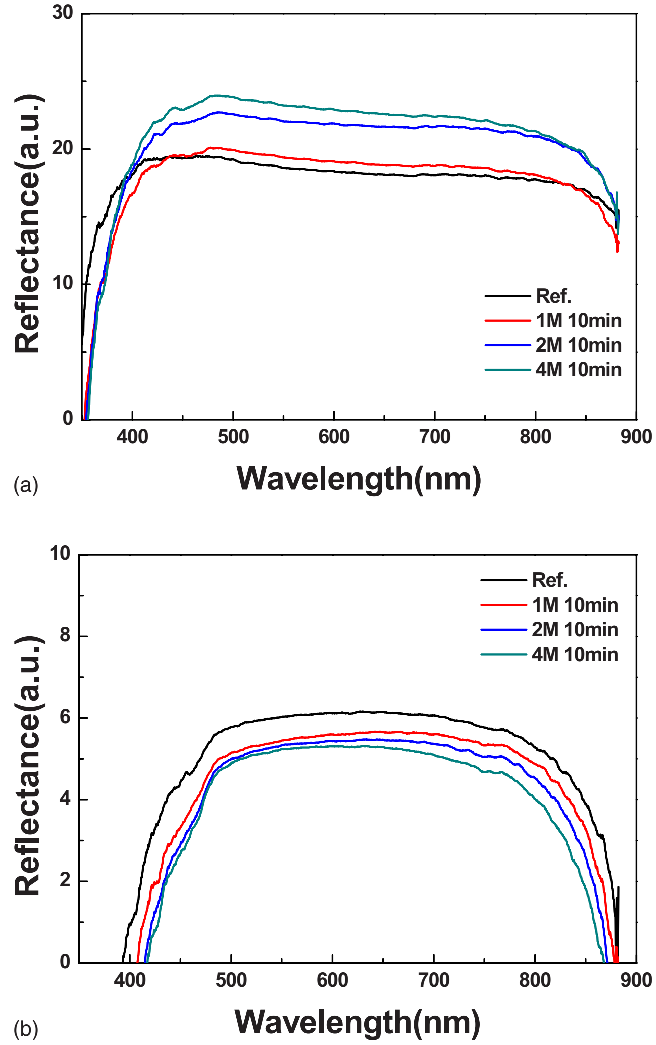

Figure 6. (Color online) (A) Reflectance data as a function of wavelength from Ga-face GaN after each PEC etch. (B) Reflectance data as a function of wavelength from N-face GaN after each PEC etch.

in 4 M KOH. Figure 5 has a 6-fold symmetry that confirms six $\{10\bar{1}\bar{1}\}$ facets (inset of Fig. 5).

The reflectance data were compared between N-polar and Ga-polar GaN at various KOH concentrations. As expected from the SEM and AFM results, the Ga-polar face showed a higher reflectance than the N-polar face (Fig. 6). Also, the reflectance was increased in Ga-polar GaN after the prolonged PEC etching because the surface became smoother. By sharp contrast, the roughened surface after PEC etch at higher KOH concentrations gave a lower reflectance because of the populated hexagonal pyramids with the sharper tips, which are beneficial to increase the light extraction efficiency in LEDs and the light absorption efficiency in the solar cells.

Conclusions

Ga-polar and N-polar GaN on sapphire substrates were compared for PEC etching characteristics at various KOH concentrations. Triple dangling bonds with negative charges prohibited etching on the chemically stable Ga-polar faces. N-polar faces were able to be chemically etched by exposing the 6-fold crystal facets. This process eliminates the high energy ions used in RIE or sputtering, which can cause severe lattice damage and create traps that degrade the performance of optical devices. Therefore, our KOH-based PEC etching on N-polar GaN has great potential for improving the efficiency of GaN-based optoelectronic devices by texturing the surface.

Acknowledgments

The research at Korea University was supported by the Carbon Dioxide Reduction and Sequestration Center, one of the 21st Century Frontier R&D Program funded by the Ministry of Education, Science and Technology of Korea.

Korea University assisted in meeting the publication costs of this article.

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