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## Selective Wet Etching of Lithium Gallate

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### ABSTRACT

Lithium gallate (LGO) is an attractive, near lattice matched substrate for the growth of GaN. In addition, LGO substrates provide a convenient route to forming thin films of GaN as used in substrate removal or lift-off processes. We report the wet etching of LGO substrates for the production of GaN thin films. Two face-selective LGO etches have been used for the processing of substrates. The etch rate of the cation face is reported here for the first time and is  $0.25 \mu\text{m min}^{-1}$  at  $50^\circ\text{C}$ . The etching solution is safe and benign to most materials including metallic bonding.

Extensive research on the group III nitride semiconductors is in progress, and efforts to date have produced the first light-emitting diodes (LEDs) and laser diodes in this material system.<sup>1,2</sup> Unfortunately, several material and device issues remain unresolved. One critical issue is the extreme difficulty in fabricating bulk, single crystals of GaN for use as substrates in the growth of epitaxial films. In place of GaN substrates, (0001)  $\text{Al}_2\text{O}_3$  substrates have been used extensively,<sup>3</sup> however, the 14% lattice mismatch with GaN produces defects and other problems. Growth on other substrates such as 6H SiC,<sup>4</sup>  $\text{MgAl}_2\text{O}_4$ ,<sup>5</sup>  $\text{LiGaO}_2$  (LGO),<sup>6</sup> ZnO,<sup>7</sup> GaAs,<sup>8</sup> and Si<sup>9</sup> is also being investigated. All these substrates, however, have logistical or growth related problems such as lattice mismatch, thermal expansion mismatch, expense, or cleaning difficulties. Lithium gallate (LGO) has by far the smallest lattice mismatch of the substrates mentioned above. The ability to chemically etch LGO for the cleaning of samples and the subsequent processing of GaN on LGO is of interest.<sup>10</sup> In addition to using LGO as the substrate, high quality single-crystal GaN substrates can be produced in thin-film form by bonding and lifting off epitaxially grown layers onto a second host substrate. Thus, the ability to etch substrates rapidly under relatively benign conditions is important.

In this article, a face-selective etch for LGO is demonstrated, and a new method for producing single-crystal GaN substrates is proposed in which the substrate is removed from the GaN epi layer. Because of the small lattice mismatch (0.19% along the *a* axis) of LGO to GaN, LGO was chosen as the initial growth substrate. However, even this small lattice mismatch is undesirable. After GaN growth on LGO, the LGO substrate is chemically removed from the thin epitaxial GaN film. The GaN is bonded to a

mechanical host that provides structural stability during the subsequent regrowth process,<sup>11</sup> and the bonded GaN epi layer then serves as the regrowth substrate. A similar substrate removal process has been applied successfully to the fabrication of GaAs and InP thin film substrates.<sup>12</sup> In those processes, selective and/or stop-etch layers were used to separate the growth substrate from the epi layers, with subsequent selective etching to produce the thin-film substrate. Since GaN is chemically inert to most wet etches, it serves as its own stop-etch layer. We focus here on a simple wet chemical etch used to remove the LGO substrate from the thin epitaxial GaN film with extremely high selectivity.

A previous LGO etching study characterized etch rates of the anion LGO face in several acids.<sup>10</sup> In that study, LGO etched rapidly in HCl and HF, although HF produced a considerably rougher surface than HCl. The disadvantage in using acidic etch solutions is the chemical attack on other materials including the metallic layers used in the epi layer bonding process. The advantages of having two-face selective etches are the ability to identify the LGO crystal face and the ability to clean and process either face of the crystal.

Crystal Photonics double-side polished LGO wafers ( $1 \text{ cm}^2$ ) were sawed into  $10 \times 1 \text{ mm}$  pieces for the etching study, which was done on both the anion and cation faces of the crystal. Half of each LGO piece was masked in wax to protect it from the etching solution. This wax also served to bond the LGO pieces to glass slides for easy immersion in the etching solutions. Three buffered solutions were made, one each at pH 7.2, 9.2, and 12.0. The buffer solutions at 7.2 and 12.0 were 0.01 N phosphate solutions, and the buffer solution at 9.2 was 0.01 N borate. The pH of the 7.2 phosphate buffer solution was increased using appropriate amounts of dilute tribasic potassium phosphate solution to yield solutions of pH 8.0 and 8.5. The pH of the 12.0 phosphate buffer solution was

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decreased using appropriate amounts of dilute phosphoric acid solution to yield solutions of pH 10.0 and 11.0.

LGO samples were suspended in the etching solutions which were positioned on a magnetic stirrer/hot plate. Etches were done at pH values of 7.2, 8.0, 8.5, 9.2, 10, 11.0, and 12.0 at a constant temperature of 50°C. The etch rate was measured at 25, 35, 50, 60, 70, and 80°C for a constant pH of 9.2. Because the pH of the borate buffer solution decreased with increasing temperature, it was necessary to add small amounts of 0.01 M NaOH to maintain the constant pH of 9.2. The solutions were slowly stirred during the etch, and each etch was performed for five minutes at which point the samples were rinsed with copious amounts of deionized H<sub>2</sub>O. On completion of the etch, the wax was removed and the etch depths were quantified using a Tencor profilometer.

When viewed under an optical microscope at 750 times magnification, the etched surfaces appeared featureless. A typical profilometer scan is shown in Fig. 1. Several LGO surfaces became heavily pitted during the etch, and although the reason for the pits is unclear at this point, it is likely that defects in the LGO are responsible. As a demonstration, experiments were performed at regions of the LGO substrate known to have a high density of defects. For example, LGO samples were masked across an LGO antiphase domain region. The etch rate at the edge of the antiphase domain was approximately four times larger than the etch rate for the same crystal in the higher quality regions, making it likely that the defects have a dominant effect on the etch rate. The ability of this etch to highlight defects in the crystal structure could be potentially useful in characterizing the material quality.

A plot of etch rate vs. pH for both the cation and anion terminated crystal faces of LGO is shown in Fig. 2. The etch rates for the cation face are larger than those for the anion face, making this etch useful for the determination of the LGO crystal face polarity. Tazoh et al. have found that a 1:1 HNO<sub>3</sub>:H<sub>2</sub>O etch preferentially attacked LGO on the anion terminated face of the crystal, speculating that the electrophilic nature of the acid caused it to attack the oxygen face with its lone pairs of electrons.<sup>13</sup> However, the actual

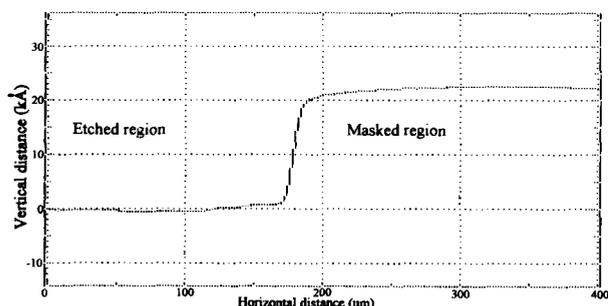


Fig. 1. Profilometer scan of LGO etched at 50°C and pH 9.2.

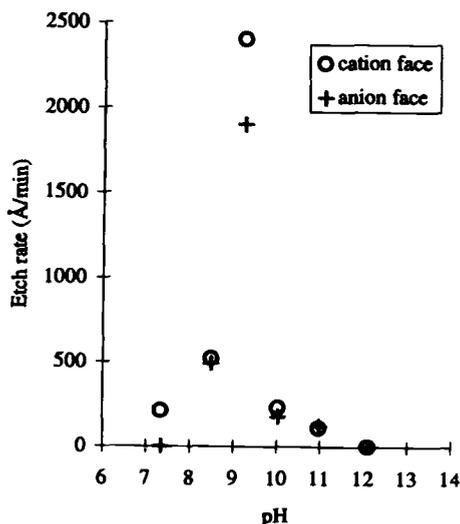


Fig. 2. Etch rate of LGO as a function of pH at a constant temperature of 50°C.

etch rates were not reported; only the etch depth was reported.<sup>13</sup> We replicated their experiment and measured an LGO etch rate of 16 kÅ min<sup>-1</sup> on the anion face and 2.5 kÅ min<sup>-1</sup> on the cation face. Thus it follows that at higher pH values, the solution preferentially etches the cation terminated face of the LGO crystal.

The mechanism for LGO etching is different from that of many other substrates. Typically, the substrate (e.g., silicon, gallium arsenide, etc.) undergoes an oxidation-dissolution mechanism. That is, the substrate is first oxidized followed by dissolution of the reaction products. The etching solution provides both the oxidant and complexing medium. For LGO etching, the substrate is already in the oxidized form, so only dissolution occurs. The dissolution of oxide salts can be kinetically slow, particularly if the ions undergo a change in the structure of the complex.

For LGO, the etch rates shown in Fig. 2 follow the same trend as the GaO<sub>2</sub><sup>-</sup> solubility which is plotted in Fig. 3. The solubility of the gallate ion was calculated at room temperature from equilibrium data.<sup>14</sup> Gallate ions are most soluble in the pH range 7.6–10.2, based on the chemical equilibria between the GaO<sub>2</sub><sup>-</sup>, GaO<sup>+</sup>, and HGaO<sub>3</sub><sup>2-</sup>. The two equilibria are shown in Eq. 1–3



$$pK_1 = \log \left( \frac{[\text{GaO}^+]}{[\text{GaO}_2^-][\text{H}^+]^2} \right) = 15.3 \quad [2]$$

$$pK_2 = \log \left( \frac{[\text{GaO}_2^-]}{[\text{H}^+][\text{HGaO}_3^{2-}]} \right) = 10.27 \quad [3]$$

The sharper slope in etch rate for pH values between 7.0 and 9.2 as compared to the etch rate slope for pH values from 9.2 to 11.0 can be seen in both Fig. 2 and 3, supporting the dissolution dependent mechanism of the etch. The experimentally determined etch rates in Fig. 2 show a large spike in the etch rate at pH 9.2 whereas the theoretical solubility does not. The reason for this discrepancy is being investigated currently.

The etch rate was also a function of temperature. Generally, the solubility of salts in aqueous solution increases as temperature increases. An expression for the solubility of salts in aqueous solution is given by Eq. 4 with the assumption that the moles of solute are much less than the moles of solvent. Etch rates at pH 9.2 as a function of temperature are shown in Fig. 4. A smaller than expected increase in the experimental etch rates was observed, indicating that an increase in mass transport of the solution may help

$$s_A = \frac{M_{APs}}{M_s} \exp \left[ -\frac{\Delta_f H^\circ}{R} \left( \frac{1}{T} - \frac{1}{T_{m,A}} \right) \right] \quad [4]$$

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical compositions of the etched LGO surfaces as well as an unetched (control) sample of LGO. The composition of the samples etched at pH values less than 12.0 were the same stoichiometry as the unetched control, whereas the lithium content of the

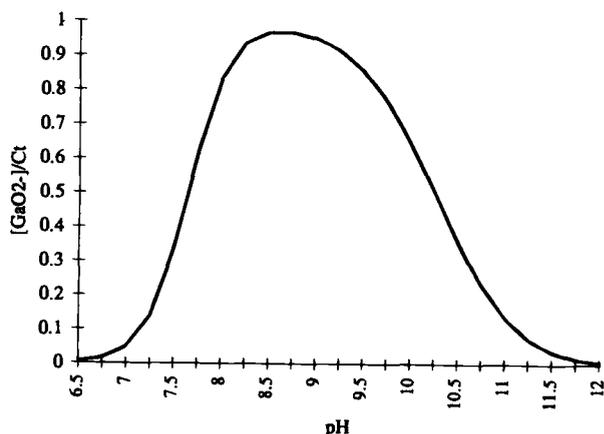


Fig. 3. Solubility diagram for the gallate anion in aqueous solution. Concentrations are presented as a fraction of the total amount of gallium (III) species in solution.

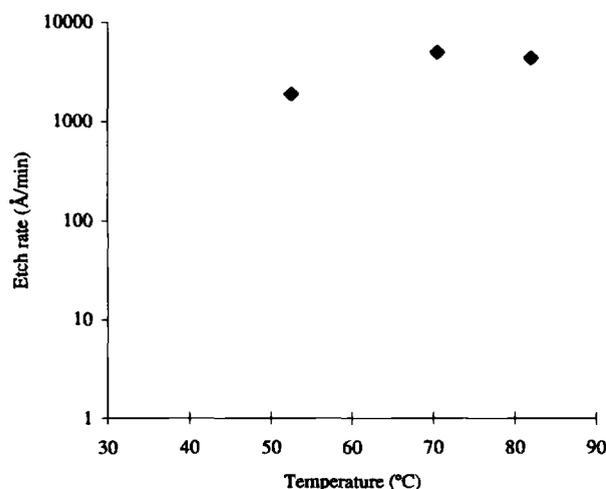


Fig. 4. Etch rate of the cation face of the LGO crystal as a function of temperature at a constant pH of 9.2.

sample etched at pH 12.0 was significantly higher. The theoretical atomic ratios of LGO are 1:1:2 for Li:Ga:O, and were measured by XPS to be 1:3.4:5.2 for the control sample. The low sensitivity of Li causes its signal to appear anomalously low. The ratio of Ga:O is 1:1.5, close to the expected ratio of 1:2. The samples etched at pH values less than 12.0 had an average atomic ratio of 1:2.8:4.7, equivalent to the control sample within experimental error. The sample etched at pH 12.0 had an atomic ratio of 1:1.3:2.1, significantly different from any of the other samples. The increased lithium content of this piece is most likely due to lithium hydroxide precipitation on the sample surface.

Using the knowledge gained in the LGO etching study detailed above, we proceeded to demonstrate the substrate removal process. An 8000 Å thick film of GaN was grown on an LGO substrate by molecular beam epitaxy (MBE) in a Riber 3200 MBE machine. Activated nitrogen was supplied by an Oxford Applied Research Cars 25 rf nitrogen plasma source operated at 600 W forward power. After growth, the substrate was removed and the GaN film was rebonded to a GaAs host wafer. The rebonded thin-film GaN had smooth morphology and was free of cracks, making this a promising technique for the realization of a thin-film GaN substrate for the homoepitaxial growth of GaN. The size of the rebonded GaN sample was 1 × 3 mm, and work is being done currently to increase this size to 1 × 1 cm. Further details of the process and device will be published elsewhere.

In summary, the benign wet etching of the cation face of LGO substrates has been demonstrated at mildly basic pH. The etch mechanism is most likely the dissolution of the substrate, corresponding to the solubility of the gallate ion at pH values ~9.2. Advantages of this etch are that it does not attack metallic layers which may be used to bond GaN thin-film substrates to mechanical host layers, and it is useful in determining crystal face polarity. When used in conjunction with the anion face etches,<sup>10,13</sup> many processes as well as definite LGO crystal face identification are possible. Finally, a thin GaN film was removed from an LGO substrate and successfully rebonded to a GaAs host wafer.

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## LIST OF SYMBOLS

$s_A$	solute solubility (g mL <sup>-1</sup> )
$M_A$	solute molecular weight (g mol <sup>-1</sup> )
$M_s$	solvent molecular weight (g mol <sup>-1</sup> )
$\rho_s$	solvent density (g mL <sup>-1</sup> )
$\Delta_f H^\circ$	solute enthalpy of fusion (kJ mol <sup>-1</sup> K <sup>-1</sup> )
$R$	universal gas constant (kJ mol <sup>-1</sup> K <sup>-1</sup> )
$T$	temperature (K)
$T_{m,A}$	solute melting temperature (K)

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