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Hydrogen etching on the surface of GaN for producing patterned structures

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A B S T R A C T

The morphology of GaN etched in hydrogen atmosphere is investigated. It is found that GaN surfaces have different profiles after being etched at different pressures. The profile resembles a surface that has been decorated with columns or mooring posts at high pressure and with deep cavities at low pressure. Etch pit density (EPD) experiment shows all dislocations have been etched to form cavities at low pressure, but not all the cavities result from etched dislocations. A model has been developed to explain the mechanism of H_2 etching. Patterned structure with a flat surface and porous inside has been produced by two-step etching which is designed according to the model.

1. Introduction

GaN is a major wide band gap semiconductor used in fabricating green to ultraviolet optoelectronic devices. Various techniques have been developed to make these nitride-based devices. Among these techniques, etching is one of the most important steps. For example, the etching process is necessary for making a patterned structure on the surface of GaN in order to reduce stress and dislocation density during the manufacturing of devices or large-area free-standing GaN substrates [1–5]. Unfortunately, due to its high chemical stability, conventional wet etching is difficult to use on GaN. The effective methods are dry etching techniques such as reactive ion etching (RIE) [6] and inductively coupled plasma (ICP) [7]. These dry etching processes produce anisotropic etching; GaN is etched in the vertical direction. However, the obtainable patterned structures are limited to the single direction etching. It is valuable to develop an etching technique having both vertical and lateral etching direction. Additionally, an in situ maskless etching will also help to simplify the manufacturing processes of the GaN substrate and device.

This is an investigation of the morphology of GaN etched in hydrogen (H_2) at high temperature. The body of literature comprises of studies on GaN decomposition in H_2 to understand the influence of H_2 during GaN growth [8–10]; surface morphology has not been investigated in detail. In order to examine the morphology, GaN has been etched in this study, where several profiles show the potential of H_2 etching for pattern producing. A model has been developed to explain the mechanism of H_2 etching. Finally, a patterned structure with vertical and lateral etching profile has been made to illustrate the applicability of the model.

2. Experiment

Samples used in this experiment were MOCVD-grown GaN templates. After ultrasonic cleaning, the sample was loaded into a home-made horizontal HVPE reactor. The first experiment was a one-step etching. The reactor was heated to 1050 °C under constant pressure. In addition to nitrogen (N_2), ammonia (NH_3) was introduced into the reactor to avoid GaN decomposition during heating. After the temperature reached 1050 °C, NH_3 was shut off and H_2 was introduced to begin etching; the flow rate of H_2 was 1 slm and the etching time was 10 min. Seven samples labeled A, B, C, D, E, F and G were etched under pressures of 700, 600, 500, 400, 300, 200 and 100 Torr, respectively. The second experiment was a two-step etching using a pressure variation. Following the same procedure as described above but with additional etching step, the sample was first etched in H_2 under a low pressure of 100 Torr for 20 min, and then under a high pressure of 700 Torr for 10 min. In etch pit density (EPD) experiment, the sample immersed in the solution of H_3PO_4 and H_2SO_4 at 220 °C for 20 min. The surface morphologies of etched samples were observed through high-resolution field emission scanning electron microscope (FE-SEM, Hitachi s-4700i).

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3. Results and discussion

Fig. 1 shows SEM images of the GaN template before etching. Fig. 2 shows the plan views (the insets), tilted views and cross-section views of the seven samples etched at different pressures. The etching profiles notably vary as the pressure changes. These profiles can be classified into three types according to their shapes, as shown in Fig. 3. At high pressure (~700 Torr), the etching depth is 200–300 nm, and the profile resembles Fig. 3(a). At intermediate pressure (~400 Torr), the surface becomes relatively flat and a few deep cavities appeared, as shown in Fig. 3(b). At low pressure (< 200 Torr), the surface becomes more flat and a lot of deep cavities appeared, as shown in Fig. 3(c).

We have developed a model attempting to explain the evolution of the surface morphology. It is proposed from the previous studies that H_2 enhances GaN decomposition [8]. H and N atoms combine to form NH_3 at high temperature, and then liquid Ga is subsequently left on the surface [8,11,12]. Ga droplet will remain as long as the Ga desorption rate is not high, which has been observed in our low temperature experiment. At high temperatures, however, Ga desorption rate is high enough to avoid Ga droplet production [8,12]. On account of H mostly reacting with N, we presume that the facet formed with N atoms (N-terminated) will be unstable during H_2 etching, while the facet formed with more proportion of Ga atom will be more stable. The as-grown surface of a MOCVD-grown c-plane GaN film is Ga-polarity (Ga-face) and the reverse side is N-polarity (N-face). The inclined {1 0 −1 1}, {1 1 −2 2} facets are mainly N-terminated. However, nonpolar (a-plane and m-plane) facets contain equal numbers of Ga and N atoms. Therefore, we suppose that during H_2 etching, the relative stabilities of facets follow the order: Ga-face > nonpolar face > inclined face > N-face. The formation of the profile in Fig. 3(a) can be explained using the concept above, and as shown in Fig. 4. As H_2 arriving at surface, it is difficult for H_2 to decompose most of GaN on the surface due to the high stability of Ga-face. Therefore, etching in the vertical direction occurs at the weak areas such as dislocation sites, as shown in Fig. 4(b) (the dotted line indicates the dislocation). N atoms are

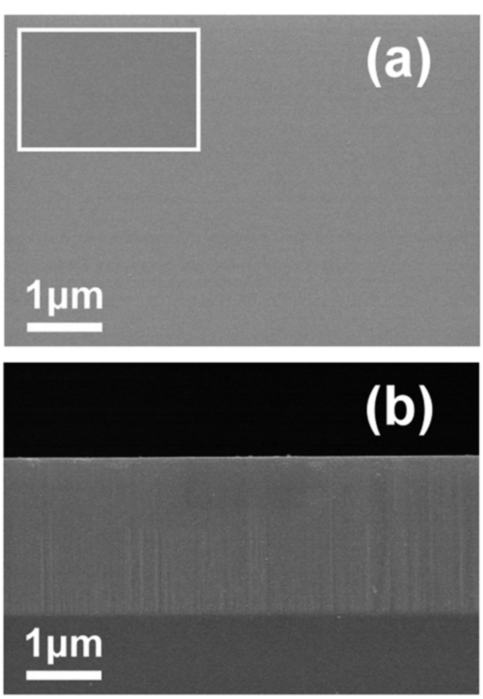

Fig. 1. SEM images of the GaN template before etching: (a) tilted view and plan view (the inset), (b) cross-section view.

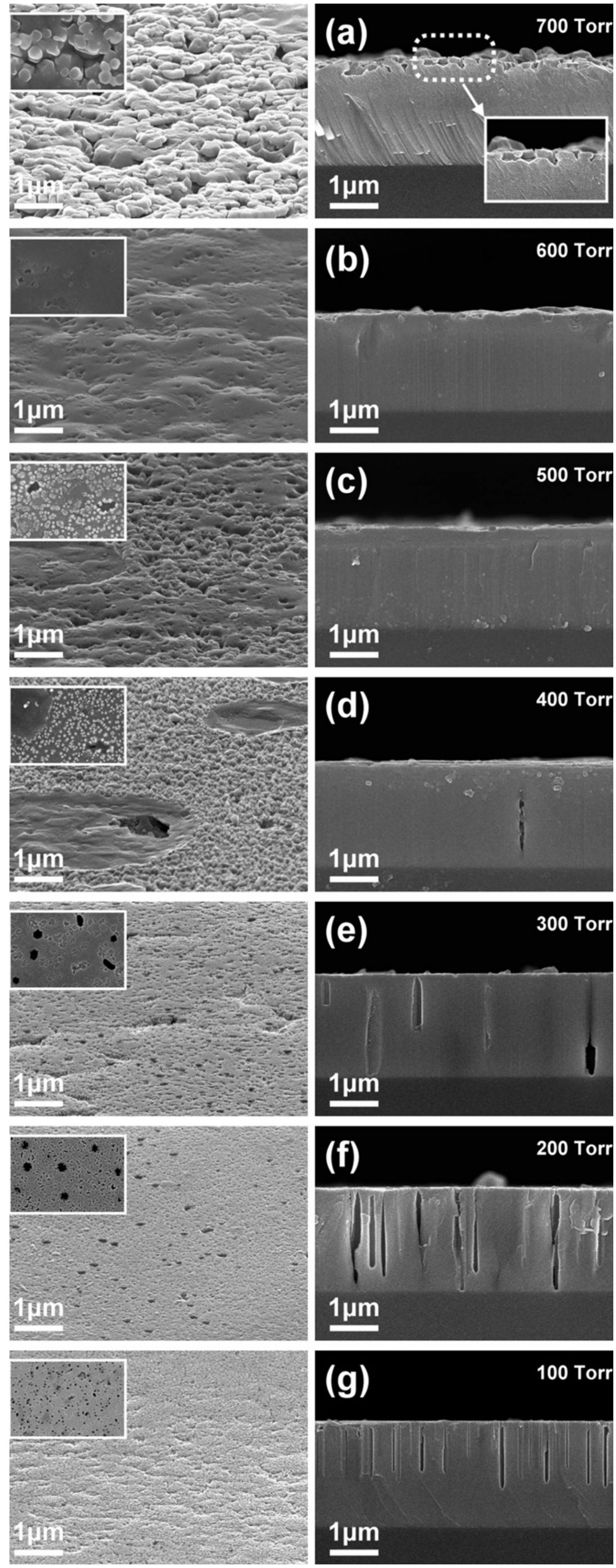

Fig. 2. SEM images of the samples etched at different pressures in plan views (the insets), tilted views (left column) and cross-section views (right column): (a) 700, (b) 600, (c) 500, (d) 400, (e) 300, (f) 200, and (g) 100 Torr. All the scale bars are 1 μm.

produced during etching and dissipate slowly at the bottom of the cavities under high pressure. It is proposed from the previous researches that the inclined face is stable under the condition of high V/III gas ratio [3,5]. Hence, we infer that the nonpolar sidewall becomes unstable in the environment of high concentration of N atoms. As a result, the lateral etching begins at the bottom of the cavities, as shown in Fig. 4(c). When the sidewall is etched for some distance, N-face facet is exposed and then etched due to its instability, therefore the etching begins in the upward direction, as shown in Fig. 4(d). The resulting etching profile is shown in Fig. 4(e). A lot of cavities with this etching profile expand and merge due to the high etching rate at high pressure, making the morphology resemble a surface that has been decorated with columns or mooring posts, as shown in Fig. 3(a). On the other hand, the etching rate is lower at intermediate pressure; therefore N atoms are produced slowly and dissipate rapidly. Nonpolar facets become stable and then some deep cavities appear, as shown in Fig. 3(b). The etching rate is lowest at low pressure; N atoms are produced more slowly and dissipate more rapidly. Nonpolar facets become more stable and a lot of deep cavities appear, as shown

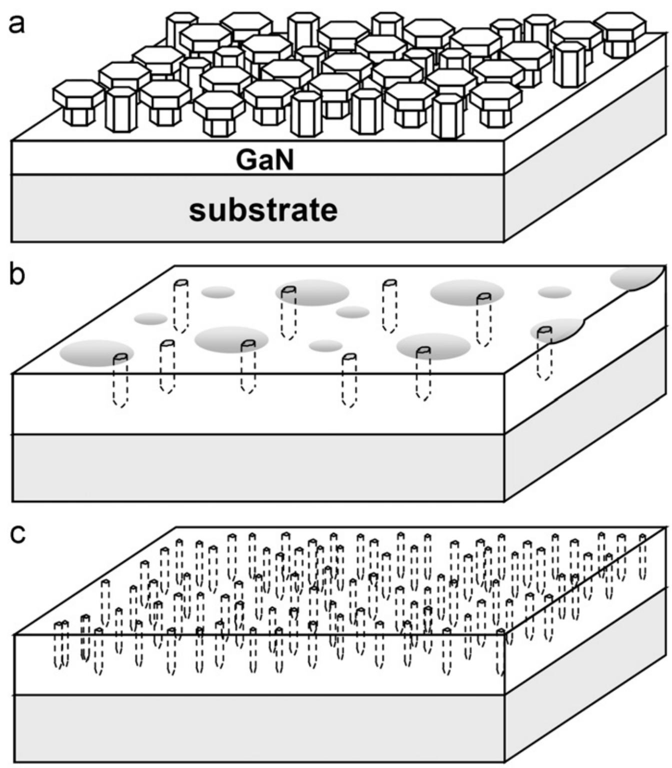

Fig. 3. Three types of profiles: (a) columns or mooring posts, (b) a few deep cavities, and (c) a lot of deep cavities.

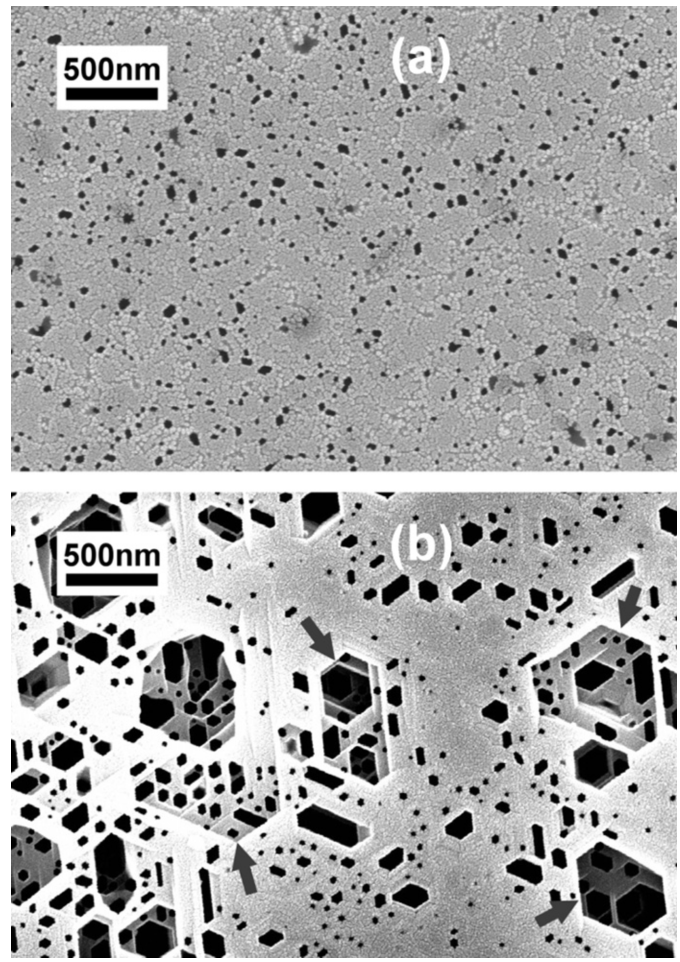

Fig. 5. Plan-view SEM images of (a) the original sample without performing EPD experiment, and (b) the sample performed EPD experiment. The arrows indicate some of the expanded tops of the cavities.

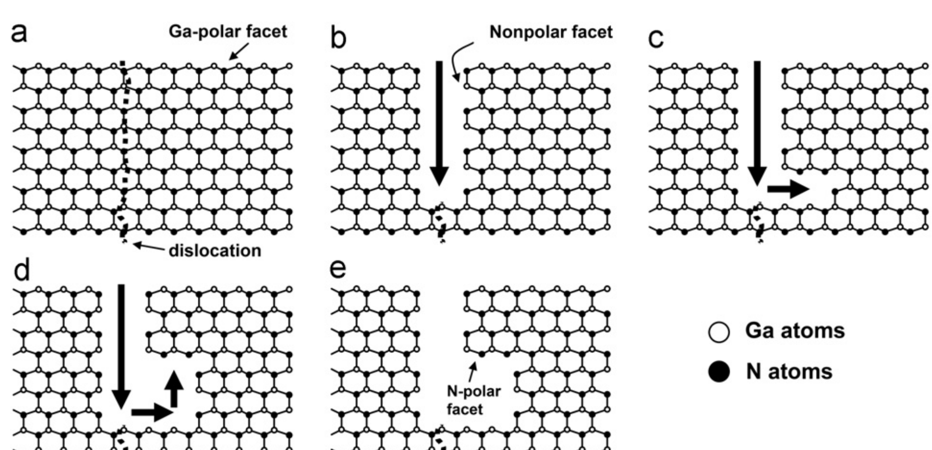

Fig. 4. The stages of H_2 etching at high pressure: (a) unetched template, the top surface is Ga-face and the dotted line indicates the dislocation, (b) H_2 etching at the dislocation site, (c) lateral etching at the bottom of the cavity, and then N-face facet is exposed, (d) etching in the upward direction due to the instability of N-face, and (e) the resulting etching profile.

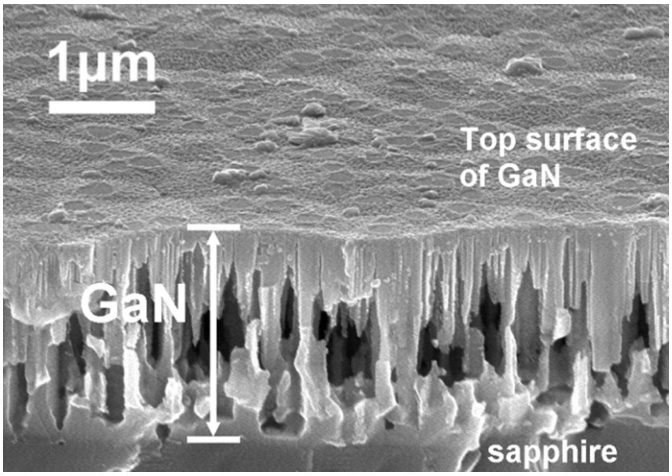

Fig. 6. SEM image of the sample etched by two-step process, the sample has a patterned structure with a flat surface and porous inside.

in Fig. 3(c). It is suggested that vertical and lateral etching direction are both dominant at high pressure. However, only the vertical etching direction is dominant at low pressure.

To determine the etching occurring at the weak areas such as dislocation sites, a piece of sample cut from sample G has been performed in an EPD experiment. Fig. 5(a) shows the surface of the original sample without performing EPD experiment. Fig. 5(b) shows the surface of sample performed EPD experiment. The top of some of the cavities were found to expand even cross over the adjacent cavities, as indicated by the arrows. However, some cavities have been observed to retain their top sizes. Also, no hexagonal V-shape pits were found on the surface of the sample used in the EPD experiment. Normally, the V-shape pits form at dislocation sites on the surface after the EPD experiment; hence we deduce that the absence of V-shape pits comes from all dislocations that are etched to form cavities. The density of the cavities shown in Fig. 5(a) is estimated to be about $7 \times 10^9\,cm^{-2}$. However, the dislocation density of the template used in this experiment is about $5 \times 10^8\,cm^{-2}$. Therefore, most cavities do not result from the etched dislocations but are most likely the ones which retain their sizes after the EPD experiment in Fig. 5(b). It can be concluded that all dislocations are etched to form cavities, but not all the cavities result from the etched dislocations. The formation of the cavities which do not result from the etched dislocations is under study.

According to the developed model, we expect that various morphologies will be produced by pressure variation etching processes. Fig. 6 shows the sample etched by two-step etching method. We deduce that the structure is formed from the following procedure: in the first step, many deep cavities are produced on the surface at low pressure. In the second step, H_2 continues to etch the bottom of the cavities at high pressure due to the weakness of these regions. A lot of nitrogen atoms are produced around the bottom of the cavities, and then the sidewalls (nonpolar facets) become unstable due to the nitrogen atoms. Consequently, lateral etching accompanied with the upward direction begins at the bottom of the cavities. As a result, the final etching profile is shown in Fig. 6, it has a flat surface but porous inside. This patterned structure may be useful in the reduction of stress and threading dislocation density during the overgrowth process. Moreover, self-separation may also occur during GaN substrate fabrication with this structure.

4. Summary

Different morphologies appear on the GaN surface etched in H_2 under different pressures at 1050 °C. It is presumed that the etching begins in certain weak areas such as dislocation sites. In addition to the vertical direction, H_2 etching also has a lateral and upward direction at high pressure. Combining the high etching rate at high pressure, the cavities expand and merge to make the surface profile resemble clustered columns or mooring posts. On the other hand, H_2 etching merely has a vertical direction at low pressure that makes the surface decorated with cavities. EPD experiment shows all dislocations have been etched to form cavities at low pressure, but not all the cavities result from etched dislocations. Two-step etching using a low and high pressure variation produces a patterned structure with a flat surface and porous inside. We anticipate that this patterned structure may be useful in the reduction of stress and threading dislocation density during the overgrowth process. Moreover, self-separation may also occur during GaN substrate fabrication with this structure.

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