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Crystallographic wet chemical etching of GaN

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We demonstrate well-controlled crystallographic etching of wurtzite GaN grown on c-plane sapphire using H_3PO_4, molten KOH, KOH dissolved in ethylene glycol, and NaOH dissolved in ethylene glycol between 90 and 180 °C, with etch rates as high as 3.2 μm/min. The crystallographic GaN etch planes are $\{0001\}$, $\{10\bar{1}0\}$, $\{10\bar{1}\,\bar{1}\}$, $\{10\bar{1}\,\bar{2}\}$, and $\{10\bar{1}3\}$. The vertical $\{10\bar{1}0\}$ planes appear perfectly smooth when viewed with a field-effect scanning electron microscope. The activation energy is 21 kcal/mol, indicative of reaction-rate limited etching. © *1998 American Institute of Physics.* [S0003-6951(98)00741-4]

Most processing of the III nitrides is currently done by dry plasma etching.[1,2] There are several disadvantages to dry etching, including the generation of ion-induced damage[3] and difficulty in obtaining smooth etched sidewalls, which are required for lasers. The typical root-mean-square (rms) roughness of sidewalls produced by dry etching is on the order of 50 nm,[4,5] although recently surfaces with an rms roughness as low as 4–6 nm have been reported.[6] Photoenhanced electrochemical (PEC) wet etching has also been demonstrated for etching of gallium nitride (GaN).[7–10] PEC etching has the advantage of relatively low equipment cost and low surface damage, but a method for producing smooth vertical sidewalls has not yet been found. Cleaved facets for GaN have also been reported, with rms roughnesses varying between 16 nm for GaN grown on sapphire substrates[11] and 0.3 nm for GaN grown on spinel substrates.[12]

While KOH-based solutions have been found to etch AlN and InAlN, no acid or base solution has previously been identified that is able to etch high-quality GaN.[13] In this letter, we have used ethylene glycol, instead of water, as a solvent for KOH and NaOH so that we are able to employ temperatures between 90 and 180 °C. These temperatures exceed the boiling point of water and are considerably higher than the temperatures used in previous references.[13] By so doing, we have developed a two-step process that etches crystallographic surfaces into III nitrides. Our samples are 2-μm-thick n-type GaN epilayers grown on c-plane sapphire by metal-organic chemical vapor deposition (MOCVD), and the films have an x-ray diffraction rocking curve full width at half maximum of ~800 arcsec.[14]

Molten KOH and hot phosphoric acid (H_3PO_4) have previously been shown to etch pits at defect sites in the c plane of GaN.[15,16] Kozawa *et al.* reported that the facets of the pits correspond to the $\{30\bar{3}2\}$ face of GaN.[16] We have observed the formation of etch pits with facets that correspond to various GaN crystal faces by etching in H_3PO_4 above 160 °C, in molten KOH above 180 °C, in KOH dissolved in ethylene glycol above 135 °C, and in NaOH dissolved in ethylene glycol at 180 °C. All of the hexagonal etch pits share a common base, i.e., the $\langle 11\bar{2}0\rangle$ direction, but intersect the c plane at a wide variety of angles. This is because the faces are actually produced by two or more competing etch planes, as can be seen in the high-resolution field-effect scanning electron microscope (FESEM) image in Fig. 1. The etchant temperatures are monitored using a thermocouple, and are accurate to within 5 °C. The etch pit density is approximately 2×10^6 cm^{-2} in H_3PO_4 and 6×10^7 cm^{-2} in hydroxide-containing etchants.

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. For our first step we have used several different processing methods, including reactive ion etching in a chlorine-based plasma, PEC etching in a KOH solution, and cleaving. The second step is done by immersion in a chemical that is able to crystallographically etch GaN. This etching step can produce smooth crystallographic surfaces, and the specific etching planes can be chosen by varying the orientation of the first step, the chemical agents, and the temperature. The etch rates and crystal planes observed for all chemicals used in this work are summarized in Table I. The etching planes listed in this table are those that appear during the etch. Because the c plane $\{0001\}$ is impervious to all of these chemicals except at defect sites where etch pits occur, it is also an etch plane, with a negligibly small etch rate.

Figure 2 displays several illustrative examples of GaN epilayers that have been crystallographically etched after cleaving. Figures 2(a) and 2(b) show a sample etched in H_3PO_4 at 132 °C. The $\{10\bar{1}3\}$ plane shown in Fig. 2(a) ap-

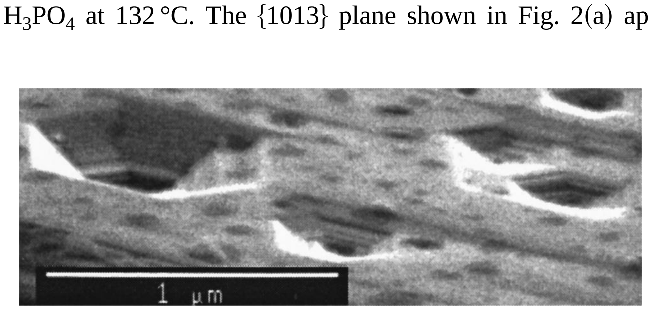

FIG. 1. High-resolution field-effect SEM image of dislocation etch pits in the c plane of GaN, produced by etching in 10% KOH by weight, dissolved in ethylene glycol at 165 °C.

TABLE I. Etch rates and observed etching planes for various chemicals.

Chemical	Temperature (°C)	Etch rate (μm/min)	Etching planes observed
Acetic acid (CH_3COOH)	30	<0.001	None
Hydrochloric acid (HCl)	50	<0.001	None
Nitric acid (HNO_3)	81	<0.001	None
Phosphoric acid (H_3PO_4)	108–195	0.013–3.2	$\{10\bar{1}2\},\{10\bar{1}3\}$
Sulphuric acid (H_2SO_4)	93	<0.001	None
Potassium hydroxide (KOH), molten	150–247	0.003–2.3	$\{10\bar{1}0\},\{10\bar{1}1\}$
50% KOH in H_2O	83	<0.001	None
10%–50% KOH in ethylene glycol (CH_2OHCH_2OH)	90–182	0.0015–1.3	$\{10\bar{1}0\}$
50% NaOH in H_2O	100	<0.001	None
20% NaOH in ethylene glycol	178	0.67–1.0	None

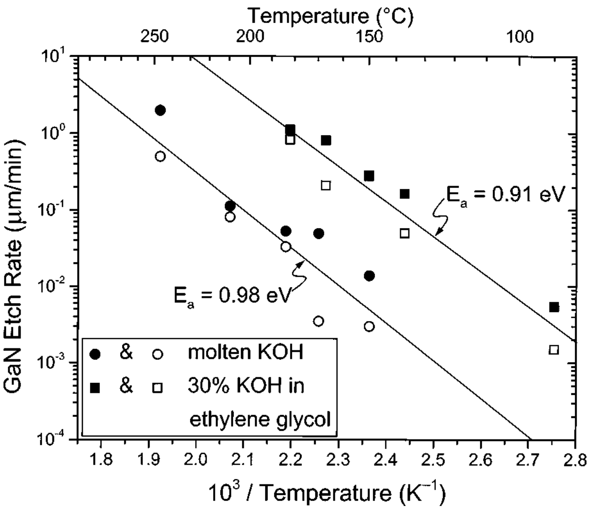

FIG. 3. Arrhenius plot of GaN etch rates in KOH and 30% KOH dissolved in ethylene glycol. Solid and hollow symbols represent etch rates measured along cleaved edges parallel to the $\{11\bar{2}0\}$ a plane and the $\{10\bar{1}0\}$ m plane, respectively.

pears along the side of the sample cleaved along the GaN a plane $\{11\bar{2}0\}$. The $\{10\bar{1}2\}$ plane shown in Fig. 2(b) appears along the side of the sample cleaved along the GaN m plane. The $\{10\bar{1}0\}$ plane shown in Fig. 2(c) was produced by etching in 10% KOH by weight dissolved in ethylene glycol at 165 °C. This plane has been examined using an FESEM with a resolution of 5 nm at 2.5 kV, and the surface appears perfectly smooth at this resolution. The $\{10\bar{1}\bar{1}\}$ plane shown in Fig. 2(d) was produced by etching in molten KOH at 184 °C.

The activation energies for etching in these various solutions is 0.9 eV, or 21 kcal/mol, as inferred from the Arrhenius plots in Figs. 3 and 4. Note that this is equal to the calculated heat of formation of GaN, 0.90 eV.[17] The activation energy indicates that the etch is reaction-rate limited. If the etching were diffusion limited, an activation energy in the 1–6 kcal/mol range would be expected.[18]

The etch rates shown in Figs. 3–5 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 of the plane is equal to the etch rate measured. For nonvertical planes, however, the etch rate of the plane is actually 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. 4 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°.

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. In fact, the etch rate as a function of concentration peaks at a value of 40% KOH by weight in ethylene glycol, as can be seen in Fig. 5. We believe that this is due to high solubility of the etch products in ethylene glycol.

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, if long etching times are used, to prevent the development of etch pits at defect sites. For this purpose we have successfully used titanium masks after annealing at 900 °C for 30 s.

In conclusion, a powerful anisotropic wet chemical etching technique is presented. Etch rates as high as 3 μm/min have been demonstrated. Because the etch is crystallographic in nature, we demonstrate smooth vertical sidewalls with an

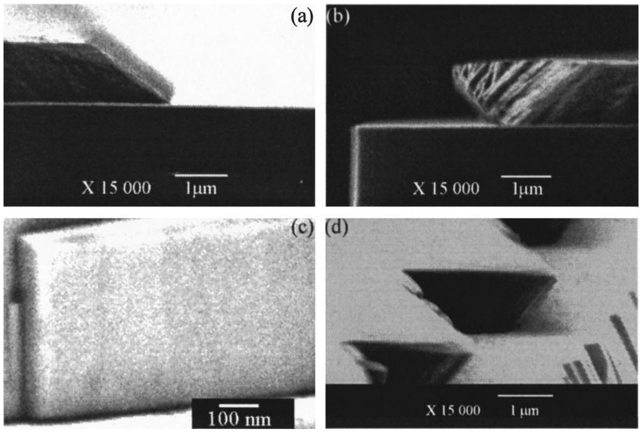

FIG. 2. SEM images of crystallographic surfaces of GaN made by wet etching. (a)$\{10\bar{1}3\}$ plane etched by H_3PO_4. (b) Undercut $\{10\bar{1}\bar{2}\}$ plane etched by H_3PO_4. (c) Vertical $\{10\bar{1}0\}$ plane etched by KOH in ethylene glycol. (d)Undercut $\{10\bar{1}\bar{1}\}$ plane etched by molten KOH.

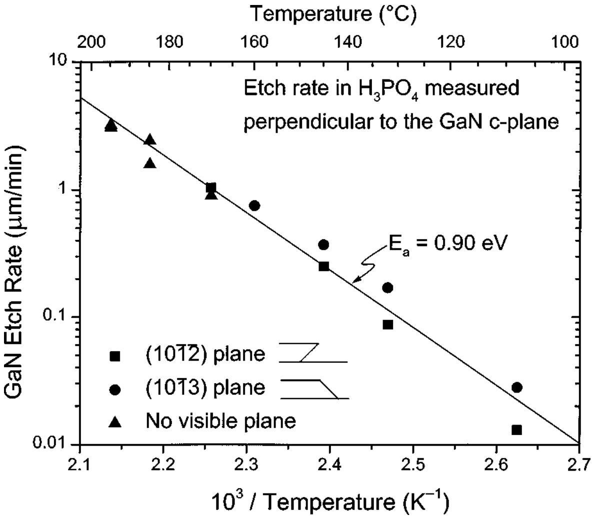

FIG. 4. Arrhenius plot of etch rates for GaN in H_3PO_4.

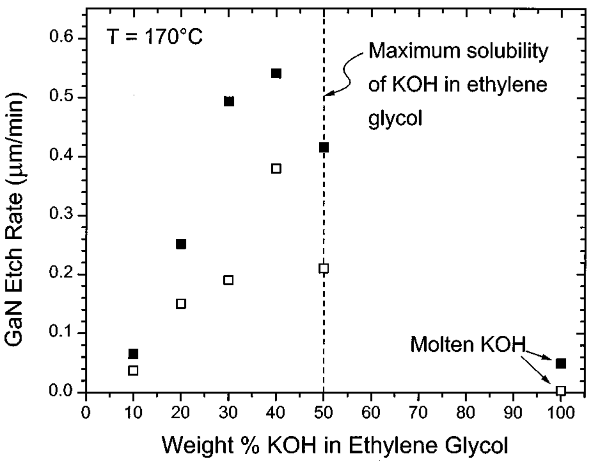

FIG. 5. GaN etch rate as a function of KOH concentration in ethylene glycol at 170 °C. Solid and hollow symbols represent etch rates measured along cleaved edges parallel to the $\{11\bar{2}0\}$ a plane and the $\{10\bar{1}0\}$ m plane, respectively.

RMS roughness smaller than the 5 nm resolution of the FESEM. This is the smallest reported roughness for etched GaN sidewalls, indicating the usefulness of this etch for high-reflectivity laser facets. The ability to undercut is also important for decreasing capacitance in applications such as bipolar transistors.

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