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Etching of GaN by microwave plasma of hydrogen

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Abstract
An etching process for GaN on a sapphire substrate using a microwave plasma of hydrogen has been studied. Scanning electron microscopy observations of the surface morphology show that the etching of GaN with H_2 plasma can lead to the formation of etch pits in hexagonal shape. The average size of hexagonal pits is greater than 200 nm. The effects of processing pressure and etching time are demonstrated.

(Some figures in this article are in colour only in the electronic version)

Introduction

Gallium nitride (GaN) is a wide band-gap (3.4 eV) semiconductor material, which finds applications in high-power and high frequency devices such as power amplifiers, and in optoelectronics for light-emitting diodes (LEDs) and laser diodes. Sapphire (Al_2O_3) and silicon carbide (SiC) are the most commonly used substrates for GaN-based LEDs, which can be used in many fields including green traffic lights, full-color displays and flat-panel room lighting to replace incandescent and fluorescent fixtures [1–5]. The most common and successful technique for the growth of epitaxial GaN films is metalorganic chemical vapor deposition (MOCVD). Etching of semiconductor materials is widely applied not only in studying of their structural, optical and electrical properties of the devices but also on fabrication processing. However, the high chemical stability of the GaN presents a technological challenge. Conventional wet-etching techniques used in semiconductor processing have not been very successful for GaN device fabrication. Due to limited wet chemical etching for the group-III nitrides, a significant amount of efforts have been devoted to the development of dry etch processing. Dry etching was initially focused on mesa structures where high etch rates, anisotropic profiles and smooth sidewalls of dissimilar materials were required. In the past few years, many research groups contributed to the development of dry plasma etching approaches. Several methods have been used for dry etching, including reactive ion etching (RIE), chemically assisted ion beam etching (CAIBE), magnetron reactive ion etching (MIE) and electron cyclotron resonance (ECR) [3, 6, 7]. In the RIE technique, halide-based (BCl_3 or HBr) plasmas have been used, and a typical GaN etch rate ∼50 nm min^{-1} has been reported [8, 9]. The highest etch rates of GaN have been obtained (>100 nm min^{-1}) by plasma-based ($CH_4/H_2/Ar$, Cl_2/H_2) ECR and CAIBE [6, 7, 10]. Eddy and Molnar had noticed that the GaN surface morphology after ECR microwave plasma reactive ion etching displays craters, most of which exhibit faceting with hexagonal symmetry resulted from preferential sputtering of nitrogen from the surface of GaN [11]. However, etching of GaN by pure hydrogen plasma has been rarely studied. The etching of GaN by hydrogen plasma may be helpful for further understanding of the processing for patterning fabrication using plasma containing hydrogen such as $CH_4/H_2/Ar$ and Cl_2/H_2. Because of the high chemical stability of the gallium nitrides, the dry etching is often employed for patterning of nitrides wafers compared to wet etching. Additional to patterning, there may be other applications of etch pits including defect revelation, and polarity identification, improving the optical qualities and surface cleaning, field emission, and so on.

In this paper, we report hydrogen plasma etching of GaN as a function of time and pressure. Microscopy observations show that the etch pits can form in a characteristic hexagonal shape. The size of etch pits was increased with time and pressure.

Table 1. Etching parameters for each process.

	H_2 gas flow (sccm)	Microwave power (W)	Pressure (torr)	Time (min)
Case I	300	600	20 (const.)	5 10 15 20
Case II	300	600	15 20 25 30	10 (const.)

Experimental details

Undoped GaN samples used in this work were grown on a 2 inch (0001) sapphire (Al_2O_3) substrate by metal-organic chemical vapor deposition (MOCVD). The GaN film thickness was about 2.5 μm. In this study, the samples were cut in a size format of 1 × 1 cm^2 from a 2 inch GaN/sapphire.

Prior to etching, the GaN/Al_2O_3 samples were ultrasonically cleaned in acetone and alcohol for ∼10 min, respectively, and dried with N_2 spray. Then, the cleaned sample (GaN/sapphire) was placed on a molybdenum holder. The etching process was carried out in an AsTeX-type microwave plasma chemical vapor deposition (MPCVD) system which had been often used for diamond deposition using mixture gases of methane and hydrogen. Here, we used the system for etching GaN film by hydrogen plasma. The hydrogen plasma was effectively generated in the reactor from a microwave power supply. The etching was done with various gas pressures and etching times. The flow rate of H_2 gas and microwave power was fixed at 300 sccm and 600 W, respectively. The H_2 gas pressure and etching times were changed from 15 to 30 torr and from 5 to 20 min, respectively (details in table 1). The substrate temperature was measured to be about 700 ± 10 °C by an optical pyrometer.

The morphology, size and composition of etch pits were analyzed by scanning electron microscopy (SEM) in a JEOL JSM-6500F-SEM equipped with an Oxford Instrument energy-dispersive x-ray (EDX) spectrometer. The surface morphology and etch depth variation were also examined in an atomic force microscope (AFM) using a Si tip in contact mode.

Results and discussion

A systematic investigation has been performed to evaluate the morphology of the etched GaN/sapphire surface. The roughness of the as-received GaN layer on the sapphire substrate was slightly more than 2 nm. The substrates (GaN/sapphire) were treated with hydrogen plasma at different pressures and etching times. We attempted to study the effect of the GaN surface by H_2 plasma in two different cases. In the first case, etching time was varied from 5 to 20 min at a constant pressure of 20 torr. In the other case, etching was performed at various gas pressures from 15 to 30 torr with fixed etching time of 10 min.

SEM plan-view and corresponding AFM images of both cases are shown in figures 1 and 2. The SEM images in figures 1 and 2 show that after etching the GaN surface morphology appears with relatively well-ordered hexagonal etch pits and polygon-shaped etch pits with clear facets. The morphology of etch pits can be distinguished from different contrast. The etch pits appear dark due to the depth, whereas the bright contrast is corresponding to surface particles which can be identified as GaN. The high-magnification SEM image (the inset in figure 1(*a*)) shows a typical hexagonal pit of a size of about 500 nm formed after 5 min etching at 20 torr. From inclined angles of etched GaN hexagonal facets, the planes are likely to be $(1\,0\,\bar{1}x)$, where $x = 1$, 2 or 3 [12]. However, the origin of the hexagonal etch pit is still unclear. Hino *et al* and Chen *et al* have demonstrated that large etch pits can be attributed to screw/mixed threading dislocations (TDs) and small ones to edge TDs [13, 14]. Therefore, it is possible that the well-defined hexagonal etch pit (∼500 nm) with a large black core (after 5 min etching, inset in figure 1(*a*)) in our case may be associated with screw-dislocation sites. For those etch pits of ∼100 nm size in unclear hexagon with a small black core and polygon as shown in figure 1(*a*), it is believed that they are mainly due to edge-type dislocations and mixed dislocations. For longer etching time, the etch pits are increased. The enlarged etch pits may result from coalescence of neighboring etch pits as shown in figures 1(*b*) and (*c*). Similar evolution of etching behavior can be observed for the pressure effect as shown in figure 2. Figure 2(*a*) shows that there are many small etch pits of ∼100 nm with a larger well-defined hexagonal pit at low pressure (15 torr). For etching at higher pressure from 20 to 30 torr, it can be seen that the etch pit size is enlarged from ∼150 to ∼320 nm (figures 2(*b*)–(*d*)). In figure 2(*c*), it can also be seen that a number of adjacent pits might be just going to merge together. It should be noted that all the small bright spots on the surface are actually GaN cones instead of metallic Ga droplets, as shown later and also confirmed from EDX results. We also noticed that the size of etch pits generally increases and the density of etch pits decreases with etching time and pressure, as shown in figures 1 and 2.

Further, cross-sectional SEM images shown in figure 3 clearly show the depth variation of etch pits. Figures 3(*a*) and (*b*) show the depth variation of etch pits with different etching times, while etch pits with pressure variation are shown in figures 3(*c*) and (*d*). Figure 3(*a*) shows that the GaN film is less etched (depth ∼300 nm) for 5 min at 20 torr. For longer treatment (15 min at 20 torr) it shows that the etch depth increases to ∼1100 nm, as shown in figure 3(*b*). Figures 3(*c*) and (*d*) show that the etch depth also increases with pressure from 20 to 25 torr for the same etching time of 10 min. Further, we noticed that the etched facets may not be smooth in both cases. After 10 min of etching, it is observed that the cone shapes of GaN exhibit inside the etch pits, as shown in figure 4. The high-magnification image in the inset of figure 4 shows that the average cone size and height is ∼150 nm and ∼03–0.5 μm, respectively. Moreover, AFM images in figures 1 and 2 show not only the overall etching

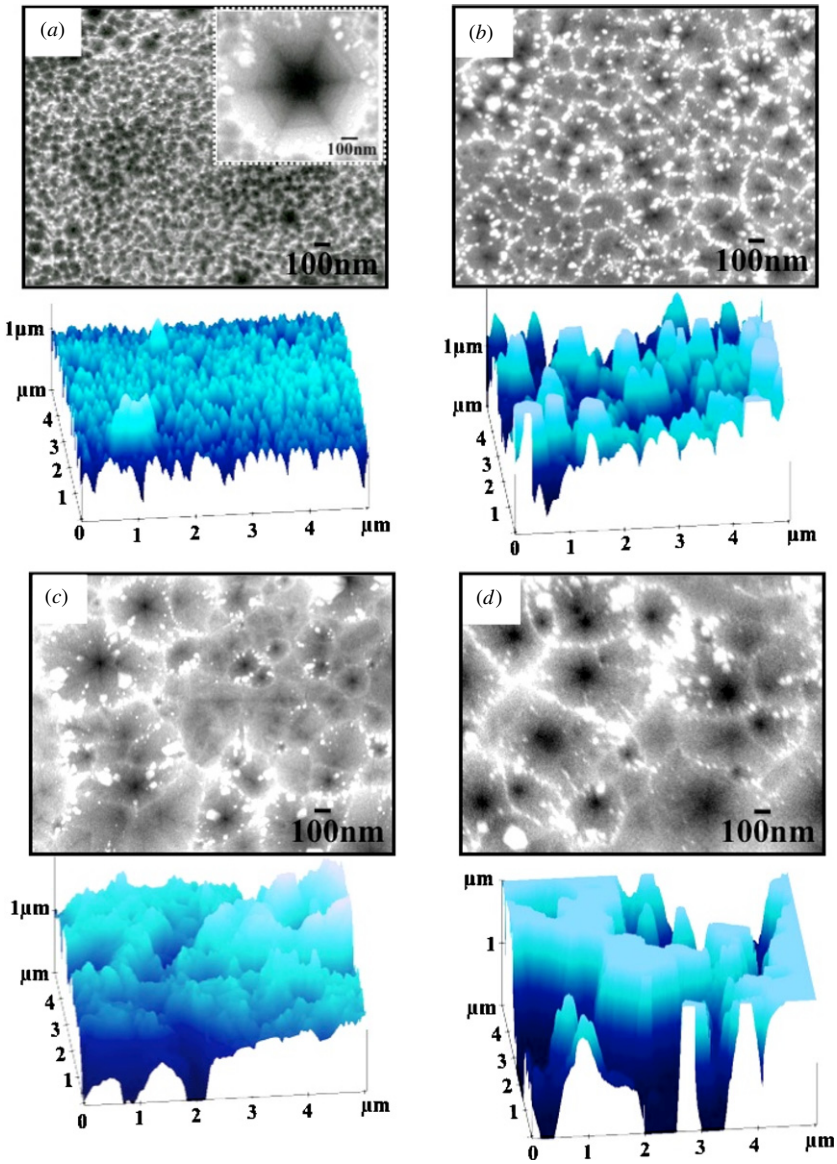

Figure 1. Plan-view SEM images with corresponding AFM images at constant pressure (20 torr) for (*a*) 5 min, (*b*) 10 min, (*c*) 15 min and (*d*) 20 min.

depth, but also the profiles. This is consistent with our SEM results.

In both cases of different etching conditions, the depth (h) and size (d) of etch pits increase with increasing etching time and gas pressure. The dislocation density in a GaN film grown by metalorganic chemical vapor deposition (MOCVD) is approximately in the order of magnitude of 10^{10} cm^{-2}. However, we observed the etch pit density ranging from $\sim 2.3 \times 10^6$ to $\sim 1.6 \times 10^9$ cm^{-2}. If we consider that one etch pit formed due to one dislocation in a short time (5 min), then the etch pit density and dislocation density would be similar. When the etching time becomes longer (10–20 min), the sizes of the etch pits are also increased, whereas the pit density is lower than the dislocation density in GaN films on sapphire. For etching time from 10 to 15 min, it is observed that the etch pit density decreases from $\sim 2.1 \times 10^8$ to $\sim 2.9 \times 10^7$ cm^{-2}. For the increase of pressure from 15 to 30 torr, it is also seen that the etch pit density is lowered from 8.2×10^8 to 5.6×10^7 cm^{-2}. Clearly, the fact that the etch pit density becomes lower at longer etching time and higher pressure is due to coalescence of small etch pits.

For a better understanding of effects of both pressure and etching time on size and shape, we plotted the average size (d) and etch depth (h) as a function of etching time and gas pressure, as shown in figure 5. The size of etch pits was measured from SEM images, while the depth of etch pits was measured from AFM images. The size and depth of etch pits were defined as shown in the inset schematic diagram in figure 5. The size and etch depth of pits are roughly proportionally increased with etching time and gas pressure. From figure 5(*a*), a typical size and depth of etch pits can be obtained as large as $\sim$620 nm and $\sim$1600 nm, respectively, after plasma etching at 20 torr for 20 min etching time. It is also found that the depth of etch pits is as large as

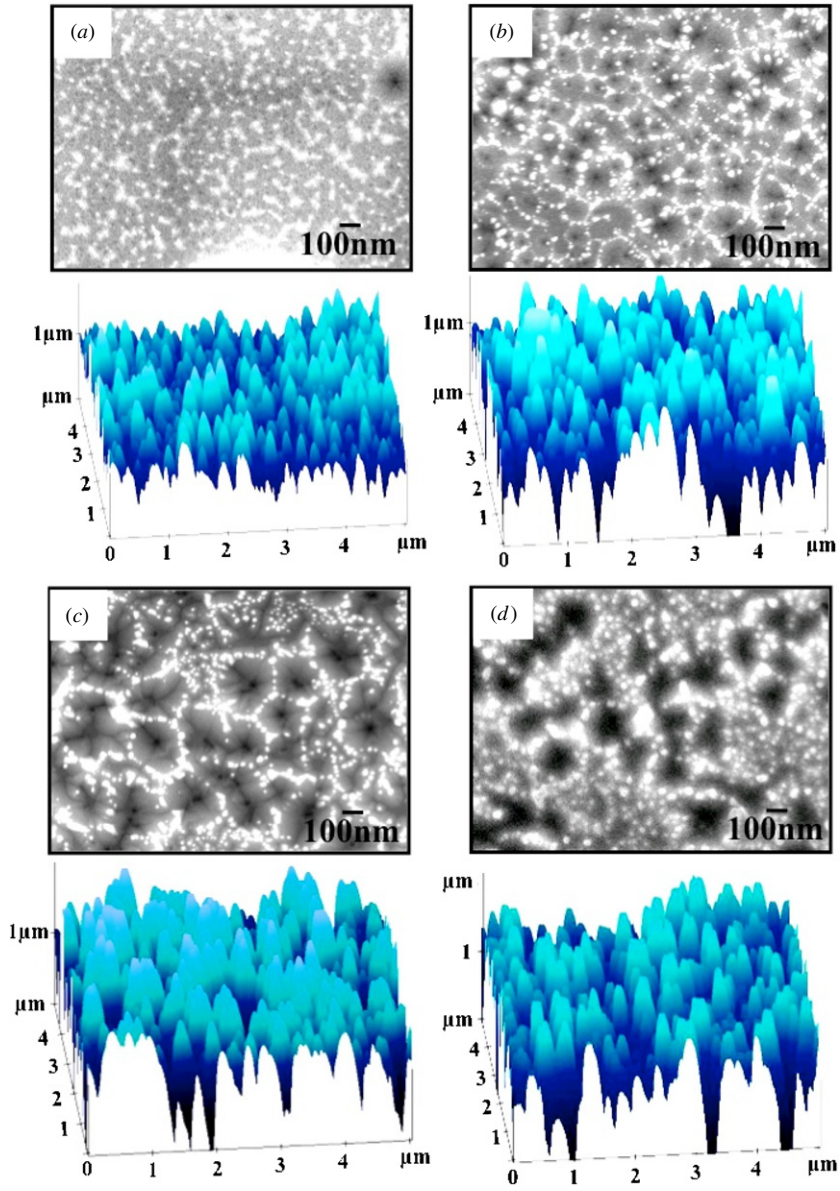

Figure 2. Plan-view SEM images with corresponding AFM images after etching for constant time (10 min) at (*a*) 15 torr, (*b*) 20 torr, (*c*) 25 torr and (*d*) 30 torr.

∼630 nm with a size of ∼320 nm after 10 min etching at 30 torr (figure 5(*b*)). It clearly indicates that the average etch rate for longer treating time (case I) and higher pressure (case II) is ∼80 nm min^{-1} at 20 torr and ∼63 nm min^{-1} at 30 torr, respectively. The depth of etch pits increases with time in a higher rate than with pressure, implying that one can use elongated etching time to obtain deep etching patterns. In addition, figure 5(*a*) suggests that the pit size may be close to a saturated value after 30 min etching at 20 torr, while the depth may still be increased. Interestingly, we have also noticed that after 10 min etching at 25 torr the size is also saturated and depth is still increased, as shown in figure 5(b). From these results, it confirms that hydrogen plasma etching prefers to depth etch after a certain size has been reached.

The depth and size of hexagonal pits may depend on reactivity of hydrogen. The mechanism of enhanced GaN decomposition with increasing pressure and time is not well understood. The etch mechanism is proposed here based on the subprocesses occurring in the hydrogen plasma. It is well known that GaN decomposes at 600 °C in hydrogen atmosphere. At 700 °C in the hydrogen plasma, GaN may decompose into individual radicals and molecules such as Ga and N. Gallium and nitrogen may react with hydrogen atom and/or ion to form volatile gallium hydride (GaH_x) compounds as well as nitrogen–hydrogen gaseous species (NH_x) as follows:

$$GaN + H^* = GaH_x + NH_3 \quad (\text{where } x = 2, 3).$$

Rebey *et al* and Kawamura *et al* reported that below 1030 °C the evaporation of GaH_x occurs in preference to the elemental

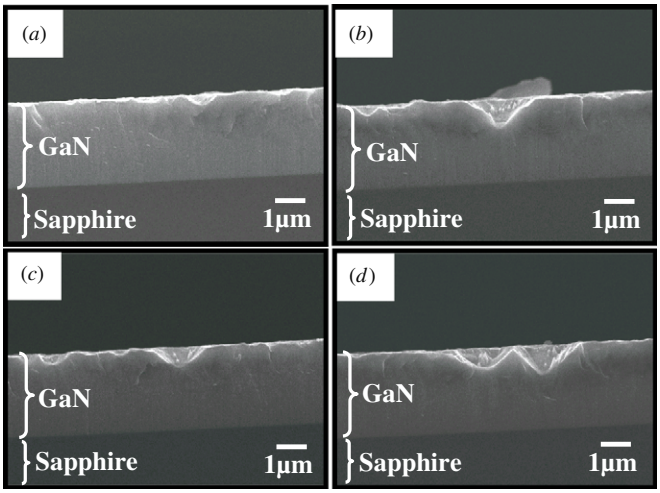

Figure 3. Cross-sectional view SEM images after (*a*) etching time of 5 min and (*b*) etching time of 15 min at 20 torr and 10 min etching at (*c*) 20 torr and (*d*) 25 torr.

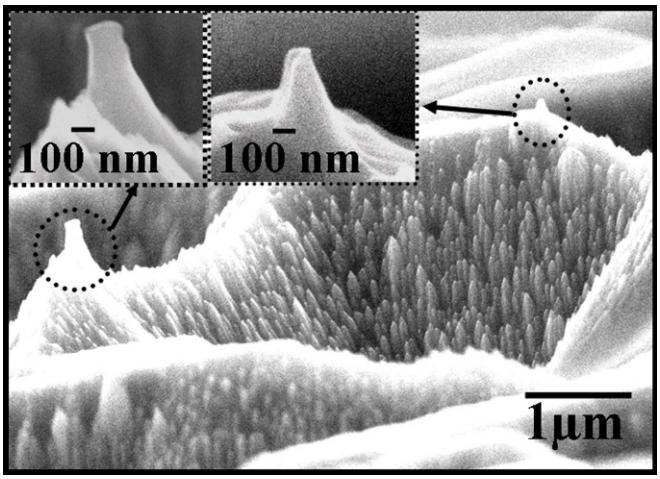

Figure 4. Cross-sectional view SEM image after 10 min etching time at 25 torr.

substance of Ga in a hydrogen atmosphere [15, 16]. We believe that the etch rate depends upon the volatile etch products. The formation of gallium hydride species (GaH_x, $x = 2, 3$) does not adsorb on the surface at 700 °C. The GaH_x species (shown in the reaction) may be weakly bound to the surface, and therefore, it has higher tendency to desorb from the surface [17]. The thermal stability of NH_3 in the microwave plasma is very low. Hydrogen plasma can induce NH_3 to dissociate effectively at temperatures between 400 and 700 °C.

It is noticed that the etch rate of GaN is higher for a longer etching time. This may occur through a surface-mediated dissociation of H_2, followed by the formation of more mobile and volatile hydrogenated N and Ga species on the rough surface of an increased area exposed to the hydrogen plasma. The hydrogen plasma density generally increases with increasing pressure (15–30 torr). Koleske *et al* showed that at higher pressure, the decomposition rate of GaN was enhanced [18]. Also, they showed that the Ga desorption rate is found

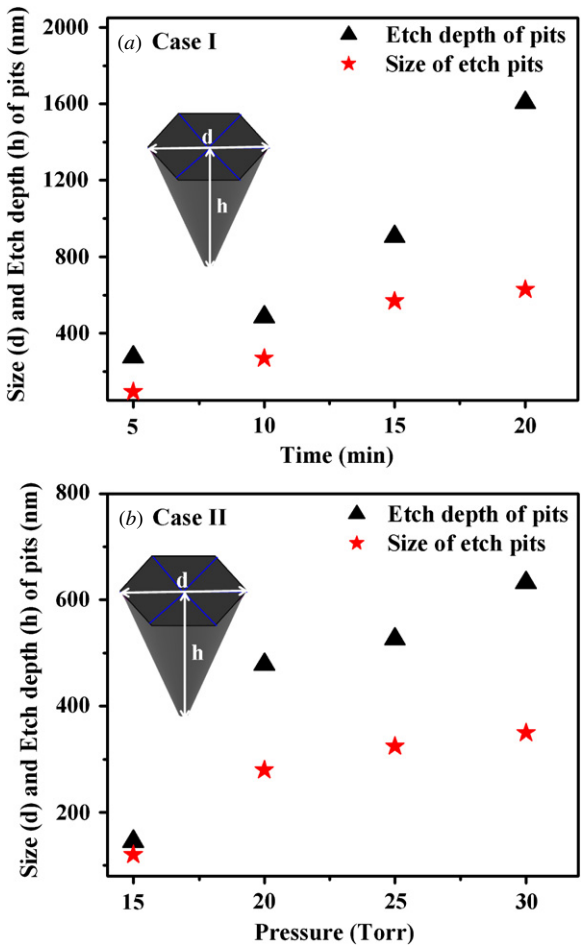

Figure 5. The variation of the size and depth of etch pits with (*a*) time and (*b*) pressure.

to be independent of pressure, and therefore, does not account for the enhanced GaN decomposition rate. This suggests that hydrogen gas acts chemically to reduce the barrier for GaN decomposition. Since the GaN surface can be chemically altered in H_2, it is possible for N to be preferentially removed from the lattice while the Ga-hydride desorption rate remains relatively constant.

Furthermore, the chemical composition of the etched/unetched GaN layer is determined by SEM-EDX spectroscopy. The EDX spectrum of unetched GaN/sapphire is shown in figure 6(*a*). The Ga/N peak ratio in the unetched GaN surface is roughly ∼3/1. After etching, the typical EDX spectrum taken from the cross-section of the etched GaN/sapphire substrate shows that the Ga/N peak ratio is ∼5/1, as shown in figure 6(*b*). However, it does not give any reliable information about the surface stoichiometry of etched GaN because nitrogen x-rays of low energy are generated in a volume of micrometer range and its intensity depends on the roughness of the surface which may strongly absorb x-rays. No metallic Ga droplets can be identified from EDX. From the etched GaN/sapphire interface, it also shows that the GaN is not yet fully etched away, indicating that the residual GaN still exists on the sapphire substrate.

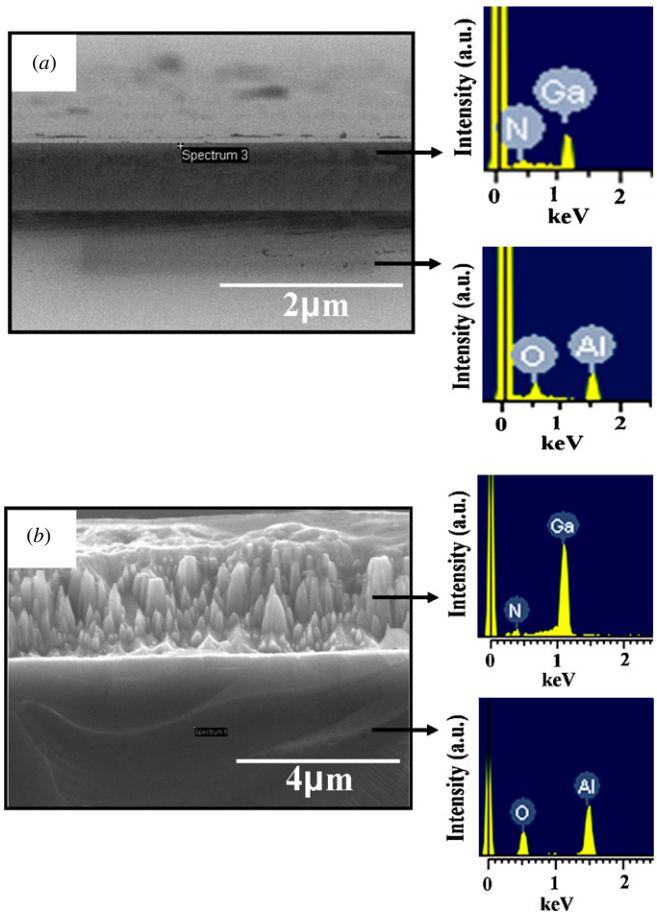

Figure 6. EDX spectra from (*a*) unetched GaN/sapphire and (*b*) etched GaN/sapphire after etching for 20 min at 20 torr.

Conclusions

The GaN layer on a sapphire substrate has been etched by a single step and facile approach with a hydrogen etching process in microwave plasma. The etch pits may display inverted hexagonal cone-like shape with facets. SEM and AFM examinations of the evolution of the surface morphology of etched GaN films reveal that the size and depth of etch pits increase with etching time and pressure.

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