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**Observation and Study of Dislocation Etch Pits in Molecular
Beam Epitaxy Grown Gallium Nitride With the Use of
Phosphoric Acid and Molten Potassium Hydroxide**

by Fred Semendy and Unchul Lee

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Observation and Study of Dislocation Etch Pits in Molecular Beam Epitaxy Grown Gallium Nitride With the Use of Phosphoric Acid and Molten Potassium Hydroxide

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14. ABSTRACT Defects continue to challenge the functionality and reliability gallium nitride (GaN)-based devices. GaN grown on sapphire by molecular beam epitaxy was investigated by wet etching in hot phosphoric acid (H ₃ PO ₄) and molten potassium hydroxide (KOH). Hexagonally shaped etch pits were formed on the etched sample surfaces. Etched samples were characterized with the use of atomic force microscopy (AFM) and scanning electron microscopy (SEM) and SEM cathode luminescence (SEM-CL). AFM images show dark spots indicating mixed dislocations. The densities of the mixed dislocations are almost ~3 x 10 ⁸ cm ⁻² . Observations were made about the three different types of etch pits distinguished as α, β, and γ. By comparing SEM and AFM, we made observations about a relationship between etch pits and dislocations. The origin of etch pits is the mixed dislocation, and the combination of KOH etching and AFM is found to be a better approach for a two-dimensional evaluation of mixed dislocations. Results showed that both H ₃ PO ₄ and molten KOH are good wet etchants for GaN and the pits created by H ₃ PO ₄ were smaller and numerous when compared to the pits created by molten KOH.					
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1. Introduction

Recently, wideband material gallium nitride (GaN)-based materials have been the subject of intensive research for opto-electronic devices and high temperature/high-power electronic devices. Ultraviolet detectors (1), aluminum nitride (AlN)/GaN field-effect transistors (2, 3) visible emitting diodes (4) and high mobility transistors (5) have been demonstrated. GaN and aluminum gallium nitride (AlGaN) materials are generally grown by metal organic vapor phase epitaxy (MOCVD), molecular beam epitaxy (MBE), and hydride vapor phase epitaxy (HVPE) (6). Because of the large lattice mismatch between GaN and sapphire and the mismatch in thermal expansion coefficient, GaN films contain dislocation densities as high as 10^8 to 10^{10} cm^{-2} . High dislocation density results in poor device characteristics and shorter life times (7). Two-dimensional surface evaluation for defects and dislocations is important in order to characterize the relationship between device performances and GaN crystal qualities.

Characterizations of dislocations (mostly threading dislocations in GaN) are mainly conducted through transmission electron microscopy (TEM). It is a process that will reveal the microscopic structure of dislocations. However, the procedure is cumbersome and time consuming. Thus, it is important that the crystal characterization be done via simple procedure, namely, chemical etching to obtain valuable information about dislocations.

Chemical etching is a useful method for crystal characterization. Etching in general is a destructive procedure. No suitable etchant has been found for GaN because of its chemical stability against various mineral acids and aqua regia. Molten sodium hydroxide, potassium hydroxide, and potassium pyrosulfate and 50 % sodium hydroxide aqueous solution (8) were the only known etchants. GaN grown on sapphire was investigated for etch pits with the use of molten KOH (9). Kozawa *et al.* found that all etch pits were hexagonal pyramids that were tentatively ascribed to dislocations in GaN layers.

Ono *et al.* (10) found that the etch pit density (EPD) of a GaN surface etched by a solution of H_3PO_4 and H_2SO_4 was reduced from 4×10^7 to $6 \times 10^6 \text{ cm}^{-2}$ when a thin layer of InGaN was inserted in the GaN layer. Yamamoto *et al.* (11) studied the etch pits in Si-doped GaN formed by molten KOH. They found hexagonally shaped etch pits with three different sizes of varying densities. The large and medium size pits were on the order of $6 \times 10^6 \text{ cm}^{-2}$ and for the smaller size, $3 \times 10^8 \text{ cm}^{-2}$. From all previous work on the etch pit studies of GaN, we can conclude that the EPD is usually 10^2 to 10^4 lower than dislocation density evaluated by TEM. Etch pit varies even in same sample, etch pit has no relation to threading dislocation, and etch pits might be related to nano pipes or threading screw dislocations. Some reports indicate that the commonly observed hexagonally shaped etch pits to dislocations (12, 13); no convincing evidence has been presented yet.

2. Experiment

GaN samples were grown on (0001) sapphire by MBE. For the experiment, samples were cut into small pieces. The layer thicknesses of these samples were less than 6 μm with unintentional doping levels of less than 10^{15} cm^{-3} . Commercial 85% phosphoric acid was heated to an etching temperature in a beaker and GaN samples were etched for various times. The etching temperature between 160 $^{\circ}\text{C}$ and 180 $^{\circ}\text{C}$ was monitored with a Pt-PtRh thermocouple. In the case of using molten KOH, the samples were held in a platinum basket and immersed in the etchant. In this case, the experiments were performed between 350 and 450 $^{\circ}\text{C}$, lasting for 10 to 20 minutes. Etching was performed in a ceramic furnace. A nickel crucible was used for the molten KOH, and thermocouples were used to monitor the temperature. Etching was performed after 30 minutes after the melting temperature reached the process temperature. The etching rate was calculated from the thickness difference before and after etching. The surface topography analysis was performed with AFM, SEM, cathodeluminescence, and surface profiling in some cases.

3. Results and Discussion

The etchants remarkably affect the etch rate and the size and shape of etch pits. Figures 1 (a) and (b) show SEM images of GaN before and after etching, respectively, in H_3PO_4 for 5 minutes at 180 $^{\circ}\text{C}$. Many darkly etched spots are observed and the dark spot density is about $4 \times 10^8 \text{ cm}^{-2}$, which is closer to the lower limit of the threading dislocation (TD) density. The scale used is 1 μm . There are mainly three types of TDs in GaN epilayers: pure edge TDS with a Burgers vector of $1/3 (11\bar{2}0)$, pure screw TDs with Burgers vector of $\langle 001 \rangle$, and mixed type TDs with Burgers vectors of $1/3 (11\bar{2}3)$. Pure screw TDs with typical densities more than one order of magnitude lower than that of the pure edge or mixed type TDs would have an average distance of less than 3 μm among each other. Pure TDs do not have a component in the C-direction and are emerged into terraces.

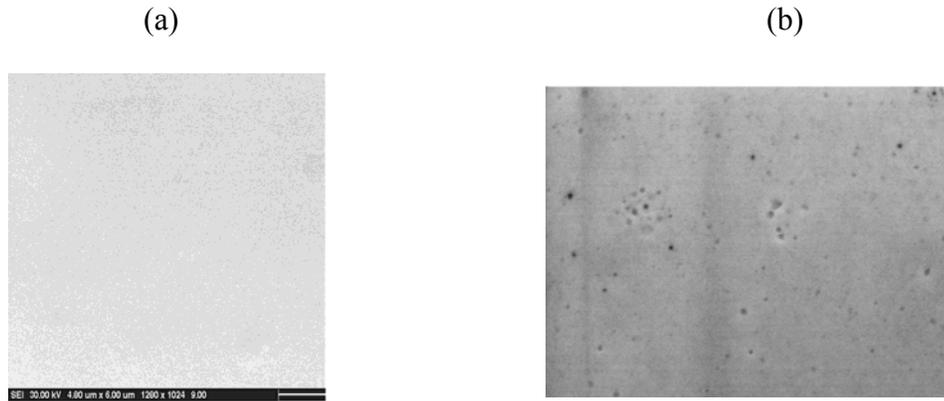


Figure 1. SEM images of GaN before (a) and after (b) etching in H_3PO_4 for 5 minutes at 180 °C.

The etched GaN samples in phosphoric acid were used to obtain panchromatic SEM-CL and the image is shown in figure 2 (b). Figure 2 (a) is an SEM image of a GaN-etched sample in phosphoric acid. The dislocations act as additional radiative recombination centers, giving rise to increased or reduced panchromatic CL intensity in the micrographs. The dislocations are clearly visible in the CL image and present all over the surface.

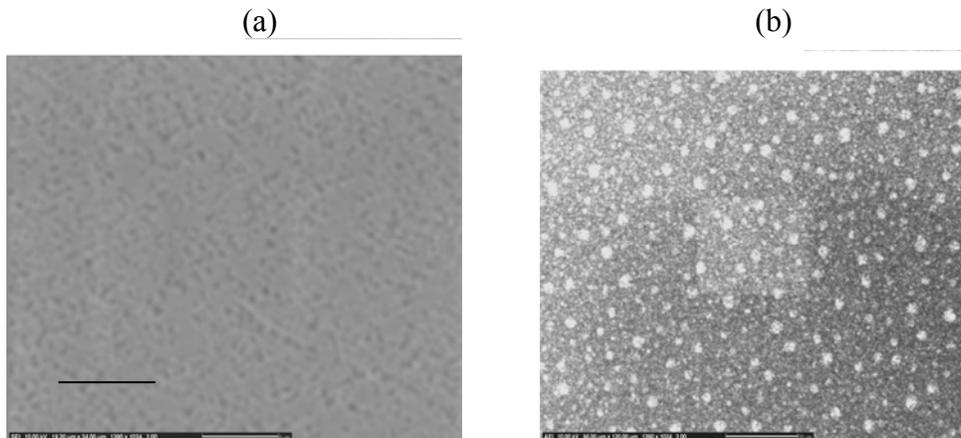


Figure 2. (a) SEM image of GaN etched in H_3PO_4 for 5 minutes at 170 °C panchromatic SEM-CL image at RT.

Figure 3 shows the hexagonal etch pits after etching the GaN samples in molten KOH at 300 °C for 10 minutes and (b) for 20 minutes. Here, the hexagonal pits seen on the surface reflect the crystal symmetry of GaN. The method indicates that the molten KOH etching is a useful method for revealing the etch pits and for characterizing the GaN surface.

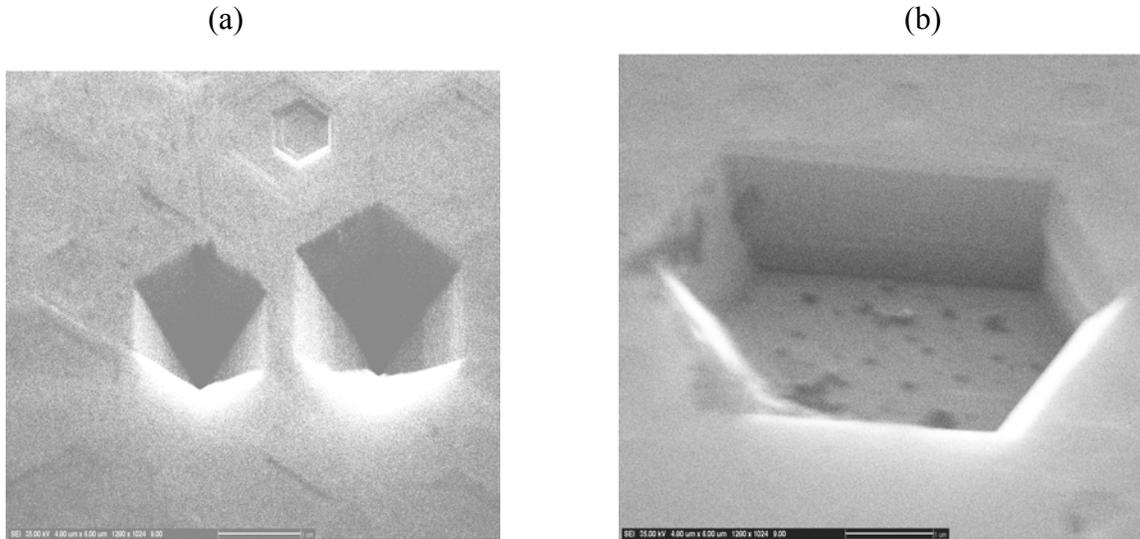


Figure 3. SEM images of GaN (a) and (b) after etching in KOH (a) for 10 minutes at 300 °C and (b) at 300 °C for 20 min.

Figure 4 gives the SEM images of GaN with couple of different angular views of the hexagonal etch pit. Figure 5 shows the schematic view of the etch pits. All pits formed hexagonal pyramids, the side of the base being along $\{11\bar{2}0\}$ and the facet being $(30\bar{3}2)$ face of GaN. In general, the shape and density of etch pits were independent of the etching temperature (300 to 400 °C). The shape of the etch pits was identical and uniform throughout the surface. When etching with phosphoric acid is compared, the shape and density were different when etched in molten KOH.

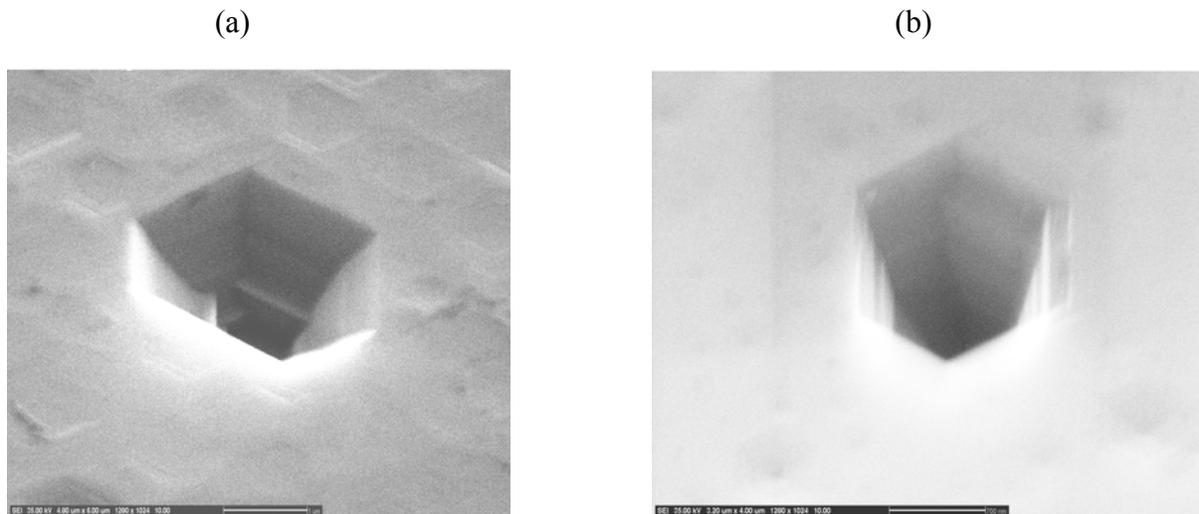


Figure 4. SEM images of GaN (a) and (b) after etching in KOH for 10 minutes at 300 °C.

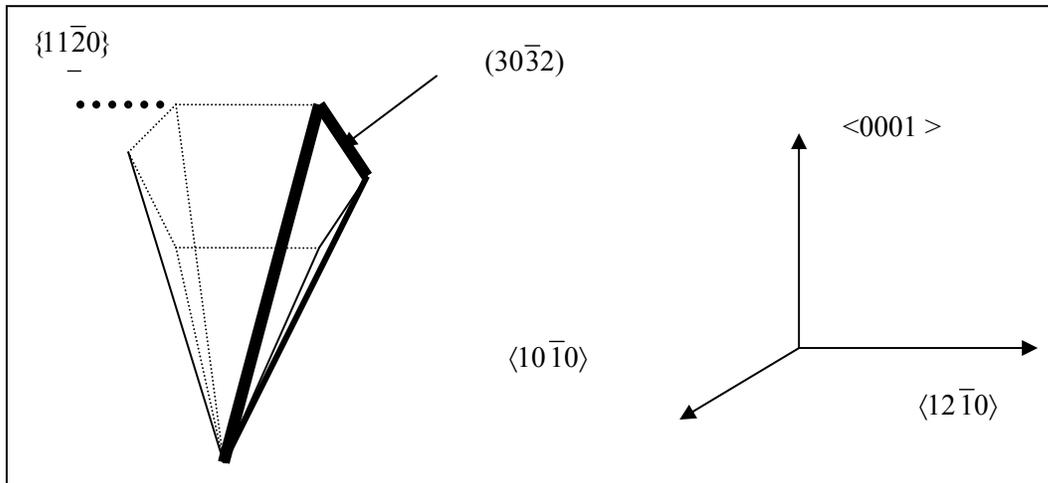


Figure 5. Schematic view of etch pits in GaN.

Samples etched in molten KOH were used for SEM-CL for the panchromatic view as shown in figure 6. These views indicate that the molten KOH etching is aggressive in nature and creates larger pits with hexagonal shapes.

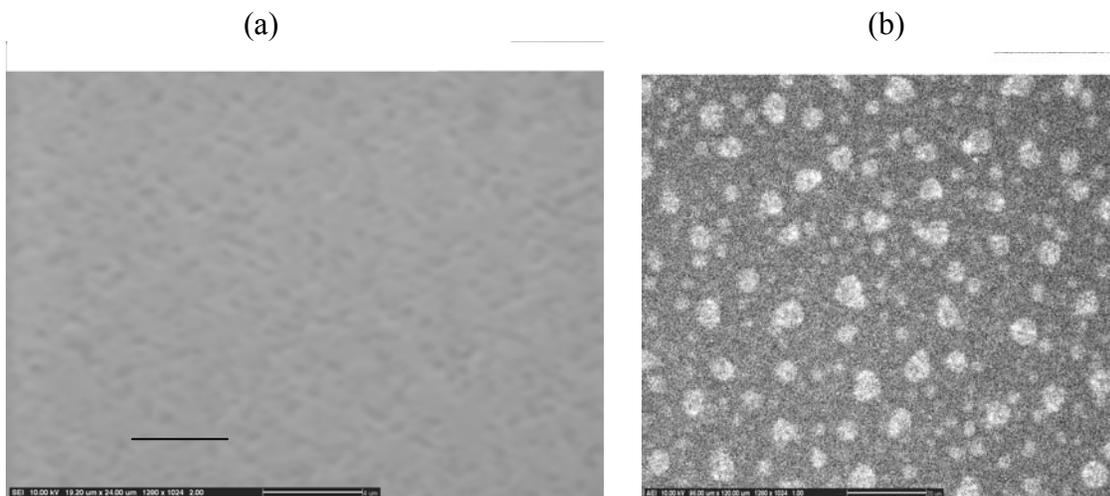


Figure 6. (a) SEM image of GaN etched in molten KOH for 5 minutes at 350 °C (b) panchromatic SEM-CL image at RT.

Figure 7 shows the AFM images of GaN with (a) and (b) showing the standard surface scan of the H_3PO_4 etched for 5 minutes at the 170 °C sample. In the first case, (a) a size of 10 μm area of the sample was scanned at 1 Hz. As can be seen, several shapes are observed when the sample is etched in hot phosphoric acid (13). Unclear etch pits can be seen in the AFM scanned (a) image. These are mainly truncated pyramid pits and conical pyramid pits along with some regularly shaped pits.

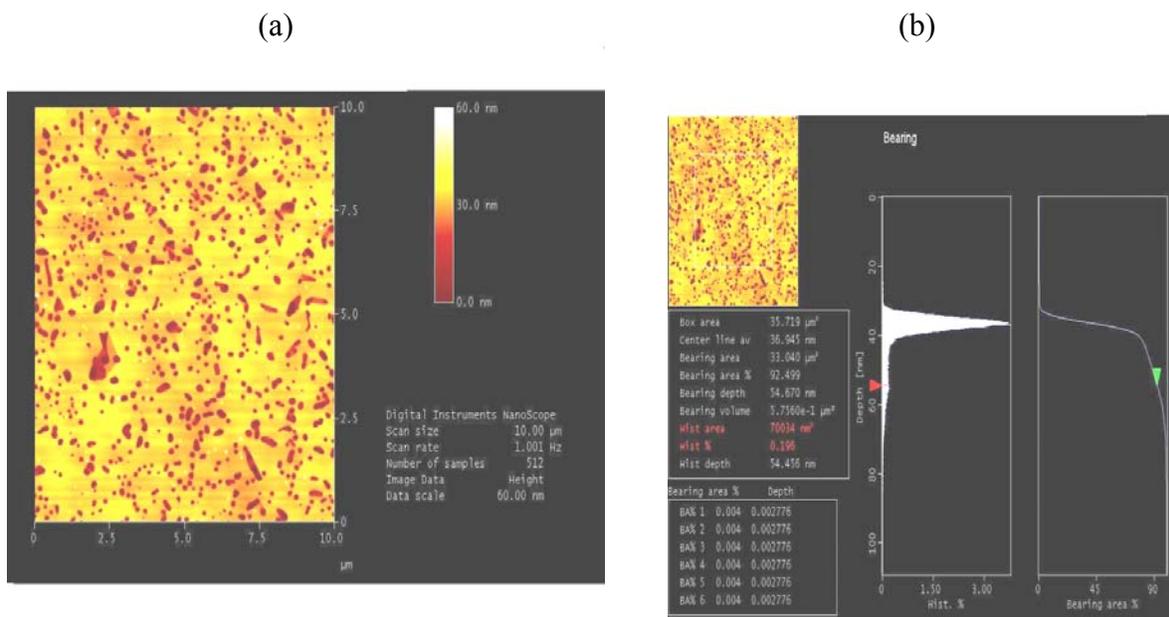


Figure 7. (a) and (b) AFM image of GaN etched in H_3PO_4 for 5 minutes at $170\text{ }^\circ\text{C}$.

Figure 8 gives the AFM analysis of GaN etched on molten KOH at $350\text{ }^\circ\text{C}$. In the case of (a) roughness analysis, the rms (root mean square) roughness for a $1\text{-}\mu\text{m}$ scan was 1.7 nm with an rms maximum value of 10 nm with an rms average value of 1.3 nm .

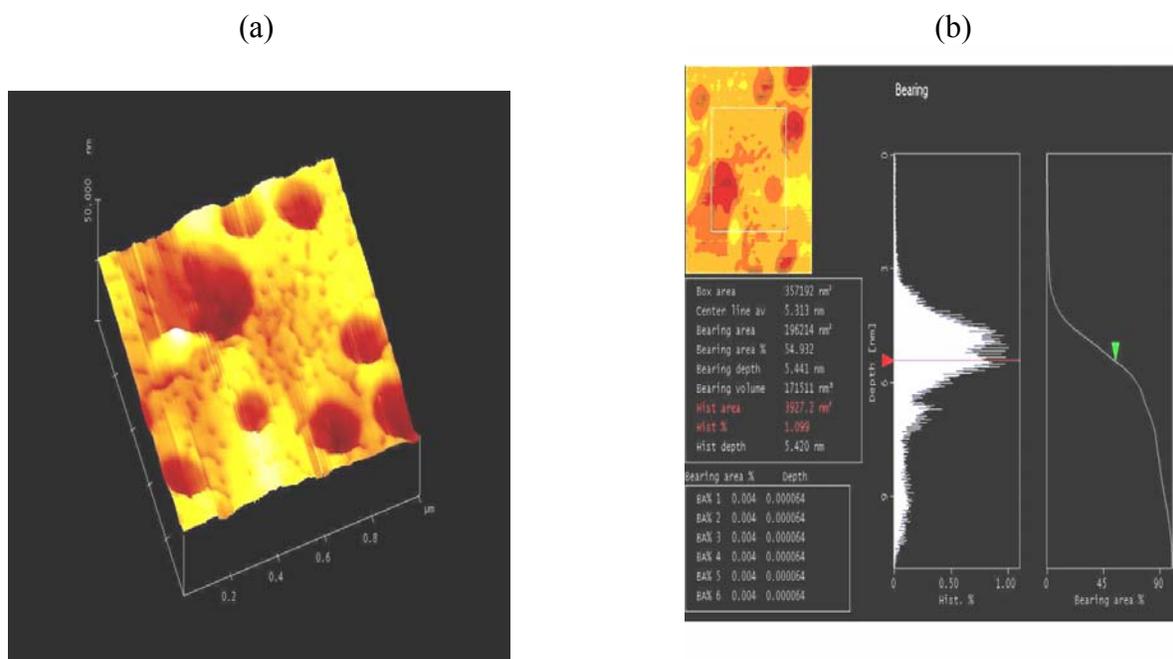


Figure 8. (a) and (b) AFM images of GaN etched in molten KOH at $350\text{ }^\circ\text{C}$.

Figure 9 gives the AFM images of GaN etched in molten KOH at 450 °C and because of the anisotropic character steps tend to align with one of three sides of the hexagon. Subsequently, dark spots disappear and hexagonal pits appear on the GaN surfaces. These pits are larger than 1 μm and smaller pits are in the nano-meter scale. However, the density of the small pits is more than that of the larger ones.

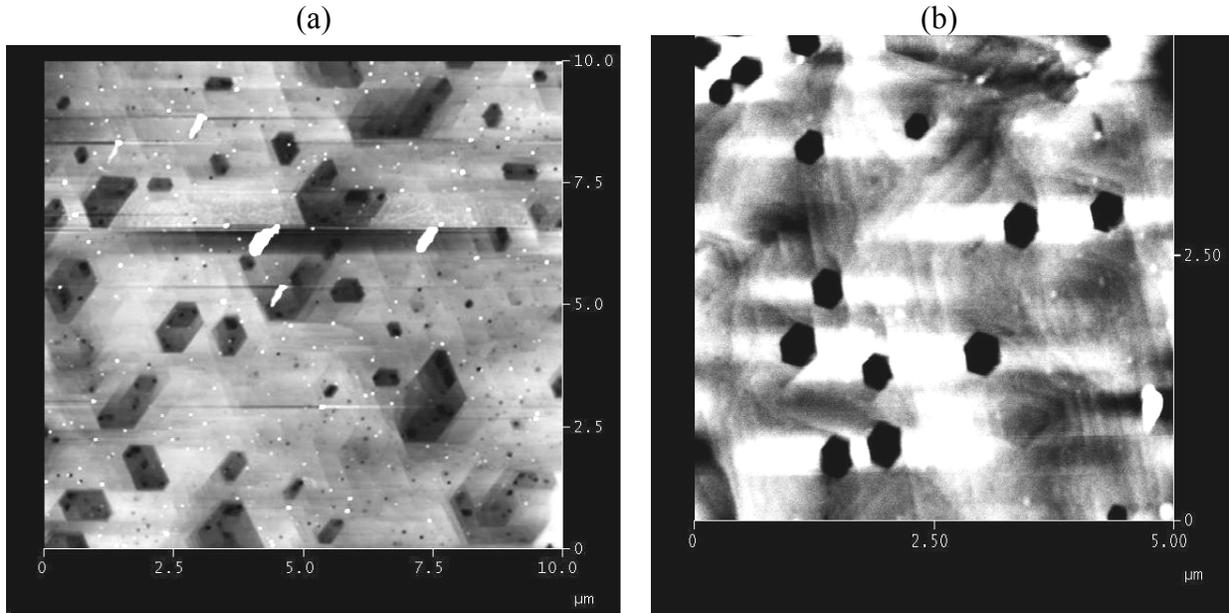


Figure 9. (a) and (b) AFM images of GaN etched in molten KOH at 350 °C.

These etch pits might be produced by threading dislocations propagating to the top surface. According to Hino *et al.* (14), there are three types of etch pits in GaN. The first type is hexagonal which is well defined with a large black core called α type, the second one is the unclear hexagon with a small black core called β type, and the last is a polygon called γ type. The α type has a triangular shape and has a facet. The β type has a combination of triangular and trapezoidal shapes, which seems to be a combination of α and β types, and the γ type has a polygonal shape.

4. Conclusions

In conclusion, both H_3PO_4 and molten KOH chemical etching were performed on MBE grown GaN samples to investigate the nature of the etch pits. GaN grown on sapphire by MBE was investigated by wet etching in hot phosphoric acid H_3PO_4 and molten potassium hydroxide (KOH). Hexagonally shaped etch pits were formed on the etched sample surfaces. Etched samples were characterized by AFM and SEM and SEM-CL. Mixed dislocations were indicated

by dark spots as shown by AFM images. The densities of the mixed dislocations are almost $\sim 3 \times 10^8 \text{ cm}^{-2}$. Observations were made about the three different types of etch pits distinguished as α , β , and γ . By comparing SEM and AFM, we made observations about a relationship between etch pits and dislocations. The origin of etch pits is the mixed dislocation, and the combination of KOH etching and AFM is found to be a better approach for 2-D evaluation of mixed dislocations. Results showed that both phosphoric acid and molten potassium hydroxide are good wet etchants for GaN and the pits created by phosphoric acid etching were smaller and numerous when compared to the pits created by molten KOH.

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