

## Anisotropic pattern transfer in GaN by photo-enhanced wet etching

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Anisotropic pattern transfer in GaN (undoped and n-type) has been performed by UV photo-enhanced wet etching in KOH, NaOH and AZ400K solutions and a comparison of these electrolytic solutions is presented. The etch mechanism was found to be diffusion-limited ( $E_a < 6 \text{ kCal}\cdot\text{mol}^{-1}$ ) under all conditions whose other characteristics were a square-root dependence of etch rate on time, the production of relatively rough surfaces with a strong dependence of rate on solution agitation, whilst significantly faster etch rates were obtained with bias applied to the sample during light exposure.

**Key words:** Photo-enhanced wet etching, GaN, UV illumination, etch mechanism, electrolytic solutions, diffusion-limited.

### Introduction

To date relatively little success has been achieved with wet chemical etching of GaN with solutions at room temperature [1]. Molten KOH and elevated temperature  $\text{H}_3\text{PO}_4$  can produce etch pits on GaN [2, 3]. Recently hot solutions (90-180°C) of KOH or NaOH in ethylene glycol and KOH or  $\text{H}_3\text{PO}_4$  at similar temperatures have been used to produce well-defined crystallographic etching of wurtzite GaN after initial formation of mesas by dry etching [4]. If the GaN near-surface region has been damaged by processes such as dry etching or high temperature annealing,  $\text{H}_3\text{PO}_4$ , NaOH or KOH solutions have been found to remove the  $\text{N}_2$ -deficient material and stop at the underlying undamaged GaN [5]. Both AlN [6, 7] and InN [8] can be etched in hot alkaline solutions of NaOH or KOH, but there has been little success with the alloy InGaN [9].

It has long been recognized that the dissolution rate of semiconductor materials may be enhanced in acid or base solutions by illumination with light whose wavelength is above the bandgap [10-14]. The basic mechanism for their photo-enhanced etching is oxidative dissociation of the semiconductor into its component elements (thereby consuming the photo-generated holes) and the subsequent reduction of the oxidizing agent in the solution by reaction with the photo-generated electrons. In most cases, n-type material is readily etched, by contrast to p-type samples where the inability to

confine photo-generated holes at the semiconductor electrolyte interface prevents etching. The first photo-enhanced wet etching of GaN at room temperature was reported using  $\text{HCl}/\text{H}_2\text{O}$  and  $\text{KOH}/\text{H}_2\text{O}$  solutions with He-Cd laser illumination [15]. Subsequently the Adesida group and others [16-24] employed broad-area Hg lamps and solutions of KOH, aqueous  $\text{H}_3\text{PO}_4$  or tartaric acid/ethylene glycol to achieve maximum room-temperature etch rates typically in the range 100-200 nm  $\text{minute}^{-1}$ . In some cases the etched surfaces are smooth, but a more general result is the appearance of a very rough microstructure. The etch mechanism appears to be the creation of  $\text{Ga}_2\text{O}_3$  on the GaN surface, and its subsequent dissolution by the acid or base solution.

In this paper we compare KOH, NaOH and AZ400K (a photoresist developer effective in etching AlN because it contains KOH) solutions for photo-enhanced wet etching of undoped and  $\text{n}^+$  GaN either with or without biasing of the samples. We find, in general, that the etch rates increase sharply when the samples are biased during UV lamp exposure. We also examined photo-enhanced wet etching of thin film InN. Since this material is degenerately doped n-type ( $>5 \times 10^{20} \text{ cm}^{-3}$ ) due to the presence of residual shallow donors (possibly nitrogen vacancies), it appears that we are unable to create enough photo-generated carriers to enhance the oxidative dissociation of the InN and no etching was observed in any of our experiments.

### Experimental

The GaN layers were  $\sim 2 \mu\text{m}$  thick and were grown on  $\text{Al}_2\text{O}_3$  substrates at 1040°C by Metal Organic Chemical Vapor Deposition. Both  $\text{n}^+$  ( $\text{n} \sim 3 \times 10^{18} \text{ cm}^{-3}$ ) and unintentionally doped ( $\text{n} \sim 3 \times 10^{16} \text{ cm}^{-3}$ ) layers

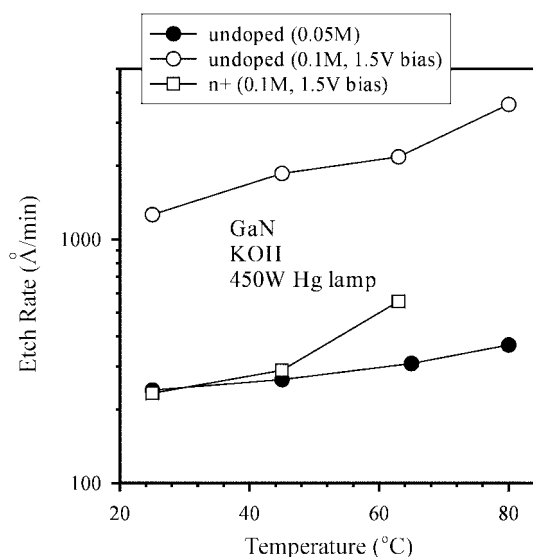
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were used in these experiments. InN layers  $\sim 1 \mu\text{m}$  thick were grown on  $\text{Al}_2\text{O}_3$  at  $\sim 650^\circ\text{C}$  by Metal Organic Molecular Beam Epitaxy. These films were degenerately n-type ( $\sim 10^{20} \text{ cm}^{-3}$ ) due to residual defects or impurities. Ti metal contacts were patterned by lift-off on the periphery of the samples, and etching performed in a standard electrochemical cell consisting of a teflon sample holder and a Pt wire cathode [2-6, 9-14]. An unfiltered 450 W Hg arc lamp  $\sim 15 \text{ cm}$  from the sample provided illumination of the samples, which were immersed in unstirred KOH, NaOH or  $\text{H}_2\text{O}/\text{AZ400K}$  solutions. Etch depths were measured by stylus profilometry, while the surface morphology was examined by both scanning electron microscopy (SEM) and tapping mode atomic force microscopy (AFM).

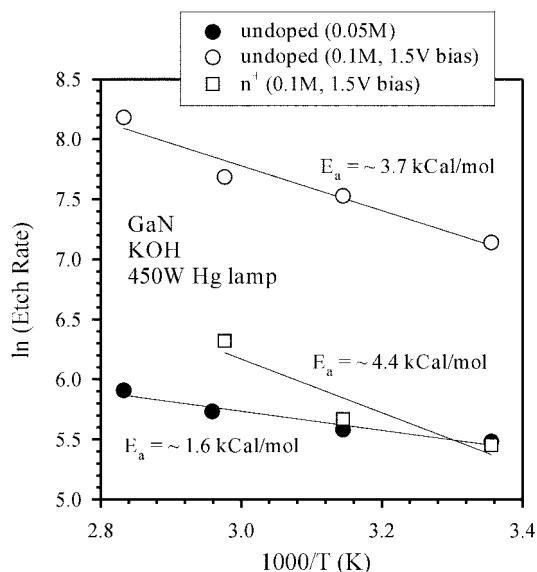
## Results and Discussion

Figure 1 shows the temperature dependence of the GaN etch rate in KOH solutions either with or without bias and at two different molarities. From separate experiments we determined that molarity had little effect on etch rate in this range, and thus that biasing and doping level in the GaN were the key parameters. This is consistent with past data on SiC [10]. The  $\text{n}^+$  GaN did not etch at all over a broad range of KOH concentrations (0.005–1 M) when no Ti metal contact was present on the sample, probably due to the inability to separate electron-hole pairs under these conditions.

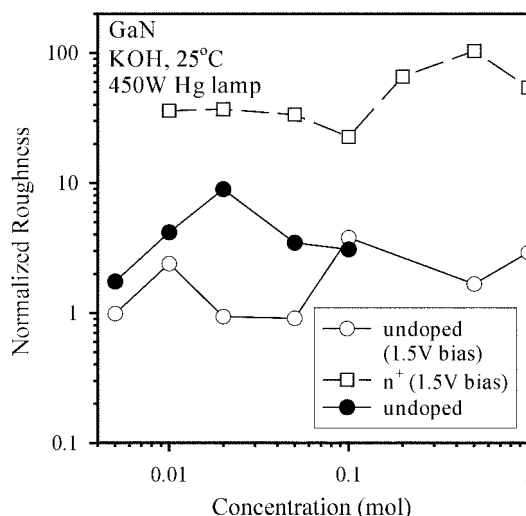
The data is plotted in Arrhenius form in Fig. 2. In all cases the activation energies are  $< 6 \text{ kcal}\cdot\text{mol}^{-1}$ , consistent with diffusion-limited etching whose other characteristics are a square-root dependence of etch rate on time, the production of relatively rough surfaces



**Fig. 1.** Temperature dependence of GaN etch rate either with or without 1.5 V bias in different molarity (0.05 or 0.1 M) KOH solutions.



**Fig. 2.** Arrhenius plot of GaN etch rate either with or without 1.5 V bias in different molarity (0.05 or 0.1 M) KOH solutions.

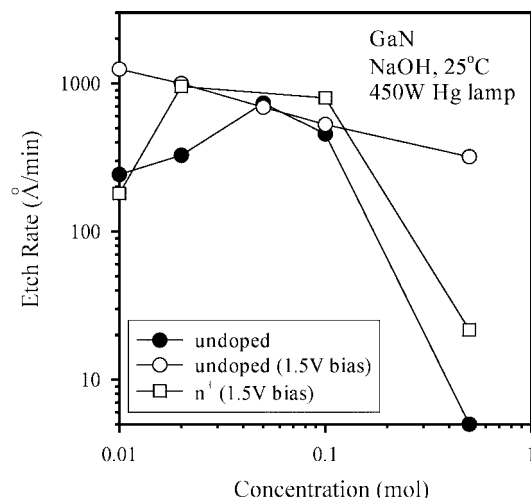


**Fig. 3.** Normalized surface roughness (control has a value of 1) of etched undoped or  $\text{n}^+$  GaN in KOH solutions at  $25^\circ\text{C}$  as a function of solution molarity.

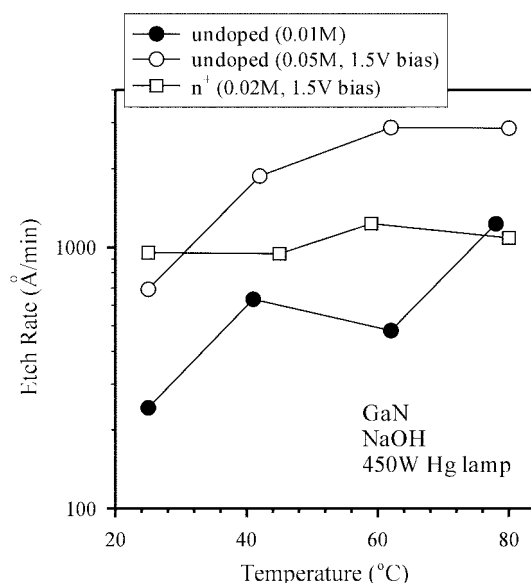
and a strong dependence of rate on solution agitation. This is consistent with the results of Youtsey *et al.* [16–18, 20].

There was also a strong dependence of etched surface morphology on doping level and presence of bias, as shown in Fig. 3. Note that in the case of the biased undoped GaN, the etched surface morphology measured by AFM is fairly similar to that of the unetched material. The role of the biasing may be to provide more efficient separation of the photo-generated carriers with a resultant improvement in uniformity of the surface oxidation reactions.

Little previous work has been performed with NaOH as the electrolyte. Figure 4 shows the influence of solution molarity on the PEC etch rates of undoped and



**Fig. 4.** Etch rate of undoped or  $n^+$  GaN either with or without 1.5 V bias in NaOH solutions at 25°C as a function of solution molarity.

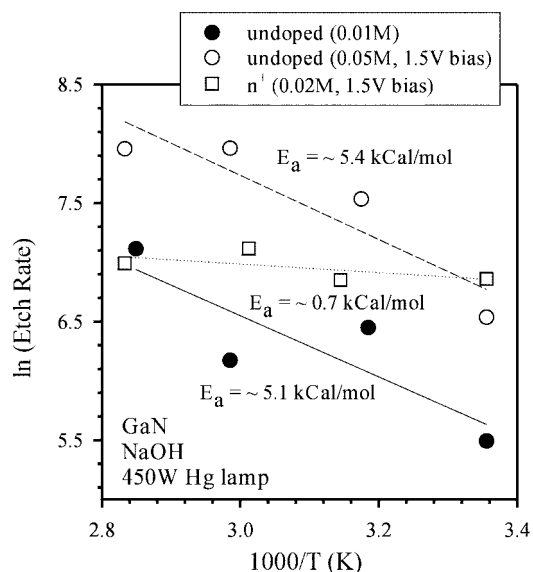


**Fig. 5.** Temperature dependence of GaN etch rate either with or without 1.5 V bias in different molarity (0.05 or 0.1 M) NaOH solutions.

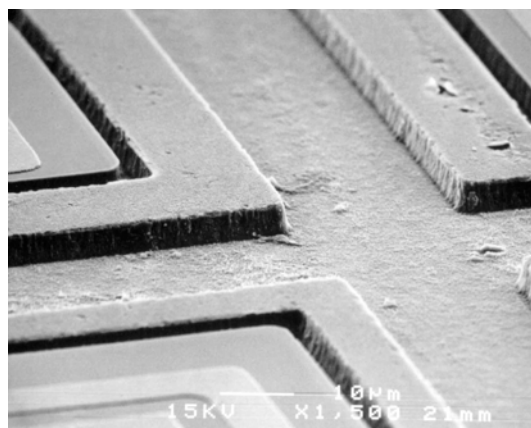
$n^+$  GaN at 25°C. The rates fall-off dramatically at high molarities ( $\geq 0.1$  M), most likely due to excessive oxidation of the surface. This effect is also seen with KOH solutions under the same conditions [21-23].

The temperature dependence of GaN etch rates in NaOH solutions is shown in Fig. 5. The application of a bias again strongly enhances the etch rates, but the temperature of the solution has little effect on  $n^+$  material. Replotting this data in Arrhenius form (Fig. 6) again shows the etching is diffusion-limited, as with KOH. Even the surface resulting from the etching is rough, quite anisotropic features can be transferred. Figure 7 shows an SEM micrograph of a sample where the entire GaN layer was etched.

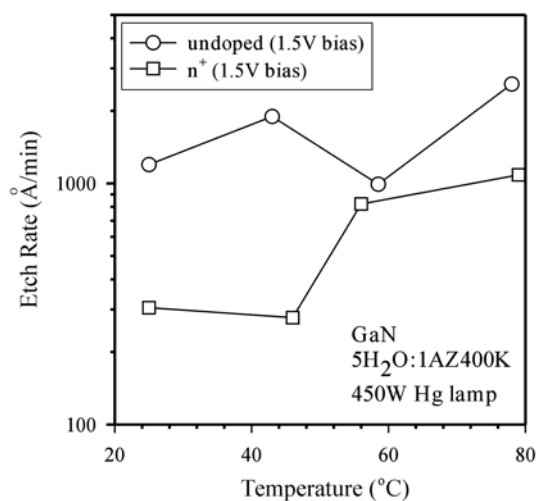
The AZ400K developer solution is a particularly convenient one since it is so commonly used in



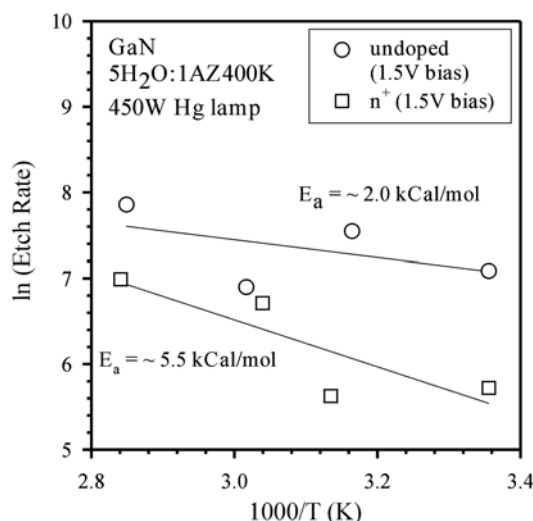
**Fig. 6.** Arrhenius plot of GaN etch rate either with or without 1.5 V bias in different molarity (0.05 or 0.1 M) KOH solutions.



**Fig. 7.** SEM micrograph of features etched into GaN with 1.5 V bias using a Ti mask and 0.02 M NaOH solution.



**Fig. 8.** Temperature dependence of GaN etch rate either with or without 1.5 V bias in  $H_2O$ :AZ400K solutions.



**Fig. 9.** Arrhenius plot of GaN etch rate either with or without 1.5 V bias in  $\text{H}_2\text{O}:\text{AZ400K}$  solutions.

lithography. We found that a  $5\text{H}_2\text{O}:\text{1AZ400K}$  mixture provided similar etch rates to KOH or NaOH solutions with low (0.01–0.1 M) molarities, as shown in Figure 8 for both undoped and  $\text{n}^+$  GaN. There was no discernible difference between the surface morphologies with KOH, NaOH and AZ400K. The etching is again diffusion-limited with the last solution as shown in the Arrhenius data of Fig. 9. Auger Electron Spectroscopy of etched surfaces generally showed that the average Ga-to-N ratio in the top 10 nm of the surface remained similar to that of the unetched control samples.

## Summary and Conclusions

The etch rate of GaN under photo-enhanced wet etching conditions in KOH, NaOH and AZ400K solutions is found to be a strong function of solution molarity, sample bias and material doping level. At high illumination intensities, etch rates for unintentionally doped ( $n \sim 3 \times 10^{16} \text{ cm}^{-3}$ ) GaN are  $\geq 100 \text{ nm minute}^{-1}$ . The etching is diffusion-limited under our conditions with an activation energy of  $< 6 \text{ kcal} \cdot \text{mol}^{-1}$ . The etched surfaces are rough, but retain their stoichiometry. The dopant-selectivity capability may be particularly useful in applications such as base mesa etching in heterojunction bipolar transistors, where exposure of a thin  $\text{p}^+$  base layer is necessary in order to make an ohmic contact.

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