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Evolution of Surface Morphology by Wet-Etching of ZnO and GaN with Different Polarity

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The surface morphologies of ZnO and GaN thin film by wet-chemical etching were investigated. While ZnO was readily etched by acidic solutions regardless of its polarity, GaN was hardly etched by acidic solutions, but etched in alkali-based solutions such as KOH, especially for N-face GaN. Furthermore, we will also discuss the micro-structural evolution of hexagonal pyramids on the O-polar (N-polar) surfaces and hexagonal pits on the Zn-polar (Ga-polar) surfaces of ZnO and GaN, respectively.

Introduction

Wide bandgap semiconductors such as GaN- and ZnO-related materials are investigated intensively for last decades in order to apply for optical and electronic devices, such as light emitting diodes (LEDs), laser diodes (LDs), high electron mobility transistors (HEMTs), and transparent thin film transistors (TTFTs), because of their physical and chemical properties of materials. For examples, GaN has a high breakdown field, greater than 50 times that of Si or GaAs, which allows for use in high power electronic applications (1). It is also applicable to the high speed electronics and UV/visible emitters due to its high electronic mobility and saturation velocity, and wide band gap energy, respectively. ZnO, which is an analogous to GaN, is of strong interest for blue/UV LEDs and thin film transistors due to its the large exciton binding energy of 60 meV and high optical transparency in visible range, respectively. Along with the availability of a large-area substrate, low growth temperature, high radiation resistance, and relatively low material costs, the fabrication of high quality multi-quantum well, by alloying with MgO, has been achieved, which opens the possibility of the development of efficient optoelectronic devices from ZnO films (2, 3). In order to achieve these advantages, on the other hand, the etching process represents a key step in the fabrication of optoelectronic devices, as well as the integration of high-speed electronic circuits. For optoelectronic applications, a higher etch rate is required and many results about etch rates of ZnO and GaN have appeared until now (1). In addition, smooth etched surfaces are also of interest in the fabrication of optoelectronic devices, since the ohmic and Schottky metals contact may be deposited on the etched surface and it would be expected that a smooth surface would enhance the optical and electrical properties, thus improving the quality and reliability of the device.

Due to the fact that ZnO and GaN has ionic nature of atomic bonding with a strong charge transfer between the electronegative oxygen (nitrogen) atoms and the relatively electropositive metal atoms, respectively, important consequences for physical and

chemical properties of materials system should be given, such as macroscopic polarizations of lattice. The direct results of these polarizations are fixed surface charge and large internal electric fields (4).

In these days, a newly developed thin-GaN LEDs structure by removal of sapphire substrate has shown great advantages over conventional LEDs schemes in the emission efficiency performances. In this structure, the sapphire substrate is removed by laser-lift-off process and the exposed surface of GaN near the sapphire/GaN interface is N-polarized face, and n-type ohmic contact should be built on this N-face GaN surface. Furthermore, in order to expose n-type GaN, undoped GaN layer should be etched away by using wet- and/or dry etching technique, and it is very important to understand the morphology of etched surface of N-face GaN in order to set-up a good ohmic contact. In case of ZnO, it is unavoidable to follow the GaN processing technology road-map for the purpose of fabricating a high-quality LEDs. However, few results about properties of Ga-/N- face GaN and Zn-/O-face ZnO surfaces etched by wet-etching methods have been known to date.

In this paper, the surface morphologies of ZnO and GaN thin film by wet-chemical etching were investigated, respectively.

Experiments

$ZnO(000\bar{1})$ and (0001) films with a thickness of ~ 1 ㎛ were epitaxially grown on a sapphire substrate by an rf magnetron sputtering method (5) and plasma assisted molecular beam epitaxy, respectively. The Zn-polar ZnO (0001) films were grown by plasma assisted molecular beam epitaxy by controlling the thickness of MgO buffer layer (6). Ga-polar GaN films were grown by metal organic chemical vapor deposition method and N-polar GaN films were produced by laser lift-off of sapphire substrate after conventional growth of Ga-polar GaN films. Conventional resist films (AZ5214) were used as masks for the etching in this experiment. The resist films, 1.5 ㎛ in thickness, were prepared on the each sample surface by spin coating. After pre-baking at 100 □ for 5 min on a hot-plate, conventional photolithography was used for preparing mask patterns. Exposed resist films were developed by dipping in a developer and post-baking was then carried out on a plate heater at 120 □ for 10 min. The samples with a patterned mask were etched by dipping in an aqueous solution of hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and hydrochloric and phosphoric acid (HCl/H_3PO_4) without any agitation at room temperature for ZnO sample. On the other hand, GaN samples were etched by using KOH and H_3PO_4 aqueous solution at elevated temperature, respectively. The etch rate was determined by averaging the etch-depths, measured with a step profiler for 10 times. The etch-depth in the masked samples was measured after removing the mask. The resulting surface morphology and anisotropy of the ZnO and GaN patterns were characterized by field emission-scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM).

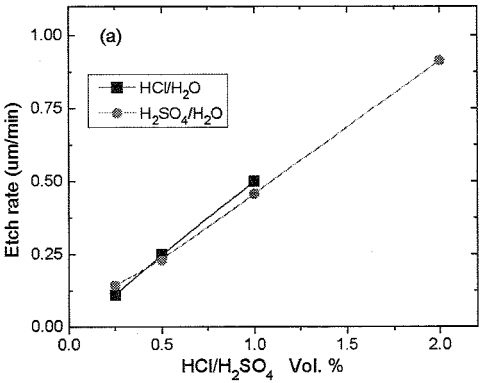
Results and discussion

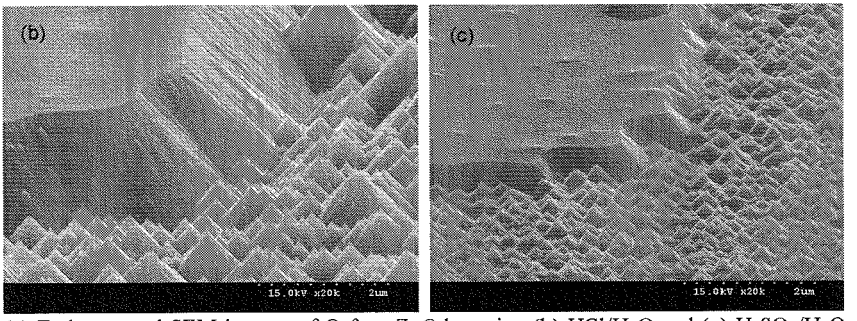
1. Zn-/O-face ZnO

Fig. 1 (a) shows the etch rate of O-face ZnO as a function of HCl and H_2SO_4 volume percentage in water. When the volume percent of the acid in an aqueous solution was increased, the etch rates were increased as the result of the increase in etchant

concentration, where the etch rate is similar to each other. However, the etch rate by using 2 % HCl solution was hard to measure because the etch rate was too fast (7) and the sharp hexagonal pyramid was predominant on the surface.

Fig. 1 (b) shows the surface of ZnO sample etched in 2 % HCl/H_2O solution. The etched surface, observed by scanning electron microscopy, showed a rough morphology with a high density of hexagonal pyramids, with sidewall angles of about ~ 47 °. This hexagonal facet of $\{10\bar{1}\bar{1}\}$ plane has been known as the slowest-etch planes, which is energetically stable due to the low bonding numbers (8). The sidewall profiles of the masked area were similar to those of the angle of the hexagonal pyramidal plane perpendicular to the surface, indicating that the sidewall profiles were closely related to the formation of hexagonal pyramids, originating from the crystallographically anisotropic etching. Furthermore, seeds which are to be developed as a tip of the hexagonal pyramid were also found in the sidewall of the masked area, as can be seen in the figure, supporting that the formation of hexagonal pyramid is the nature of crystallographic anisotropy, not originated from the redeposition of etched or external particles. Although the etch rate of H_2SO_4 is similar to that of HCl solution, the surface morphology, shown in Fig. 1 (c), was somewhat different from those produced by HCl etching. The shapes of hexagonal pyramids became irregular and the size was decreased.





(a) Etch rate and SEM images of O-face ZnO by using (b) HCl/H_2O and (c) H_2SO_4/H_2O solution, respectively.

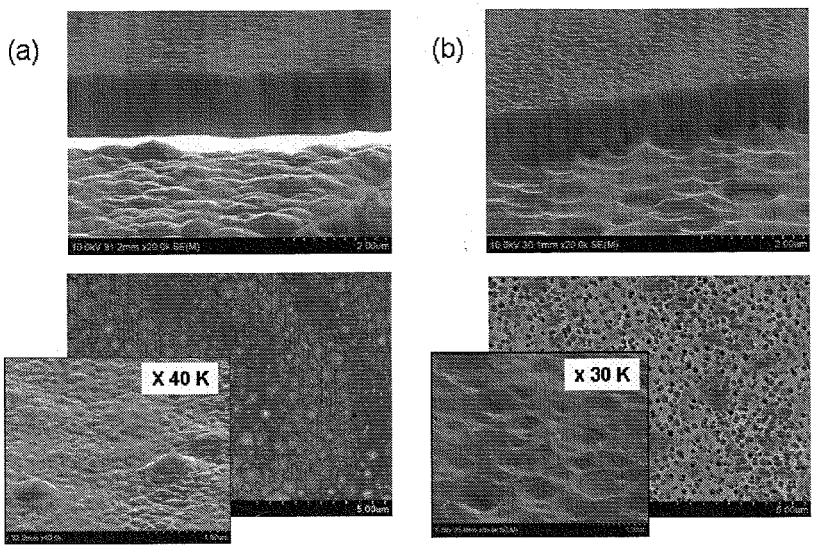


Figure 2. (a) Etched surface morphology of (a) O-face ZnO and (b) Zn-face ZnO by using HCl/ H_3PO_4/H_2O solution.

Because the viscous acids can suppress the lateral etching rate due to the slow consumption of active etchant (9) and the vertical etch rate could be, at least, maintained, the size of the hexagonal pyramids can be shrink, as shown in the figure.

Figure 2 shows the etched surface profile of the O-face and Zn-face ZnO surface by using $HCl/H_3PO_4/H_2O$ solution. In our previous study, we have found that the $HCl/H_3PO_4/H_2O$ solution was favorable in order to achieve a smooth etched surface morphology of O-polar ZnO surface (10). The as-grown O-polar and Zn-polar surface, which is the masked regions shown in Fig. 2 (a) and (b), show smooth surfaces. While the etched Zn-polar surface was relatively smooth in contrast to those etched by using HCl/H_2O solution as in Fig. 1, the small pyramid or bumps still exist on the surface.

On the contrary, Zn-polar surface showed a stepped hexagonal hole or pits as shown in the Fig. 2 (b). It was known that the ZnO was etched through the reaction of aqueous proton ions with oxygen ion in ZnO to make a Zn cation and water (11).

$$ZnO(sol.)+2H^{+}(aq)\rightarrow Zn^{2+}(aq)+H_2O(liq.) \qquad [1]$$

The surface of the O-polar sample, etched with a $HCl/H_3PO_4/H_2O$ solution, is active because there exists a excess oxygen to be reacted with aqueous proton. The etching process is occurred with relatively fast rate. However, the slowest-etch plane $\{10\bar{1}\bar{1}\}$ suppressed the lateral etching of O-polar ZnO, indicating the formation of sharp-tip hexagonal pyramid on the surface. On the contrary, Zn-polar ZnO surfaces are relatively inactive due to their shortage of oxygen. The etching would be occurred with low etch rate on the vertical direction. However, if there are defects, such as pits or threading

dislocations, the etching would be enhanced by an existence of oxygen under-layer. Dulub *et al.* (12) reported that the surface of Zn-face ZnO(0001) had been characterized by the presence of nanosized islands and triangular holes with single-height, O-terminated step edges, in accordance with our AFM results. Furthermore, due to the existence of the slowest-etch plane $\{10\bar{1}\bar{1}\}$, the lateral etch is also prohibited from ongoing etching, resulting in the formation of hexagonal pits on the Zn-face ZnO(0001) surface.

In an effort to clarify the origin of the morphology evolution, we studied the initial stage of etching of ZnO with less than 60 sec of etching time using mixed solutions of HCl, H_3PO_4, and H_2O. Figure 3 shows the SEM photographs of as-grown, 30 sec etched and 60 sec etched surface of ZnO samples. The RMS roughness values of as-grown O-polar and Zn-polar sample, seen in Fig. 3, were measured to be about 5 nm and 10 nm, respectively. Along with a SEM image in Figure 2, the roughness of the surface of an as-grown Zn-polar ZnO is rougher than that of O-polar surface, maybe due to the surface defects. While the both surfaces of the sample were slightly roughened with 30 sec of etching, the morphologies were observed to be completely different from each other. When the O-polar surface was etched for 30 sec, the bumps which might be a seed for pyramid was developed on the surface. After the 60 sec etching, the sizes of the bumps were increased as shown in the figure. On the contrary, the surface of Zn-polar surface which was etched for 30 sec shows high densities of pits. As the etching times were increased, the depth and lateral sizes of the pits were also increased, which is corresponding to the result in Figure 2. These are the confirming evidences that the formation of the hexagonal etch pits on the etched Zn-polar surface was enhanced by the surface defects such as pits or threading dislocations.

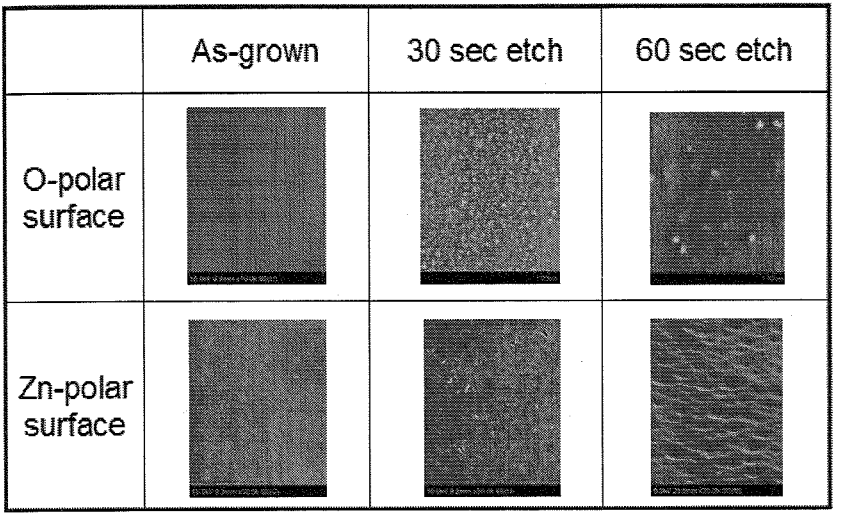


Figure 3. (a) Etched surface morphology of (a) O-face ZnO and (b) Zn-face ZnO by using HCl/ H_3PO_4/H_2O solution.

2. Ga-/N-face GaN

Fig. 4 shows the etch rate of Ga-face GaN using KOH and H_3PO_4 as a function of etching temperature. While the etch rate of Ga-face GaN by using H_3PO_4 was measured to be 30 nm/min at the temperature of 300 ℃, the etch rate by using KOH was 8 nm/min, which are lower than that of previous report by Stocker *et al.* (13). In order to calculate the activation energy, Arrhenius equation was used as follows;

$$R = R_0 \exp\left(\frac{-E_a}{kT}\right) \quad [2]$$

where E_a, k, and T are activation energy, Boltzmann constant, and absolute temperature, respectively. As can be seen in the graph, the activation was calculated to be about 3 kcal/mol irregardless of an etchant solution. This result indicates that that the etch rate is primarily dependent on the inherent nature of thermodynamic reaction and/or materials quality (14).

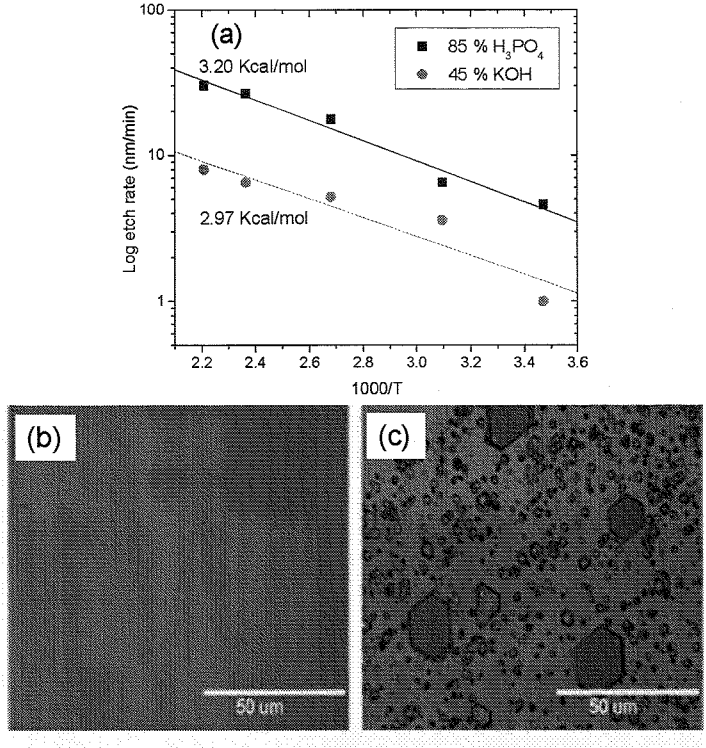


Figure 4. (a) Arrhenius plot of etch rate versus time dependent on etchant solution, (b) Optical microscopic image of etched Ga-face GaN by (a) KOH and (b) H_3PO_4 for 20 min.

Fig. 4 (b) and (c) show the surface of Ga-face GaN sample etched in KOH and H_3PO_4 solution, respectively. While the KOH-etched surface, observed by optical microscopy, showed a smooth surface morphology with a few small etch pits, the H_3PO_4-etched surface shows a high density of hexagonal pits, indicating that the etching process by H_3PO_4 solution had already started on the surface. Note that the shape of etch pits on the H_3PO_4-etched Ga-face GaN is similar to those of Zn-face ZnO which were discussed early, indicating that the etch mechanism might be similar to each other.

In order to clarify the etch mechanism, we studied morphology evolution with increasing time and the results are shown in Fig. 5. The RMS roughness of as-grown sample was measured to be less than 5 nm. With increasing the etching time, the a number of etch pits were appeared on the sample, without any regular shape [Fig. 5 (b)]. However, the etching time reached at 40 min, high density of hexagonal hole of pits were formed on the etched surface with bimodal size of 15 ㎛ and 3 ㎛, respectively, as shown in Fig. 5 (c). As the etching increased further, the lateral size of the hexagonal holes or pits were increased, specially for smaller ones [Fig. 5 (d)], and finally, joined and merged together at the time of more than 80 min, as shown in Fig. 5 (e) and (f).

These results indicate that the etching of Ga-face GaN by phosphoric acid solutions proceeded through the lateral widening and the merging of initial holes and pits.

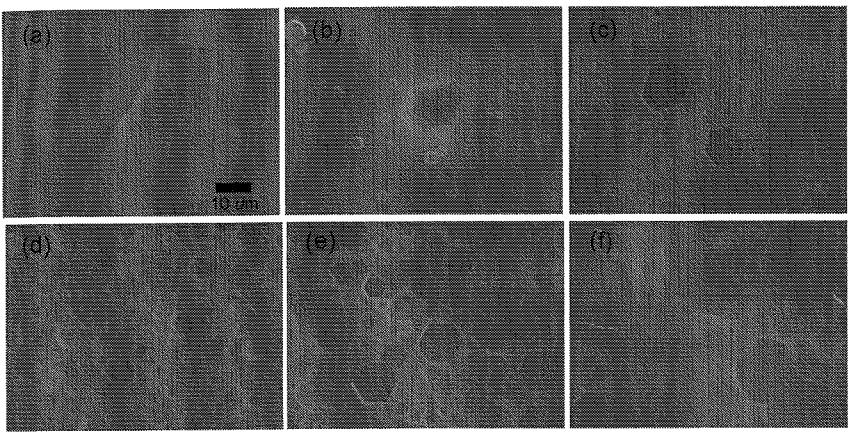


Figure 5. SEM images of (a) as-grown and etched Ga-face GaN surface by 85 % H_3PO_4 for (b) 20, (c) 40, (d) 60, (e) 80, and (f) 100 min at 180 ℃. (the dark area in Fig. (a) is masked region).

Figure 6 shows the morphological evolution of N-face GaN surface by KOH-based etching method. The surface of reference sample after laser-lift off process was smooth as shown in Fig. 6 (a) and the RMS roughness valued was measured to be about 30 nm due to the dry-etching process for the purposed of exposing n-type GaN. As the etching time increased, high densities of hexagonal pyramid were found on the N-face GaN surface. The angle between base and pyramid facet was calculated to be about 60 ~ 62 ° from the SEM image of the isolated hexagonal pyramid (not shown), indicating that the Miller indices of the facet is $\{10\bar{1}\,\bar{1}\}$, which is the same to those of O-face ZnO, corresponding to the results of other researchers (15).

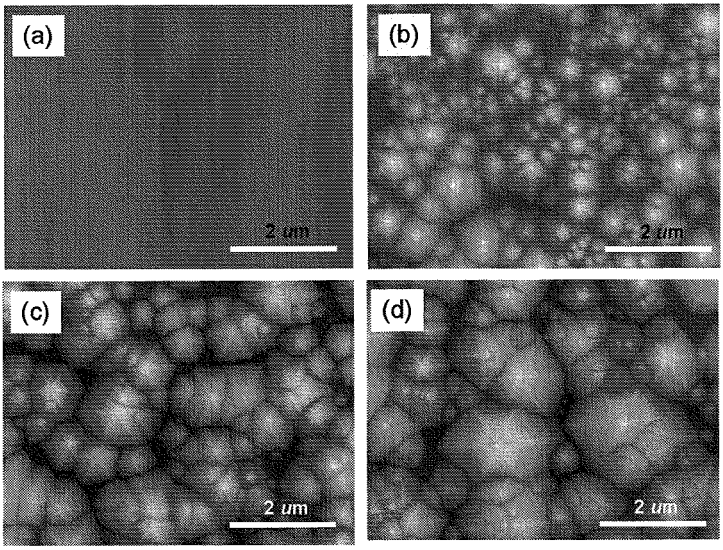


Figure 6. SEM images of (a) reference and etched N-face GaN surface by KOH for (b) 2, (c) 3, (d) 4 hours of etching at room temperature.

As the etching time was increased the sizes of the hexagonal pyramid were increased and the density of the pyramid was decreased indicating that the pyramids might be joined and emerged as a result of etching. These results indicate that the etching of N-face n-type GaN by KOH solutions proceeded through the evolution of hexagonal pyramids, such as formation, dissociation and enlargement of pyramids.

Summary

The surface morphologies of ZnO and GaN thin film by wet-chemical etching were investigated. While ZnO was readily etched by acidic solutions regardless of its polarity, GaN was hardly etched by acidic solutions, but etched in alkali-based solutions such as KOH, especially for N-face GaN. Furthermore, the formation of the hexagonal etch pits on the etched Zn-polar surface was enhanced by the surface defects such as pits or threading dislocations. the etching of N-face n-type GaN by KOH solutions proceeded through the evolution of hexagonal pyramids, such as formation, dissociation and enlargement of pyramids.

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