GaN hexagonal pyramids formed by a photo-assisted chemical etching method*

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A series of experiments were conducted to systematically study the effects of etching conditions on GaN by a convenient photo-assisted chemical (PAC) etching method. The solution concentration has an evident influence on the surface morphology of GaN and the optimal solution concentrations for GaN hexagonal pyramids have been identified. GaN with hexagonal pyramids have higher crystal quality and tensile strain relaxation compared with as-grown GaN. A detailed analysis about evolution of the size, density and optical property of GaN hexagonal pyramids is described as a function of light intensity. The intensity of photoluminescence spectra of GaN etched with hexagonal pyramids significantly increases compared to that of as-grown GaN due to multiple scattering events, high quality GaN with pyramids and the Bragg effect.

Keywords: hexagonal pyramids, GaN, photo-assisted chemical etching

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1. Introduction

Because of excellent physical and chemical properties, GaN-related materials have been intensively investigated in recent decades for application in optical and electronic devices, such as light emitting diodes (LEDs), laser diodes, high electron mobility transistors, and transparent thin-film transistors.[1] However, the total light output from these LEDs is still rather low.[2,3] Enhancing the efficiency of GaN-based LEDs is an area of active study.[4] There are two principal approaches for improving LED efficiency: the first is increasing the internal quantum efficiency, which is determined by the crystal quality and epitaxial layer structure, and the second is increasing the light extraction efficiency, which is primarily limited by the total internal reflection of the light generated from the active region at the semiconductor-air interface.[5] Many approaches have been carried out to increase the external efficiency, including roughening the surface of the LED.[6–9] The roughened top surface reduces internal light reflection and scatters the light outward. In particular, a hexagonal pyramid structure assists in the escape of photons which are caught inside due to total internal reflection. The etched surface morphology proves to be useful for enhancing the extraction efficiency of LEDs, increasing the light extraction efficiency by a factor of 2–3 times.[5] In addition, micrometer-size GaN pyramids of a high optical quality can be used to form efficient microcavities for multiple-mode optical resonance.[10] Another area of application for these structures is quantum dots that are formed on top of the GaN pyramids by depositing, for example, AlGaN/GaN/AlGaN or GaN/InGaN/GaN layers.[11]

GaN pyramids are usually formed through selective growth of GaN on patterned substrates by metalorganic chemical vapor deposition (MOCVD)[12–14] or hydride vapor-phase epitaxy (HVPE).[15] GaN pyramids fabricated from this method are usually lateral epitaxial overgrown on a sapphire substrate with a SiO_2 mask. The dislocation originated from the interface between the GaN and the sapphire substrate can easily penetrate into the as-grown GaN crystal due to lattice and thermal mismatch, even though it can be artificially controlled to spread horizontally.[16] These dislocations are detrimental to the device lifetime and its efficiency, since they provide nonradiative electron–hole recombination centers that dissipate energy in the form of heat instead of as photon emissions.[17,18] In addition, the strain distribution along the axial direction of GaN pyramids is quite non-uniform and thus leads to the different optical emissions within the crystal, which strongly affects the performance stability of GaN-based optoelectronic devices.[19,20] Also, the existing lithogra-

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phy is both complicated and costly. Therefore, it is definitely required to search for another effective method to synthesize GaN pyramids with improved crystal quality for the high-performance GaN nanodevices. The photo-assisted chemical (PAC) etching method provides a low-cost, effective and feasible approach for the realization of GaN pyramids with enhanced crystal quality and uniformity of light emission. In our research, an oxidizing agent has been used to the aqueous solution, which can effectively consume the photoexcited electrons. Compared with dry etching, wet chemical etching on a semiconductor induces much less damage. Wet etching for GaN has been extensively studied because of its low cost and large area fabrication. Using such a property, defect-selective etching of GaN has been reported[21] and applied in GaN-based laser diodes emitting in violet.[22] Several groups have investigated contactless GaN etching in a solution containing $K_2S_2O_8$ and KOH.[23–32]

In this paper, we obtained well-defined GaN with pyramids by photo-assisted chemical etching in KOH solution, with $K_2S_2O_8$ as the oxidizing agent. We have systematically studied the PAC etching for GaN, including the effects of the conditions (the etching time, solution concentration, and light intensity) on surface morphology, crystal quality, stress state and optical properties.

2. Experimental procedures

Photo-assisted chemical (PAC) etching consists of an ultraviolet (UV) light source and $K_2S_2O_8$/KOH solution, as originally reported by Bardwell *et al.*,[23] where a UV light is used for the photo-excitation of GaN. In n-type materials, photo-generated holes are pushed to the surface by band bending at the semiconductor/electrolyte interface, where they oxidize the semiconductor surface. The surface oxide then dissolves in the alkaline solution. Excess electrons are consumed by the reduction of the oxidizing agent in the electrolyte.

C-plane GaN substrate produced by HVPE and laser lift-off (LLO) process from sapphire was used in our experiments. The samples were cleaned using a standard process, and then immersed in KOH and $K_2S_2O_8$ mixed solutions. The solutions were made up freshly, as peroxydisulfate was subject to slow thermal decomposition.[33] All the reagents were analytically pure and used without further purification during the procedure. Ultrapure distilled water was used in all the reaction processes. A Xe lamp (330 W) with the alterable light intensity was used as the source of UV light. All experiments were carried out at room temperature. The sample was kept about 7 cm from the light source.

A series of experiments were performed to change the controllable parameters of the experiment: solution concentration, the etching time, and light intensity. These were manipulated by changing one parameter while keeping the other two parameters constant. Hexagonal pyramids structure, crystalline quality, stress state, and optical property were proved by the combined results of scanning electron microscopy (SEM) images, X-ray rocking curves (HRXRD) analysis, micro-Raman spectra, and photoluminescence (PL). The formation mechanism and feature were rationally discussed.

3. Results and discussion

3.1. Effect of the electrolyte concentration on the etching of GaN

The electrolyte concentration has been found to be a very important parameter in synthesis of pyramids. Figure 1 shows SEM images of the etching morphology in different KOH concentrations. The images were obtained with the sample tilted up by 30°. Keeping the $K_2S_2O_8$ concentration at 0.05 M, the KOH concentration was varied between 0.1 and 1 M under a continuous UV irradiation (70 mW/cm^2) for 2 h. At a low concentration of 0.1 M, protruding grains with the rough surface distribute sparsely on the surface of the film (Fig. 1(a)). As the concentration is increased to 0.5 M, the protruding grains become bigger and higher, looking like circular truncated cones (Fig. 1(b)). Further increase of the KOH concentration clearly changes the morphology of the GaN from circular truncated cones to cones, as shown in Fig. 1(c). Most of the cones possess sharp tips and a smooth surface. This is clear evidence of the preferential formation of the cones at 1 M KOH.

Another series of experiments was conducted by varying the $K_2S_2O_8$ concentration while keeping the KOH concentration at 1 M. The cones became sharper, smaller and smoother with the increase of the $K_2S_2O_8$ concentration from 0.01 M to 0.1 M, as shown in Fig. 2. A clear change in morphology with lots of pyramids is observed with higher $K_2S_2O_8$ concentration. Figure 2(c) shows the pyramids are well-distributed over the etched GaN with a density of $\sim 10^8$ cm^{-2}. The pyramid consists of six identical triangles with extremely smooth faces, as is shown in the inset of Fig. 2(c). The faces of the pyramids are the $\{10\bar{1}\bar{1}\}$ planes, as evidenced by the angle between the inclined edge and the base of the pyramid. This facet could give rise to the formation of hexagonal pyramids during the etching process. Wurtzite GaN can be preferentially wet-etched to form the hexagonal pyramid structure depending on the facets and polarity.[34–37] According to the Wulff theory,[38] the equilibrium shape of a crystal is determined by both the surface energy and the area to achieve the lowest total energy. This means that the $\{10\bar{1}\bar{1}\}$ planes of the isolate hexagonal pyramid have the lowest surface energy with respect to the corresponding surface area. A detailed discussion has been described in Ref. [39]. We believe that the etching agent $K_2S_2O_8$ plays a key role, because aqueous $K_2S_2O_8$ is a neutral solution and $S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$ in the etching process. The above-mentioned results indicate that the optimum

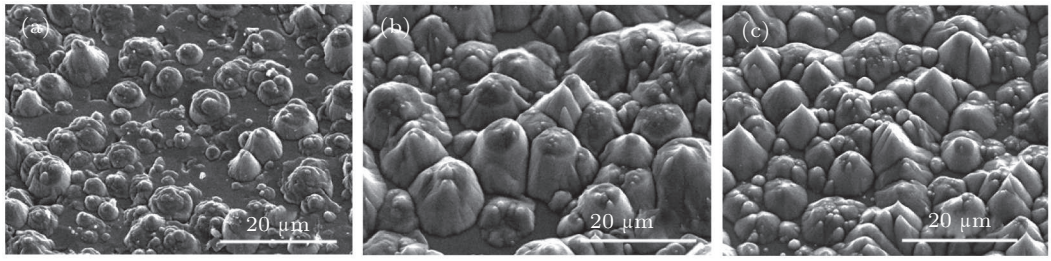


Fig. 1. SEM images of GaN samples etched in varying KOH concentrations keeping the $K_2S_2O_8$ concentration at 0.05 M: (a) 0.1 M KOH; (d) 0.5 M KOH; (c) 1 M KOH.

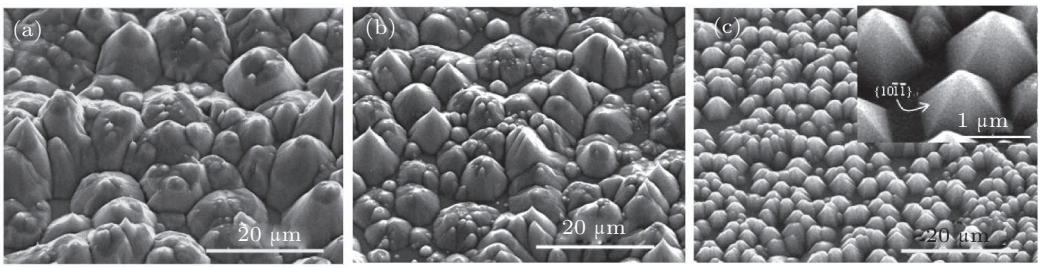


Fig. 2. SEM images of GaN samples etched in different $K_2S_2O_8$ concentrations keeping KOH concentration at 1 M: (a) 0.02 M $K_2S_2O_8$; (b) 0.05 M $K_2S_2O_8$; (c) 0.1 M $K_2S_2O_8$. The inset at the top right corner is the corresponding high magnification image of panel (c).

concentration of fabricating GaN hexagonal pyramids is 1 M KOH and 0.1 M $K_2S_2O_8$.

3.2. Effect of the etching time on GaN pyramids

GaN samples were etched for different times in a solution (1 M KOH and 0.1 M $K_2S_2O_8$) under a continuous UV irradiation (70 mW/cm^2). From Fig. 3, we note that these figures highlight the pyramid-like surface morphology. After etching for 1 h (Fig. 3(a)), both of the isolated and adjacent hexagonal pyramids show a symmetric hexagonal structure and well-defined crystallographic planes. It is also noted that the tip of the pyramid is very sharp, which may enhance the field of field emitters.[40] The sharp tips of the pyramids are maintained with prolonged etching. By comparing Fig. 3(b) with Fig. 3(a), it is evident that the size of the hexagonal pyramids increases with the etching time. However, a further increase of the etching time results in the formation of smaller pyramids, as shown in Figs. 3(b) and 3(c). The size of the pyramids decreases ($\sim$ 2 μm to $\sim$ 1 μm) and the density of pyramids increases ($\sim 10^7$ cm^{-2} to $\sim 10^8$ cm^{-2}), while the etching time increases from 2 to 4 h. Gao *et al.*[29] reported that the hexagonal pyramids increased in size and the density of pyramids decreased with prolonged etching time. Ng *et al.*[30] reported that the density of pyramids decreased with increasing etching duration, and the size of pyramids decreased with prolonged etching. In the present study, the hexagonal pyramids increased in size and then decreased with a prolonged etching time. The physical explanation is that in the early etching process, the small pyramids are observed on the surface of the material and represent sites where the initiation of the etch process has taken place. So the tips of the pyramids form throughout the surface. As the etch proceeds, with a crystallographic preference, the pyramids coalesce. This consolidation process of pyramids repeats itself until an isolated pyramid is formed. These results indicate that etching of N-polar GaN using KOH solutions proceeded through the stages of pyramidal evolution, such as formation, growth, dissociation, and isolation of pyramids.[31] Further etching will eventually etch away all the isolated pyramids.

The crystalline quality of GaN with pyramids was determined using ω-rocking curves of the symmetric (002) and asymmetric (102) reflections. Figure 4 shows the full width at half maximum (FWHM) of X-ray rocking curve for hexagonal GaN (002) and (102) diffraction from etched GaN as a function of the etching time. It is obvious that FWHMs for all reflections in the etched GaN decreased in comparison with the as-grown GaN. The decrease of FWHM values reveals the crystal quality improvement due to the defects of as-grown GaN being etched. In addition, the FWHM decrease of the (002) planes is more than that of the (102) planes. It has been reported that the width of the (002) peak reflects lattice distortion from screw dislocations or mixed dislocations, while that of the (102) asymmetric peak is associated with lattice distortion from edge dislocations.[41] So screw dislocations or mixed dislocations are effectively eliminated by PAC etching. It is worth mentioning that the minimum XRD FWHM values of the (002) planes are obtained for the etched GaN for 2 h, which clearly indicates the pyramids etched after 2 h have a higher crystal quality.

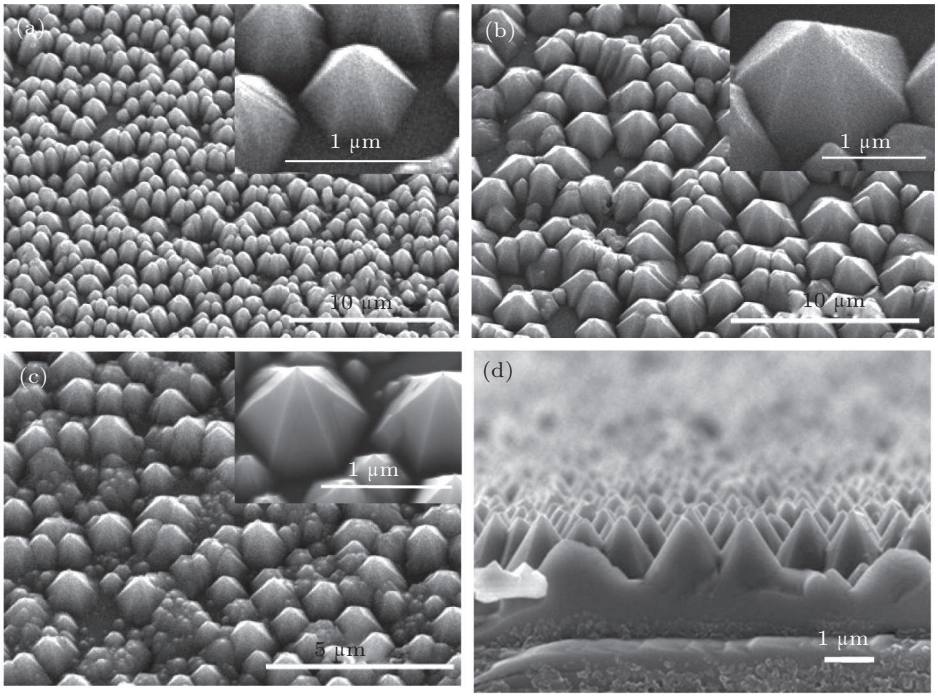


Fig. 3. The morphologies obtained after the samples etched for different time: (a) 1 h; (b) 2 h; (c) 4 h. The insets at the top right corner are the corresponding high magnification images. (d) Cross-sectional SEM image of (b).

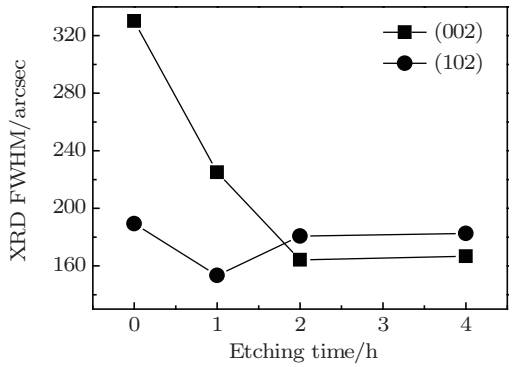


Fig. 4. FWHM of X-ray rocking curve of the samples etched for different time.

Stress is known to perturb the band structure and modify the optical properties in semiconductor films. The residual strain of these samples was measured by micro-Raman scattering spectroscopy with the E_2 (high) phonon frequency. Raman spectra were conducted at room temperature, excited by an argon ion laser ($\lambda = 514$ nm). As shown in Fig. 5, the positions of E_2 mode of as-grown GaN and etched GaN for 1 h, 2 h and 4 h are 563.8, 564.8, 565.7 and 565.1 cm^{-1}, respectively. So the peaks of GaN with pyramids tend to have a smaller wave number,[42] which indicates that tensile stress is still present but reduced in GaN with pyramids. Using this relation,[43] $\sigma = (\Delta\omega/4.3)$ (cm^{-1}·GPa^{-1}), where σ is the biaxial stress and ω is the E_2 phonon peak shift, we could estimate that the residual tensile stress for the as-grown GaN and etched GaN for 1 h, 2 h, and 4 h is about 0.86, 0.63, 0.42 and 0.56 GPa, respectively.

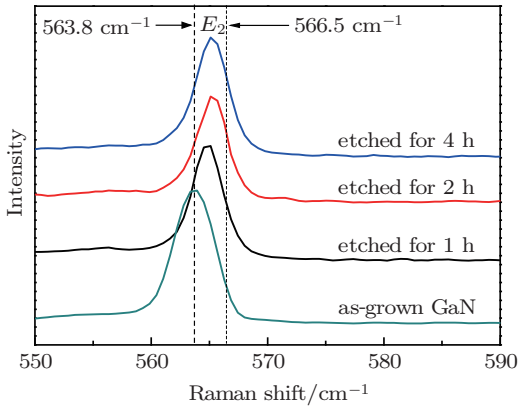


Fig. 5. (color online) Raman spectra of as-grown GaN and GaN with pyramids etched for different time.

3.3. Effect of the UV light intensity on GaN etching

The incident light intensity has a profound effect on the size and density of GaN pyramids. The etched GaN still maintains the hexagonal pyramids at different incident light intensities (Figs. 6(a)–6(c)). The density of GaN pyramids obviously increases and the lateral size of GaN pyramids reduces with increasing the incident light intensity as shown in Fig. 6(d). The high light intensity produces more electron–hole pairs and accelerates the etching of GaN, leads to the separation of conjoint pyramids, which make the hexagonal pyramids denser and smaller.

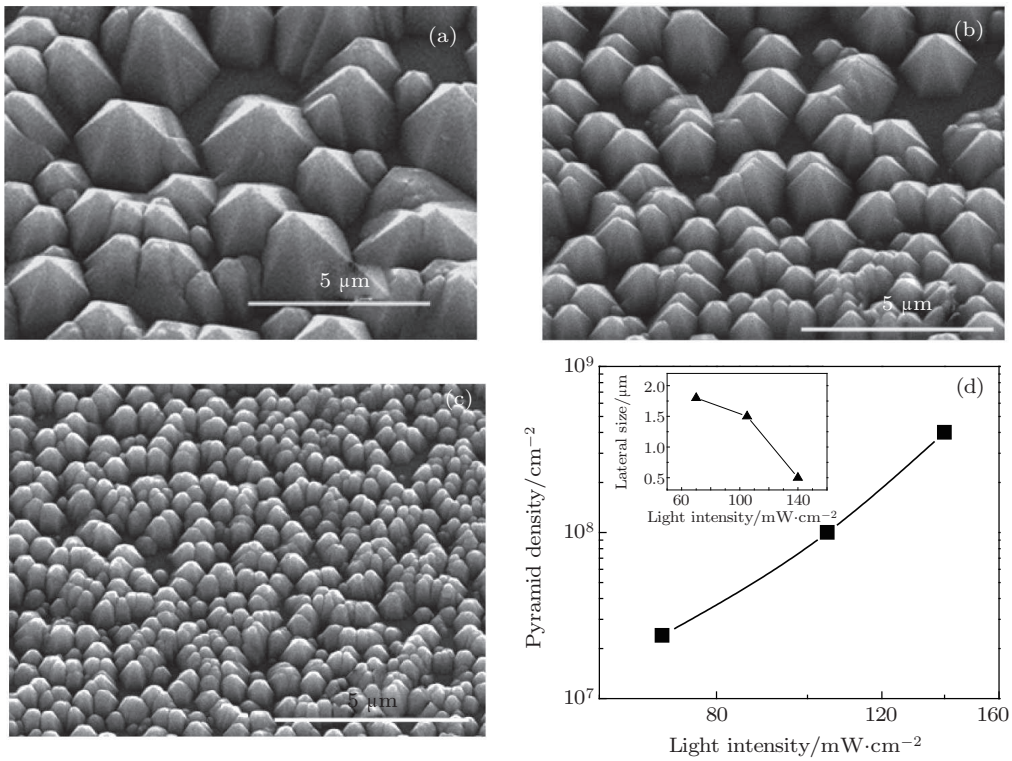


Fig. 6. SEM images of GaN etched at different light intensities: (a) 70 mW/cm^2; (b) 105 mW/cm^2; (c) 140 mW/cm^2. (d) Plot of the pyramid density as a function of UV light intensity. The solid line is an exponential fit to the data points. The inset shows the lateral sizes as a function of UV light intensity.

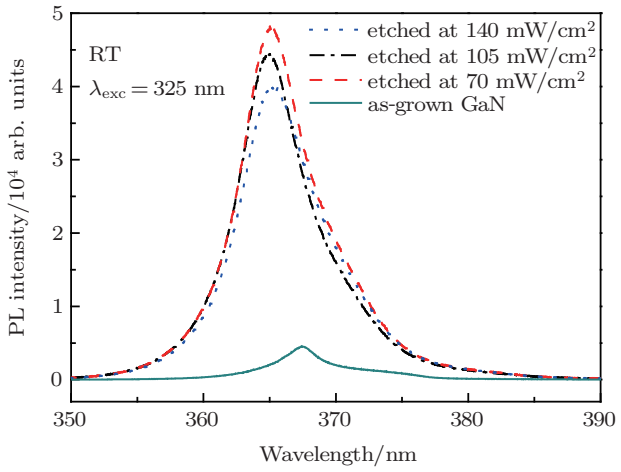


Fig. 7. (color online) Room temperature PL spectra of as-grown GaN and GaN with hexagonal pyramids etched at different intensities.

The measurement of photoluminescence (PL) spectra was performed at room temperature with a 325-nm He–Cd laser as the excitation source. Figure 7 shows only a band-edge emission of GaN. It can be seen that the PL intensity of GaN with pyramids is about ten times that of as-grown GaN, which means that the number of emitted photons for GaN with hexagonal pyramids is much higher. Three different mechanisms can be invoked to explain the increase in PL intensity. Firstly, GaN with hexagonal pyramids allows photons to escape easily because it can reduce the total reflection by increasing the number of the reflection events and randomizing the angles of the light rays.[44] So the hexagonal pyramid structure is considered be important for the emission intensity. Secondly, the partial defects of as-grown GaN are preferentially etched away. The defects of GaN films tend to generate electronic surface levels that capture carriers, resulting in nonradiative recombination and degradation of the light emitting efficiency. The nonradiative recombination related to defects would be reduced after the etching, which consequently enhances photon emission at room temperature. Lastly, because there are some smaller pyramids after the etching, the Bragg effect may account for the partial enhancement of the emission.

In addition, the blue shift of the band-edge PL peaks of hexagonal pyramids with respect to the flat GaN further supports the conclusion about relaxation of tensile stress.

4. Conclusions

In summary, this work provides a systematic study on GaN with hexagonal pyramids etched by a simple photo-assisted chemical etching. The size and density of the hexagonal pyramids were observed to depend strongly on the etching conditions (the etching time, solution concentration and light intensity). The photoluminescence intensity of GaN with hexagonal pyramids significantly increases compared to as-grown GaN, which indicates that GaN with hexagonal pyramids has great potential for improving the light extraction efficiency in GaN-based LEDs. It is indeed exciting.

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