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Dislocation Etch Pits in GaN Epitaxial Layers Grown on Sapphire Substrates

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ABSTRACT

Dislocations in GaN epitaxial layers grown on sapphire substrates have been studied by chemical etching. We have examined molten KOH as a defect etchant and characterized the etch pits on GaN layers. By use of molten KOH etching, etch pits were revealed on the surface of the GaN layer. All pits were hexagonal pyramids, which reflect the crystal symmetry of GaN. Results showed that molten KOH etching might be a useful method for the evaluation of the dislocations in GaN layers. The etch pit density (EPD) was typically 2×10^7 cm^{-2}.

Gallium nitride (GaN) is one of the most interesting materials for blue light emitting devices because it has a direct energy bandgap of 3.39 eV at room temperature. Recently, the crystal growth of high-quality GaN was achieved by metallorganic vapor phase epitaxy (MOVPE)[1-3] or molecular beam epitaxy (MBE),[4,5] and high-brightness LEDs based on GaN have been developed.[6,7] However, GaN epitaxial layers are normally grown on sapphire or SiC, and there is no ideal substrate material with lattice constant and thermal expansion coefficient matched to GaN at present. Therefore, the epitaxial layers contain a high density of dislocations resulting from the lattice mismatch and the difference in the thermal expansion coefficients between the epitaxial layer and the substrate. Until now, there have been only a few reports about the dislocations in GaN epitaxial layers.[8-10]

In this study, the dislocation etch pits revealed by chemical etching on the surfaces of GaN epitaxial layers grown on sapphire substrates by MOVPE were investigated. Although chemical etching is a useful method for the evaluation of the dislocations and has been widely used in III-V compound semiconductors,[11-14] no suitable etchant for GaN has been found because of its chemical stability to various mineral acids and aqua regia. The chemical etching using an aqueous sodium hydroxide solution[8] and hot phosphoric acid[9] were reported for GaN grown by vapor phase epitaxy (VPE). However, these etchant are not able to reveal etch pits on MOVPE-grown GaN, those surfaces were smooth and pinhole free.[15] We have examined molten potassium hydroxide (KOH) as a defect etchant for GaN epitaxial layers, and characterized the etch pits revealed on GaN layers. Molten KOH etching has been used to evaluate dislocations in GaAs,[14] however, there are no reports for defect etching using molten KOH in GaN to our knowledge. The density of etch pits revealed by molten KOH was compared to the dislocation density measured by transmission electron microscopy (TEM) method.

GaN epitaxial layers were grown on sapphire substrates by MOVPE. The Ga, Al (for the AlN buffer layer), and N source gases were trimethylgallium (TMG), trimethylaluminum (TMA), and ammonia (NH_3), respectively. The thin AlN (50 nm) layer was deposited at 400°C as a buffer layer just before the growth of the GaN at 1150°C. The growth conditions were the same as those reported previously.[16,17] The thickness of the GaN layer was about 2 μm. The chemical etching using molten KOH was carried out to reveal the dislocation etch pits. The etching time and temperature were typically 10 min and 360°C. The shape and density of etch pits were observed by Nomarski microscopy and scanning electron microscopy (SEM). The dislocation density in GaN layer was measured from the plan-view TEM image. The TEM specimen was prepared by mechanical thinning followed by ion milling. The GaN epitaxial layer was thinned from the substrate side so that only the dislocations at the upper epitaxial surface region were imaged.

Molten KOH etching was performed on the GaN epitaxial layers. The SEM images of as-grown and etched surfaces of GaN epitaxial layers are shown in Fig. 1. No hillocks or pits were observed on the as-grown surface of the GaN epitaxial layer. On the other hand, hexagonal pits, which reflect the crystal symmetry of GaN, are observed on the etched surface. This result indicates that molten KOH etching is a useful method for revealing etch pits and characterizing GaN layers. To clarify the detailed shape of the etch pits, we cleaved the etched sample and analyzed through a 60°-tilted view, as shown in Fig. 2. 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 (see Fig. 3). The shape and density of the etch pits were independent of the etching temperature (300-450°C), and the background of the etched surface has no emerging pits even in further etching and under enlarged view. The shape of each pit was almost identical, and the density of the etch pits was uniform across the sample. The shape and density of the etch pits are dif-

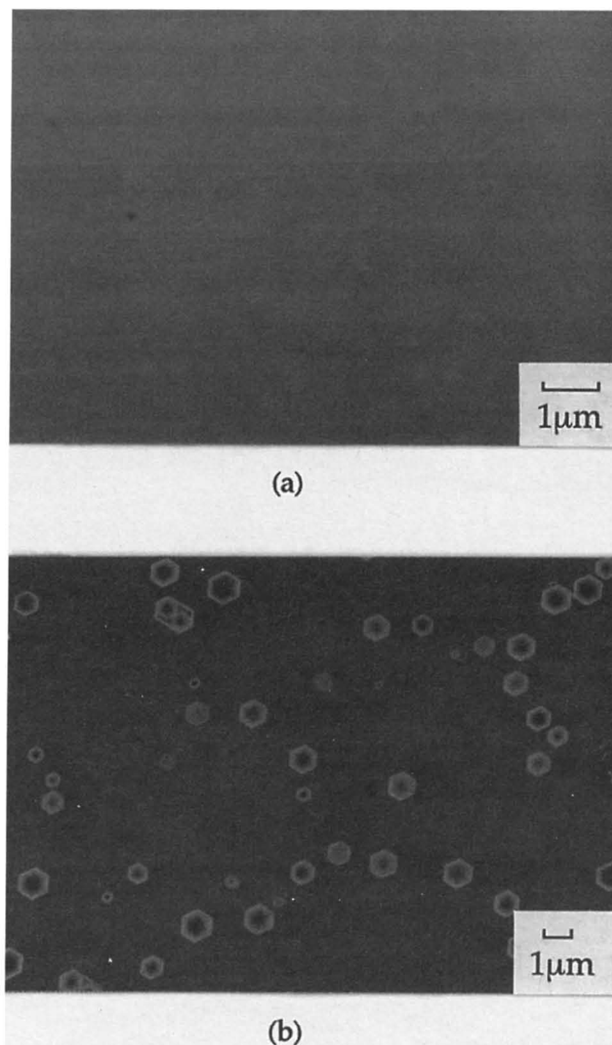

Fig. 1. The SEM images of (a) as-grown and (b) molten KOH-etched surface of GaN layers.

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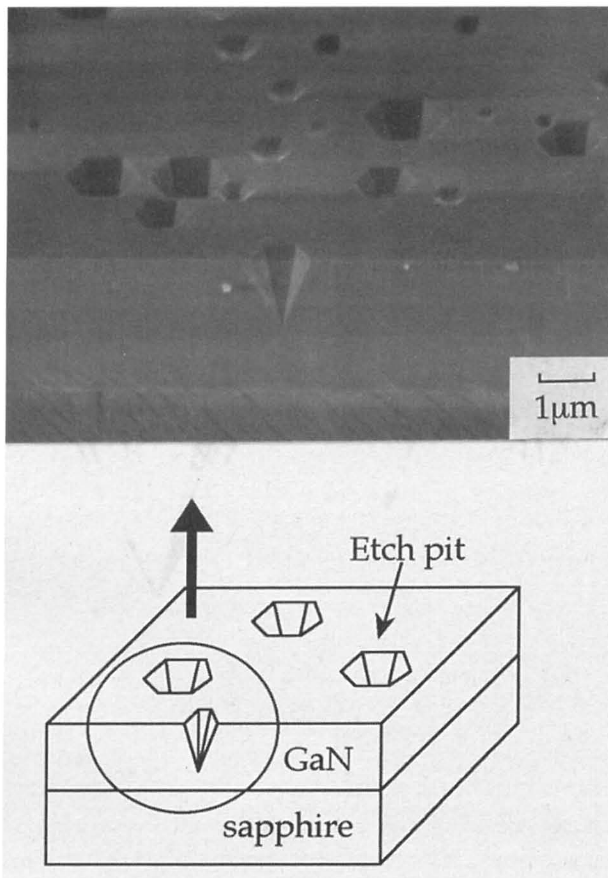

Fig. 2. The cleaved etched sample through a tilted view of SEM.

ferent from those reported by Shintani *et al.*[9] using hot phosphoric acid. They reported that the various shapes of pits, such as truncated hexagonal pits and conical pits, were observed on the etched surface of the GaN layers, and etch pits were partly arranged along a direction of crystal growth step lines or edge of spiral hillock. The GaN layers they used were grown by a conventional vapor phase epitaxy (VPE) method without any buffer layers. Unintentionally doped GaN layers showed n-type conductivity with a high residual donor concentration of more than 10^{18} cm^{-3}. Moreover, many hillocks with various sizes, resulting from three-dimensional growth, were observed on the as-grown surface of their sample. On the other hand, no hillocks were observed on the as-grown surface of our sample, which were grown with an AlN buffer layer by MOVPE, and no etch pits were revealed on our

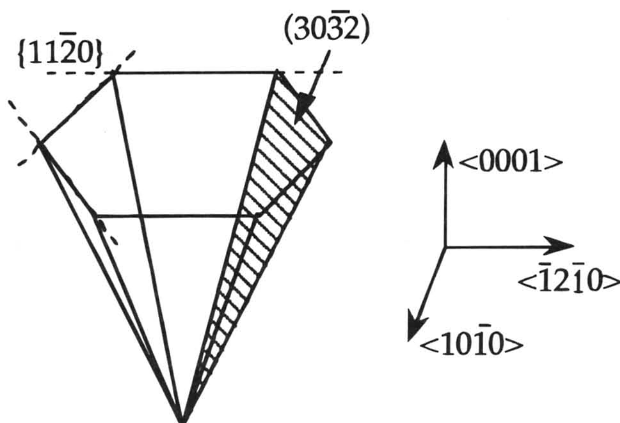

Fig. 3. Schematic view of etch pit.

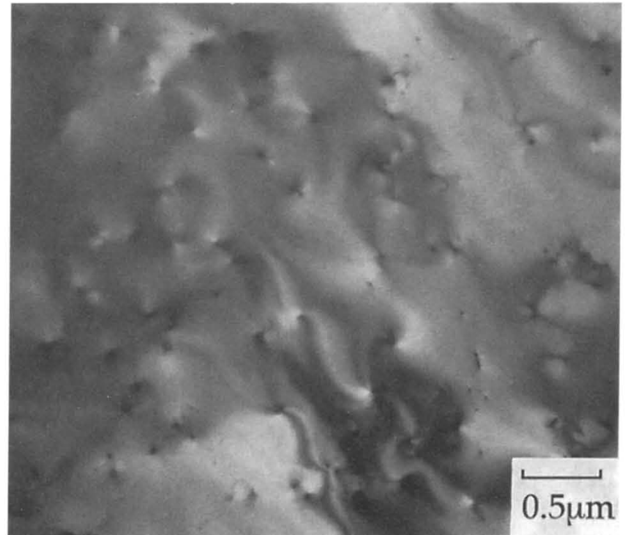

Fig. 4. The plan-view TEM image of GaN near surface region.

sample by hot phosphoric acid. This discrepancy is thought to be caused by the difference in crystal quality of the samples.

Molten KOH etching produces crystallographically oriented etch pits also in GaAs.[14] However, the etch pits revealed on the GaN layer formed sharp and deep pyramids as compared with that on GaAs. This feature of etch pits might be caused by the defect structure and etching reaction. Lester *et al.*[10] characterized the dislocations in GaN epitaxial layers grown on a sapphire substrate by TEM. They reported that dislocations in the GaN layer propagate in the direction normal to the substrate. The etch pits were thought to follow the continuous dislocation line into the GaN layer, so etch pits might have developed normal to the surface. In addition, dislocation sites of the GaN layers were etched fast by molten KOH. Therefore, etch pits on GaN layer were supposed to form sharp pyramids. Evidence of pits with different sizes is also noted in each etched surface. As shown in Fig. 1, the pit size (diagonal line length of hexagonal pit base) ranged from 0.3 to 1.2 μm. However, the reasons for the deviation of the pit size are not clear.

The etch pit density (EPD) was measured at several areas. The observed EPD was typically 2×10^7 cm^{-2}, and did not change substantially with position across the sample and from sample to sample. To evaluate dislocations, it is important to confirm that the EPD correlates with the dislocation density in the GaN layer. Therefore, we also characterized the GaN layer by TEM. Figure 4 shows a plan-view TEM of the threading dislocations in the near-surface region of GaN. The image was taken under bright-field conditions. Dislocations are supposed to propagate normal to the substrate and are seen as dark spots in Fig. 4. The dislocation density measured from the TEM image was 2×10^8 cm^{-2}, and this value was inconsistent with the EPD. This result suggests the possibility that some dislocations were not revealed by molten KOH etching. Similar observations have been reported in defect etching of GaAs grown on Si substrates.[18] In fact, the molten KOH etching of GaAs on Si led to serious discrepancies in defect densities measured by etch pits (~10^3 cm^{-2}) and TEM (~10^7-10^8 cm^{-2}) at an early stage.[19] Subsequent investigations[20] showed that the molten KOH etching revealed a high density of small etch pits, which were buried in the rough background, in addition to large etch pits which had features similar to that revealed in bulk GaAs. Even when this was done, there might be an underestimate ~0.3-0.5 in the ratio of EPD to dislocation density (TEM) value in GaAs on Si. These etching results might be explained by the characteristics of molten KOH etching depending on the Burgers vectors of dislocation.[21] It is supposed that there might be some kind of dislocations, which belong to different Burgers vectors, and some of the dislocations were not revealed by etching. Moreover, the dislocation density in GaN layer measured by TEM was small compared with the reported value (2-10 $\times$ 10^{10} cm^{-2}) by Lester *et al.*[10] They characterized LEDs, which contained a double heterostructure, by cross-sectional TEM. The dislocation density might change due to sample layer structure and TEM observation method. However, further study is required to clarify the discrepancy of the results of EPD and TEM, and to evaluate the exact value of dislocation density in GaN layers.

In summary, we have studied the dislocations in GaN epitaxial layers grown on sapphire substrates by chemical etching. Molten KOH was examined as a defect etchant for GaN, and characterized the etch pits in the GaN layer. By use of molten KOH etching, etch pits were revealed on the GaN surface, and all pits formed hexagonal pyramid pits, which reflect the crystal symmetry of GaN. Results showed that molten KOH etching might be a useful method for evaluating the dislocation in GaN layers. The etch pit density (EPD) was typically 2×10^7 cm^{-2}. The EPD value was small compared with the dislocation density (2×10^8 cm^{-2}) measured by TEM, which was smaller than the reported value (2-10 $\times$ 10^{10} cm^{-2}). Further study is required to clarify the discrepancy of the results of EPD and TEM, and to evaluate exact value of dislocation density in GaN layers.

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