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Crystallographic Wet Chemical Etching of p-Type GaN

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We demonstrate crystallographic wet chemical etching of p-type GaN with etch rates as high as 1.2 μm/min. Etchants used include molten KOH, KOH dissolved in ethylene glycol, aqueous tetraethylammonium hydroxide, and phosphoric acid (H_3PO_4), at temperatures ranging from 90 to 260°C. The observed crystallographic p-GaN etch planes are (0001), $\{10\bar{1}0\}$, and $\{10\bar{1}\bar{2}\}$. The etch rates follow an Arrhenius characteristic with activation energies varying from 21 kcal/mol for KOH-based solutions to 33 kcal/mol for H_3PO_4. The etch rate and crystallographic nature for the various etching solutions are independent of conductivity, as shown by seamless etching of a p-GaN/undoped, high-resistivity GaN homojunction and by comparison of the etch rates of p-GaN with n-GaN.

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Most etching of the III-nitrides is currently done by dry processes.[1] While dry etching has many desirable properties, including high etch rate and ability to obtain vertical walls, there are several disadvantages to dry etching, including the generation of ion-induced damage[2] and difficulty in obtaining smooth etched sidewalls, which are required for lasers.[3] Photoenhanced electrochemical (PEC) wet etching has also been demonstrated for etching of GaN,[4-7] but in most cases the surfaces created are very rough. Recently, a two-step process including crystallographic wet chemical etching has been demonstrated for n-type GaN.[8] This process involves one conventional etching step, such as dry etching, followed by a second, crystallographic wet etching step. The two-step process provides smooth surfaces and can be used to create undercut, overcut, or vertical sidewalls. However, this technique has not yet been demonstrated for p-type GaN; this publication reports on the first crystallographic wet etching of p-type GaN.

The first of the two etching steps in the crystallographic etching process is used to establish the etching depth, and it can be performed by several common processing methods, including dry etching, PEC etching, and cleaving. This first step is required because the *c* plane (0001) is impervious to all chemical agents that have been investigated,[9,10] except at defect sites where etch pits occur.[11,12] For all of the samples reported on here, cleaving has been used as our first step. The second step is done by immersion in a hot chemical etchant that is able to crystallographically etch GaN. This etching step can produce smooth crystallographic surfaces, and the resulting etching planes can be controlled by varying the orientation of the first step, the chemical agents, and the temperature.

The Mg-doped p-type GaN samples are grown by metallorganic vapor phase epitaxy on *c* plane sapphire substrates. The samples consist of a p-type GaN layer with a carrier concentration determined by Hall measurements to be 7×10^{16} cm^{-3}, grown on a 1 μm thick undoped, high resistivity layer on a 300 Å AlN buffer layer, for a total thickness of 2 to 2.5 μm. Etching is done in Pyrex beakers on a hot plate. The temperature is monitored using a thermocouple immersed next to the samples and is accurate to within 5°C.

Crystallographic etching is demonstrated in molten KOH, KOH dissolved in ethylene glycol, H_3PO_4, and tetraethylammonium hydroxide (TEAH). Etching occurs "horizontally," *i.e.*, normal to [0001]. The thickness of the GaN epi layers as measured with a scanning electron microscope (SEM), however, do not change. The etch rate in the "vertical" [0001] direction is therefore at least two orders of magnitude lower than the etch rate in the horizontal direction. Because the *c* plane is impervious to all of the chemicals used in this study, no etch mask is required for the crystallographic etching step. The *c* plane itself acts as a mask. An etch mask may be necessary, however, to prevent the development of etch pits at defect sites. For this purpose we have successfully used 60 nm thick nickel masks after annealing at 650°C for 2 min in a nitrogen atmosphere and titanium masks after annealing at 900°C for 30 s in a nitrogen atmosphere. The annealed nickel masks can be removed by etching in a 1:1:3 solution of HCl, HNO_3, and H_2O, and the annealed titanium masks can be removed by etching in buffered oxide etchant. No surface damage is observed after mask removal.

SEM images of the two etch planes observed after crystallographic wet etching of p-type GaN are shown in Fig. 1. Only the top portion of the epi layers is doped p-type; the lower 1 μm is undoped. The seamless morphology of the surfaces displayed in Fig. 1 indicates that the change in doping does not affect the etch plane or the etch rate. The most commonly observed etching planes formed by H_3PO_4, TEAH, and KOH dissolved in ethylene glycol, and in molten KOH under some conditions, are $\{10\bar{1}\bar{2}\}$, as shown in Fig. 1a. The $\{10\bar{1}0\}$ planes shown in Fig. 1b are also observed after etching in molten KOH.

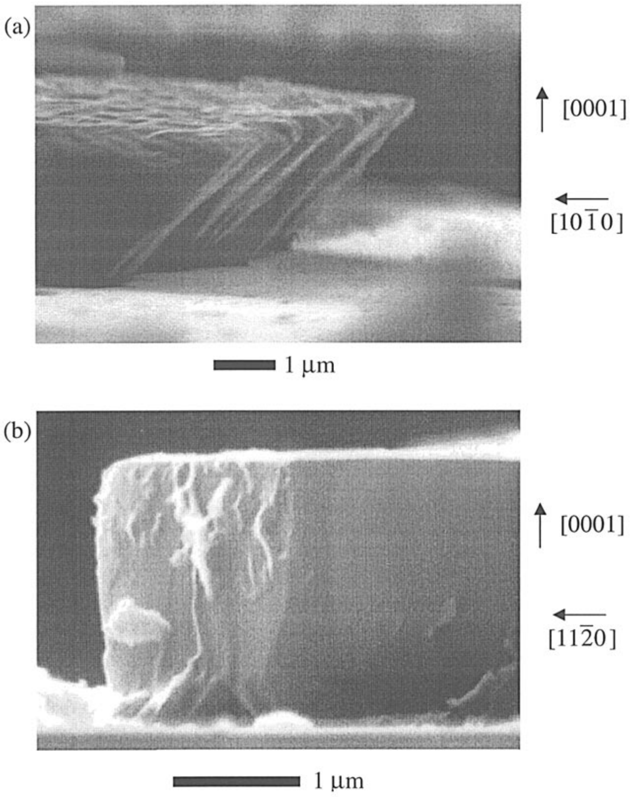

Figure 1. SEM images of crystallographic surfaces of GaN made by wet etching. (a) $\{10\bar{1}\bar{2}\}$ plane etched by molten KOH at 243°C. (b) $\{10\bar{1}0\}$ plane etched by molten KOH at 197°C.

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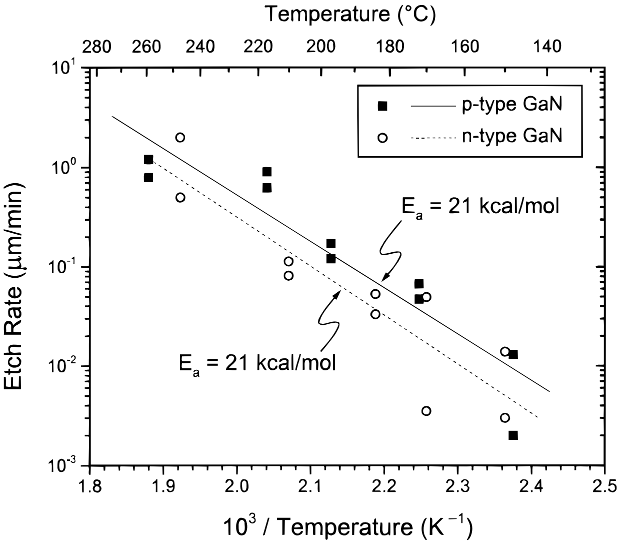

Figure 2. Arrhenius plot of n- and p-type GaN etch rates in molten KOH. The etch rates for the n-type GaN are taken from Ref. 8.

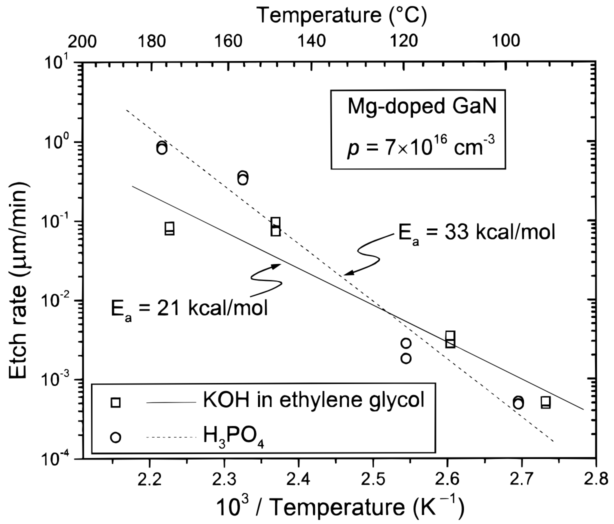

Figure 3. Arrhenius plot of p-type GaN etch rates in H_3PO_4 and in 30% KOH by weight dissolved in ethylene glycol.

Etch rates and activation energies in molten KOH for p-type GaN and for n-type GaN are nearly the same, as can be seen from the Arrhenius plots shown in Fig. 2. The activation energy observed in both samples is 21 kcal/mol, or 0.9 eV. In Fig. 2 and 3, two different etch rates are recorded for each sample at any given temperature. The faster etch rate is measured at the side of the wafer cleaved along the GaN {1120} *a* plane, and the slower rate is measured at the side of the wafer cleaved along the GaN {1010} *m* plane. As inferred from the Arrhenius plots in Fig. 3, the activation energy for the p-type GaN in 30% KOH in ethylene glycol is 21 kcal/mol, or 0.9 eV, and the activation energy in H_3PO_4 is 33 kcal/mol, or 1.3 eV. For all of the etchants used, the activation energy is equal to or slightly higher than the calculated heat of formation of GaN, 0.90 eV.[13] These high activation energies indicate that the etching is reaction-rate limited. If the etch rate were diffusion limited, an activation energy in the 16 kcal/mol range would be expected.[14]

It is interesting to note that the etch rate of KOH dissolved in ethylene glycol is higher than the etch rate of molten KOH at the same temperature, which can be seen by comparing Fig. 2 and 3. Originally it was thought that this could be due to high solubility of the etch products in ethylene glycol.[8] This is not likely, however, because the etch rate is not diffusion limited. Instead, the ethylene glycol seems to be playing an active role in the etching mechanism.

The suitability of aqueous TEAH for crystallographic etching was investigated. The etch rate of p-type GaN in aqueous TEAH is approximately 0.007 μm/min at 91°C. The TEAH solution is initially 40% aqueous, but becomes more concentrated as the etch progresses, due to evaporation. Difficulties arise when attempting a systematic study to determine the activation energy of etching in this solution due to the low etch rate near the boiling point of the solution.

The planes which are revealed by crystallographic etching are the slowest etching planes. For undercut planes, the etch rate is found by measuring the etch rate of the farthest protruding point; in Fig. 1a, this point is at the top of the epi layer. The originally vertical sidewalls are undercut by fast etching planes, which expose the slowest etching plane. Measuring the minimum distance etched, from the cleaved edge of the sapphire to the farthest protruding point of the GaN, and dividing by the etching time gives the etch rate of this plane. Measuring the distance from the cleaved edge of the sapphire to the deepest etched region, *e.g.*, the bottom of the epi layer in Fig. 1a, would give an etch rate higher than that of the exposed plane. The etch rates shown in Fig. 2 and 3 are measured perpendicular to the growth direction, *i.e.*, in the horizontal *c* plane. For vertical planes, such as the $\{10\bar{1}0\}$ plane, the actual etch rate normal to the plane is equal to the measured etch rate shown in Fig. 2 and 3. For nonvertical planes, however, the etch rate normal to the plane is less than the measured etch rate. The etch rate perpendicular to the $\{10\bar{1}\bar{2}\}$ plane, for instance, is the etch rate shown in Fig. 3 multiplied by cos(46°), because the $\{10\bar{1}\bar{2}\}$ plane intersects the vertical $\{10\bar{1}0\}$ plane at an angle of 46°.

In conclusion, a crystallographic wet chemical etching technique is able to etch p-type GaN at rates as high as 1.2 μm/min perpendicular to the growth direction. The activation energy of etching is 33 kcal/mol in H_3PO_4 and 21 kcal/mol in KOH and KOH dissolved in ethylene glycol. Etching was also achieved in tetraethylammonium hydroxide. The observed crystallographic GaN etch planes are (0001), $\{10\bar{1}0\}$, and $\{10\bar{1}\bar{2}\}$. Because the *c* plane of GaN is impervious to the etchants, no etch mask is required except to prevent the formation of etch pits at dislocations. When required, annealed nickel and annealed titanium are effective masks even at the highest temperatures employed in this study. The etch rates of p-type material are similar to those of the n-type material investigated previously. Undoped GaN/p-type GaN homojunctions etch seamlessly, and can form vertical sidewalls or undercut sidewalls, depending upon the chemistry used. The ability to etch smooth vertical sidewalls independent of conductivity type shows that crystallographic etching may be useful for fabricating facets for GaN-based laser diodes.

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