

Etching Behavior of GaN/ GaAs(001) Epilayers Grown by MOVPE*

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Abstract: Wet etching characteristics of cubic GaN (ζ -GaN) thin films grown on GaAs(001) by metalorganic vapor phase epitaxy (MOVPE) are investigated. The samples are etched in HCl, H₃PO₄, KOH aqueous solutions, and molten KOH at temperatures in the range of 90~ 300 °C. It is found that different solution produces different etch figure on the surfaces of a sample. KOH-based solutions produce rectangular pits rather than square pits. The etch pits elongate in $[1\bar{1}0]$ direction, indicating asymmetric etching behavior in the two orthogonal $\langle 110 \rangle$ directions. An explanation based on relative reactivity of the various crystallographic planes is employed to interpret qualitatively the asymmetric etching behavior. In addition, it is found that KOH aqueous solution would be more suitable than molten KOH and the two acids for the evaluation of stacking faults in ζ -GaN epilayers.

Key words: cubic GaN; MOVPE; wet etching; asymmetry

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1 Introduction

Considerable progress has been made recently in the areas of growth, dry etching, and doping of the III-nitrides and their ternary alloys. This has resulted in GaN-based blue light emitting diodes and laser diodes^[1,2]. Despite the great success achieved so far, there are still many problems to be solved. The epitaxial layers invariably contain high densities of defects resulting from the large lattice mismatch between epilayers and substrates^[3]. Therefore, the availability of reliable and quick methods to investigate the defects in GaN is of great interest.

Wet-chemical etching is a useful method for surface

defect investigation and has been widely used in III-V compound semiconductors. However, there has been little success in the development of wet etching techniques for III-nitrides which have excellent chemical stability^[4]. Mileham *et al.*^[5] reported the etching of AlN defective single crystals in KOH-based solutions at etch temperatures in the range of 23~ 80 °C. They found decreasing etch rates with increasing crystal quality, as the reactions occurred favorably at grain boundaries and defect sites. InN in aqueous KOH solutions was reported to etch at a few nm/min at 60 °C^[6]. For GaN, there were several early reports of wet etching in NaOH that hindered by formation of an insoluble gallium hydroxide (GaOH) coating^[7]. Others have reported that H₃PO₄ can remove GaN at a very slow rate. Although GaN can not be etched with vari-

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ous conventional chemical solutions at room temperature, some hot etching solutions, such as hot H_3PO_4 (215 °C) and molten KOH (360 °C) have been able to etch pits at defect sites on the c -plane of GaN epilayers grown on sapphire^[8,9]. More recently, photoenhanced wet etching of GaN has been regarded as a means of greatly improving the chemical reactivity of GaN at room temperature. Ultraviolet (UV) illumination is used to generate electron-hole pairs at the semiconductor surface, which enhance the oxidation and reduction reactions within an electrochemical cell. The photoelectrochemical (PEC) etching can produce anisotropic^[10], dopant selective^[11], and uniform etching^[12,13]. Most of the PEC etching experiments were performed at room temperature using KOH aqueous solution as electrolyte with no bias. Under some special conditions, the dislocation microstructure in the GaN can be revealed by selectively removing material between the dislocations, resulting in whisker formation^[14]. Up to now, however, there are no reports for wet etching of c -GaN epilayers grown on GaAs (001) substrates.

In this study, in order to investigate preliminarily the etching behavior and defect revealing, we performed wet chemical etching on (001) surfaces of MOVPE grown c -GaN epilayers. We etched c -GaN epilayers by using HCl, H_3PO_4 , KOH aqueous solutions and molten KOH in the temperature range of 90~ 300 °C. Asymmetric etching behavior in the two orthogonal $\langle 110 \rangle$ directions was observed.

2 Experimental procedure

GaN epilayers used for wet etching were grown on GaAs (001) substrates in a horizontal MOVPE reactor operating at low pressure (10^4 Pa). TEGa and NH_3 were used as the precursors for Ga and N, respectively. The GaN epilayers were grown in H_2 ambient at 820 °C for 1h after growing the GaN buffer layers at 550 °C. All the films were 0.6 μm in thickness. The unintentionally doped GaN films

were measured to be n -type with a carrier concentration of $\sim 10^{17} \text{ cm}^{-3}$. Typical full width at half of maximum (FWHM) of double-crystal X-ray diffraction (002) ω scan, from GaN films was about 25°. Our plan-view TEM studies of the as-grown epilayers indicated a defect density in the range of $10^9 \sim 10^{10} \text{ cm}^{-2}$. Commercial 36% HCl, 85% H_3PO_4 , and 5M KOH aqueous solution were heated to etching temperatures 90, 140 and 120 °C, respectively. The samples were immersed in the chemical etchants, which were not stirred during etching. Molten KOH etching was also performed on the c -GaN films. KOH was melted in a platinum beaker and the etch temperature was about 300 °C. JEOL-6301F scanning electron microscopy (SEM) was employed to examine the surface morphology of the as-grown and etched GaN samples. The plan-view TEM specimen was prepared by mechanical thinning followed by ion milling. The GaN epilayer was thinned from the substrate side so that only the defects near the surface region were imaged. Plan-view TEM observation was carried out on a Hitachi H-800 TEM with an accelerating voltage of 200kV.

3 Results and discussion

Figure 1 shows plan-view SEM images of as-grown c -GaN epilayer and layers wet etched in several acid and base solutions at temperatures in the range of 90~ 300 °C for 5min. The surfaces of the samples are mirror-like before etching. However, as can be seen in Fig. 1(a), ridges and pits on the surfaces can be observed by SEM. Figure 1(b) shows a SEM image of a sample after it was etched in commercial 36% HCl at 90 °C. Sawtoothed etch figures developed on the sample surface. Figure 1(c) is for a sample immersed in commercial 85% phosphoric acid (H_3PO_4) at 140 °C for 5min. After it was etched in this etchant, spindle-shaped etch pits developed on the sample's surface. These pits elongate in $[110]$ direction. A typical SEM micrograph of the GaN surface after molten KOH etched is shown in Fig. 1(d). As it can be seen,

molten KOH produced rectangular etch pits on the sample surface. It is well known that molten KOH has been used successfully in evaluation of dislocations in wurtzite GaN grown on sapphire. In our etching experiment, however,

molten KOH produced residual complex on the surface of the sample. In the view point of revealing defects, molten KOH is not suitable for evaluating the defects in c-GaN epilayers.

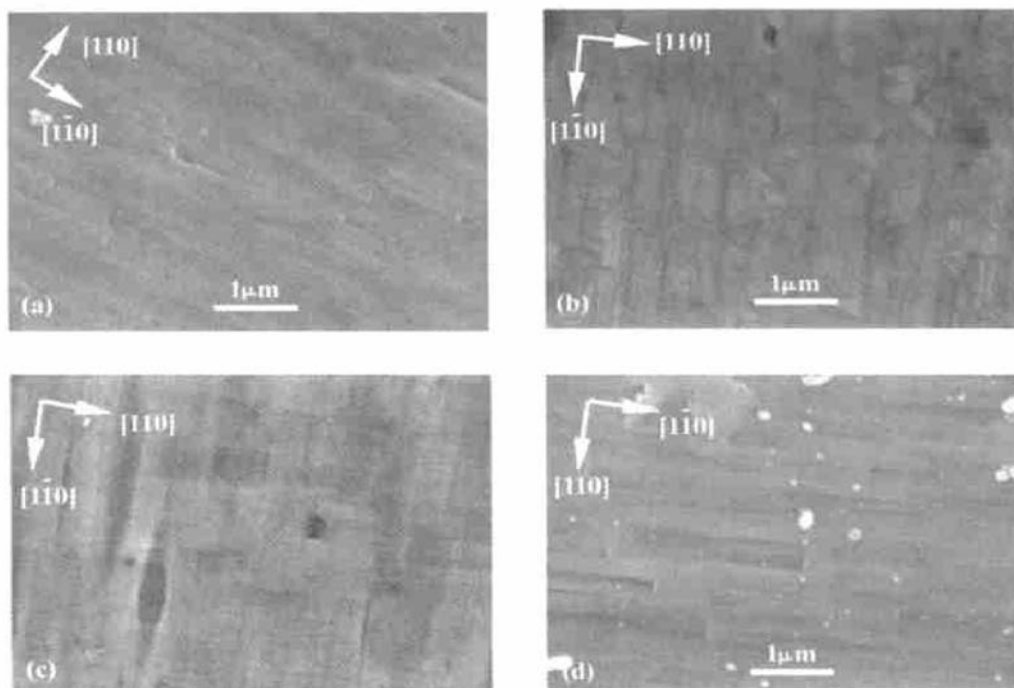


Fig. 1 SEM images of surfaces of as-grown GaN and GaN epilayers after wet chemical etching in acid and base solutions at temperatures up to 300 °C for 5min (a) As-grown; (b) 36% HCl, 90 °C; (c) 85% H₃PO₄, 140 °C; (d) Molten KOH, 300 °C

Figure 2 shows the SEM images of the surfaces of GaN etched in 5M KOH aqueous solutions at 120 °C with different etch times. As in the case of molten KOH etching, aqueous KOH solutions can also produce rectangular pits on the surfaces of c-GaN epilayers. After being etched for 5min, elongated etch pits were visible on the surfaces of the GaN epilayers, as shown in Fig. 2 (a). The etch figures grew in size and merged into each other with the increasing of etch time, as can clearly be seen in Fig. 2 (b) and (c). In addition, steps both in [110] and $[\bar{1}\bar{1}0]$ directions can be observed on the surfaces, especially in Fig. 2(c).

As described above, different chemical solutions produce different etch figures on the GaN surfaces. Hot HCl develops sawtoothed figures which align the edges of original pits (Fig. 1(a) and (b)). Hot H₃PO₄ produces spindle-shaped etch pits on the surface. On the other hand, KOH-based solutions produce rectangular etch pits, which are consistent with the crystallographic symmetry of c-GaN with zinc-blende structure. This is different from the wet chemical etching of wurtzite GaN grown on sapphire, in which both acid and base solutions produce hexagonal etch pits, which reflect the crystallographic symmetry of wurtzite GaN. Here, we only try to discuss the rectangular etch pits produced by molten KOH and aqueous KOH solution.

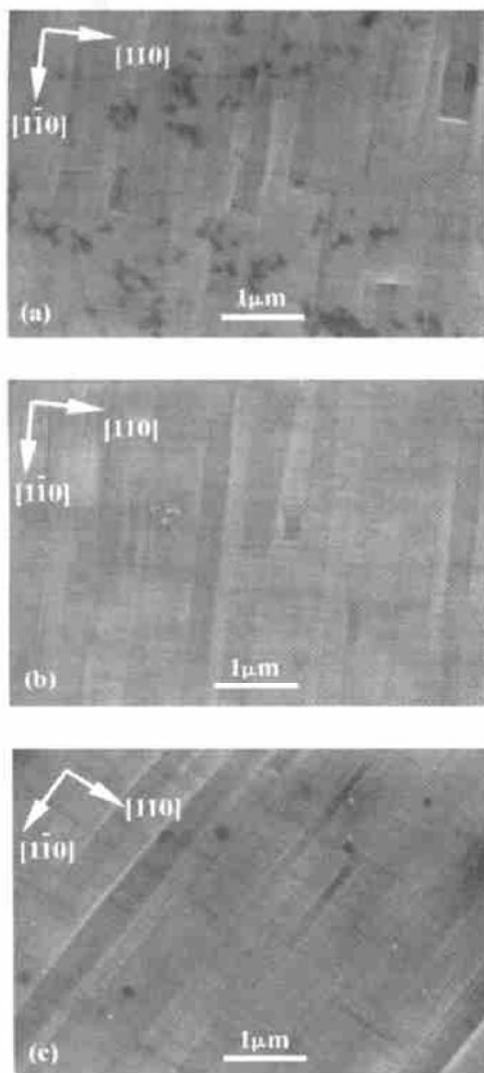


Fig. 2 SEM images of GaN epilayer etched by KOH aqueous solution with different etch times (a) 5min; (b) 10min; (c) 20min

It is well known that the zinc-blende structure exhibits no polarity in the $\langle 001 \rangle$ directions, differences in etching behavior are not expected among the various $\{001\}$ surfaces. In certain etchants, however, $\{111\}$ facets develop on the $\{001\}$ surfaces, and consequently the $\langle 111 \rangle$ polarity of zinc-blende structure is reflected in the etching behavior of these surfaces. Like most of the III-V compound semiconductors, c -GaN has two types of $\{111\}$

surfaces, $(111)A$ and $(111)B$ surfaces. The two types of surfaces, resulting from the crystallographic polarity of the $\langle 111 \rangle$ directions, exhibit markedly different physical and chemical properties. It was found that the $(111)B$ surfaces are far more reactive than the A surfaces in most chemical agents^[15, 16]. Grabmaier *et al*^[15], etched GaAs utilizing molten KOH, they found molten KOH etchant attacks the $(111)B$ surfaces more rapidly. Gatos *et al*^[16], investigated the etching behavior of the (110) and (001) surfaces of InSb. The reactivity of the principal crystallographic planes of InSb decreases in the following order.

$$(111)B \gg (001) > (110) > (111)A$$

We assume this order of reactivity can also be applied to the present case, therefore, the $(111)B$ surfaces are more chemically reactive than the $(111)A$ surfaces. The difference in reactivity was considered the controlling factor for the differences in etching behavior between the two types of surfaces^[16]. Therefore, once small pits with $\{111\}$ facets form at the defect sites in the initial stage of the wet etching, they will gradually develop into larger rectangular pits. The preferential etching of $(111)B$ surfaces is shown schematically in Fig. 3. The etch figures grow in size and merge into each other preferentially in the $[110]$ direction, due to the faster etching of $(111)B$ surfaces, as shown in Fig. 2(b) and (c).

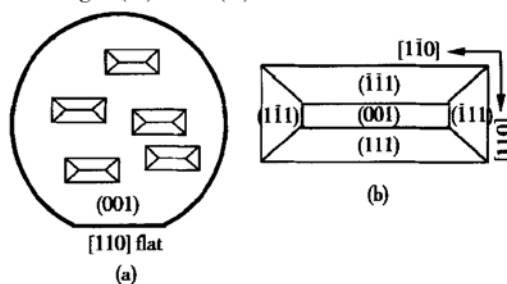


Fig. 3 Schematic diagram of KOH based solutions producing etch pits on (001) surface of GaN epilayer grown on GaAs(001)

In addition, KOH aqueous solution wet etching might be a useful method for evaluating the surface defects of c -GaN epilayers. Steps both in $[110]$ and $[\bar{1}10]$ directions

can be observed in Fig. 2(c). These steps probably correspond to the intersection of stacking faults lying on {111} planes with the (001) surfaces of zinc-blende GaN. Figure 4 shows a plan-view TEM (PV-TEM) image of the same GaN film near the top surface. Bands composed of black-white fringes can be observed in this figure which are formed by inclined stacking faults in the PV-TEM observations^[17]. It is noteworthy that the distribution and density of the striations in Fig. 2 are very similar to that of the stacking faults in Fig. 4. Therefore, we conclude that KOH aqueous solution wet etching can probably be used to reveal surface defects of *c*-GaN epilayers grown on GaAs.



Fig. 4 PV-TEM micrograph of as-grown GaN epilayer near the surface. The dark-bright fringes originate from the inclined stacking faults in the GaN epilayer.

4 Conclusion

We have reported on the etching characteristics of GaN epilayers grown on GaAs (001) substrates by LP-MOVPE. That KOH-based solutions etch rectangular parallelogram pits rather than square pits on the sample surfaces indicates asymmetric etching behavior in the two

different $\langle 110 \rangle$ directions. The asymmetry was attributed to the different reactivity between (111) A and (111) B planes. (111) B planes are more chemically reactive than (111) A planes resulting in the elongated etch figures on the GaN surfaces. In addition, we noticed the similarity between the step distribution of the sample etched in SEM images of hot KOH aqueous solution and the distribution of the stacking faults revealed by PV-TEM observation. Therefore, the etching of KOH aqueous solution can probably be used to reveal surface defects of GaN/GaAs(001) system.

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GaN/ GaAs (001) 外延薄膜的湿法腐蚀特性*

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摘要: 对在 GaAs (001) 衬底上用金属有机物气相外延(MOVPE)方法生长的 GaN 薄膜的湿法腐蚀特性进行了研究. 所用腐蚀液包括 HCl H₃PO₄ KOH 水溶液以及熔融 KOH, 腐蚀温度为 90~ 300 ℃. 实验发现不同的腐蚀液在样品表面腐蚀出不同形状的腐蚀坑. KOH 溶液腐蚀出长方形的坑, 长边平行于 (111) A 面, 表明沿相互垂直的 <110> 晶向的腐蚀特性不同. 用不同晶面相对反应性的差别定性解释了腐蚀的这种非对称性. 此外, 还发现 KOH 水溶液更有可能用于显示立方相 GaN 外延层中的层错.

关键词: 立方相 GaN; MOVPE; 湿法腐蚀; 非对称性

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