

## UV-PHOTOASSISTED ETCHING OF GaN IN KOH

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### ABSTRACT

The etch rate of GaN under UV-assisted photoelectrochemical conditions in KOH solutions is found to be a strong function of illumination intensity, solution molarity, sample bias and material doping level. At low e-h pair generation rates, grain boundaries are selectively etched, while at higher illumination intensities etch rates for unintentionally doped ( $n \sim 3 \times 10^{16} \text{ cm}^{-3}$ ) GaN are  $\geq 1000 \text{ \AA} \cdot \text{min}^{-1}$ . The etching is diffusion-limited under our conditions with an activation energy of  $\sim 0.8 \text{ kCal} \cdot \text{mol}^{-1}$ . The etched surfaces are rough, but retain their stoichiometry.

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## INTRODUCTION

The dissolution rate of semiconductors may be altered in acid or base solutions by illumination with above bandgap light.<sup>(1-8)</sup> The mechanism for photo-enhanced etching involves the creation of e-h pairs, the subsequent oxidative dissociation of the semiconductor into its component elements (a reaction that consumes the photo-generated holes) and the reduction of the oxidizing agent in the solution by reaction with the photo-generated electrons. Generally, n-type material is readily etched under these conditions, while p-type material is not due to the requirement for confining photo-generated holes at the semiconductor-electrolyte interface.

Minsky et. al.<sup>(9)</sup> reported the first photo-enhanced wet etching of n-GaN at room temperature in HCl/H<sub>2</sub>O and KOH/H<sub>2</sub>O solutions. A He-Cd laser with typical energy density  $\sim 0.6\text{W}\cdot\text{cm}^{-2}$  was employed to create e-h pairs, and rates up to a few thousand angstroms per minute were obtained. Youtsey et. al.<sup>(10-14)</sup> employed a broad-area Hg lamp and KOH solutions to demonstrate dopant-selective photo-enhanced wet etching of n-GaN. Ti metal contacts provided electrical contact to the GaN, while a Pt wire was used as the system cathode. Smooth etching was achieved under high light intensity, low KOH concentration conditions. Strong evidence was found that the dislocation microstructure could be revealed by selective etching of material between dislocations.<sup>(14)</sup> Lu et. al.<sup>(15)</sup> reported photo-assisted anodic etching of n-GaN in tartaric acid/ethylene glycol solutions at room temperature, with rates up to  $1600\text{\AA}\cdot\text{min}^{-1}$ . Peng et. al.<sup>(16)</sup> were able to use aqueous H<sub>3</sub>PO<sub>4</sub> and KOH solutions with UV illumination to etch GaN. The etch rates were strongly dependent on the pH value of the solutions, peaking at  $\sim 1000\text{-}1200\text{\AA}\cdot\text{min}^{-1}$ <sup>1</sup> for pH of 1 for H<sub>3</sub>PO<sub>4</sub> and 14 for KOH. The photoelectrochemical process was found to

create  $\text{Ga}_2\text{O}_3$  on the GaN surface, that was subsequently dissolved by the acid or base solution. Pulsed electrochemical etching with  $\text{H}_3\text{PO}_4$ /ethylene glycol/ $\text{H}_2\text{O}$  solutions was found to etch both p-GaN and the InGaN active region in light-emitting diode structures, providing a simple and controlled method of exposing the underlying n-GaN for contacting.<sup>(17)</sup>

Conventional wet etching without photo- or current-enhancement has proven relatively ineffective for GaN.<sup>(18)</sup> Molten KOH and elevated temperature  $\text{H}_3\text{PO}_4$  has been reported to produce etch pits on GaN<sup>(19,20)</sup>, and Stocker et. al.<sup>(21)</sup> have used similar solutions in glycol at typical temperatures of  $\sim 180^\circ\text{C}$  to produce well-defined crystallographic etching of wurtzite GaN. Kim et. al.<sup>(22)</sup> found that  $\text{H}_3\text{PO}_4$ , NaOH and KOH solutions at these temperatures are useful for removing  $\text{N}_2$ -deficient surface layers on GaN induced by processes such as high temperature annealing or dry etching. After removal of this damaged material, selective etching began to reveal etch pits.

In this paper we report on some of the characteristics of photo-assisted etching of GaN in KOH solutions, as a function of UV illumination intensity, KOH concentration and solution temperature. The etch rates increase strongly when the samples are biased during light exposure. No etching of degenerately-doped InN ( $n \sim 10^{20}\text{cm}^{-3}$ ) was obtained under our conditions.

## EXPERIMENTAL

GaN layers  $\sim 2\mu\text{m}$  thick were grown on  $\text{Al}_2\text{O}_3$  substrates at  $1040^\circ\text{C}$  by Metal Organic Chemical Vapor Deposition. Both  $n^+$  ( $n \sim 3 \times 10^{18}\text{cm}^{-3}$ ) and unintentionally doped ( $n \sim 3 \times 10^{16}\text{cm}^{-3}$ ) layers 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 are 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.<sup>(2-6,9-14)</sup> An unfiltered 450W Hg arc lamp  $\sim 15\text{cm}$  from the sample provided illumination of the samples, which were immersed in unstirred KOH 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). The near-surface stoichiometry was examined by Auger Electron Spectroscopy (AES).

## RESULTS AND DISCUSSION

For low Hg lamp powers ( $\leq 100\text{W}$ ), we did not observe any macroscopic etching of the GaN (or InN), but there was selective etching at grain boundaries to reveal the hexagonal nature of the GaN (Figure 1). This would be expected since the defective regions should contain a higher density of dangling or weakened atomic bonds that are more readily attacked by the KOH than the lower defect density material in between grains.

At higher lamp powers significant etch rates were obtained for both types of GaN used, as shown in Figure 2. As the KOH solution molarity increases, the etch rates of both n and  $\text{n}^+$  GaN increase, and then saturate before decreasing at the highest molarities. The higher lamp power clearly provides sufficient photo-generated electron-hole pairs to promote the oxidation-reduction reaction necessary at the GaN surface. Higher etch rates

were obtained when the sample was biased, consistent with past data on SiC.<sup>(5)</sup> The n<sup>+</sup> GaN did not etch at all over a broad range of KOH concentrations (0.005-1M) when no Ti metal contact was present on the sample, probably due to the inability to separate e-h pairs under these conditions. Similarly, InN was also not etched in these experiments, possibly as a result of the high intrinsic electron concentration in the material. It is difficult to create enough extrinsic carriers to promote the dissociative oxidation of this material. The roll-off of etch rate at high KOH solution molarity in Figure 2 is probably due to excessive oxide formation on the surface.<sup>(16)</sup>

The temperature dependence of n-GaN etch rate in 0.05M KOH solutions without applied bias is shown at the top of Figure 3. As expected, the GaN dissolution occurs faster at elevated temperatures. As Arrhenius plot of the data (bottom of Figure 3) reveals an activation energy of  $\sim 0.8\text{ kCal}\cdot\text{mol}^{-1}$ . This is typical of diffusion-limited etching, whose other characteristics are a square-root dependence of etch rate on time, relatively rough surfaces and a strong dependence of rate on solution agitation. This is consistent with the results of Youtsey et. al.<sup>(11)</sup>

AFM scans of the etched n-GaN surface morphology are shown in Figure 4. The etched surfaces are rougher than those of the control sample under all the conditions we examined. This is fairly typical of photo-enhanced etching of semiconductors, and only Youtsey et. al. have reported a small window of conditions where good morphologies for GaN were achieved.<sup>(12)</sup> Figure 5 shows the root-mean-square surface roughness measured by AFM and normalized to that of the control sample, as a function of KOH solution molarity. The best surfaces were obtained at either low or high molarities.

Some typical features formed in  $n^+$  GaN using a 0.01M KOH solution at 25°C (450W of Hg lamp power) are shown in the SEM micrographs of Figure 6. The rough morphologies are typical of those reported previously for GaN<sup>(11,13,15,16)</sup> and SiC<sup>(6)</sup>, and probably represent the micro-crystallites in the material.<sup>(14)</sup> We believe the PEC process is useful only in particular device fabrication steps where morphology will not be an issue. These would include mesa isolation of electronic devices, selective removal of n-type GaN from an underlying p-GaN layer (such as in revealing the base region of a heterojunction bipolar transistor) or in shallow etch situations, such as removal of dry etch damage.

AES surface scans of an unetched GaN control sample (top) and one etched at 25°C in a 0.01M KOH solution (bottom) are shown in Figure 7. The Ga-to-N ratios are approximately the same, indicating that Ga and N are removed at essentially the same rate during the PEC process. Notable is the fact that there is more oxygen detected on the etched sample, consistent with the expected etch mechanism.

## SUMMARY AND CONCLUSIONS

PEC etching is found to selectively reveal grain boundaries in GaN under low light illumination conditions. At high lamp powers the rates increase with sample temperature and the application of bias to the PEC cell, while they go through a maximum with KOH solution molarity. The etching is diffusion-limited, producing rough surface morphologies that are suitable in a limited number of device fabrication steps. The surfaces however appear to remain relatively close to their stoichiometric composition.

## ACKNOWLEDGMENTS

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## References

1. J. van de Ven and H.J.P. Nabben, *J. Electrochem. Soc.* 137 1603 (1990).
2. M.N. Ruberto, X. Zhang, R. Scarmozzino, A.E. Willner, D.V. Podlesnik, and R.M. Osgood, Jr., *J. Electrochem. Soc.* 138 1174 (1991).
3. R. Khare and E.L. Hu, *J. Electrochem. Soc.* 138 1516 (1991).
4. J.S. Shor, R.M. Osgood and A.D. Kurtz, *Appl. Phys. Lett.* (1992).
5. J.S. Shor, X.G. Zhang and R.M. Osgood, *J. Electrochem. Soc.* 139 (1992).
6. J.S. Shor and R.M. Osgood, Jr., *J. Electrochem. Soc.* 140 (1993).
7. F.W. Ostermayer and P.A. Kohl, *Appl. Phys. Lett.* 39 76 (1981).
8. M.J. Grove, D.A. Hudson, P.S. Zory, R.J. Dalby, C.M. Harding and A. Rosenberg, *J. Appl. Phys.* 76 587 (1994).
9. M.S. Minsky, M. White and E.L. Hu, *Appl. Phys. Lett.* 68 1531 (1996).
10. C. Youtsey, I. Adesida and G. Bulman, *Electron. Lett.* 33 245 (1997).
11. C. Youtsey, I. Adesida and G. Bulman, *Appl. Phys. Lett.* 71 2151 (1997).
12. C. Youtsey, I. Adesida, L.T. Romano and G. Bulman, *Appl. Phys. Lett.* 72 560 (1998).
13. C. Youtsey, G. Bulman and I. Adesida, *J. Electron. Mater.* 27 282 (1998).
14. C. Youtsey, L.T. Romano and I. Adesida, *Appl. Phys. Lett.* 73 797 (1998).
15. H. Lu, Z. Wu and I. Bhat, *J. Electrochem. Soc.* 144 L8 (1997).
16. L.-H. Peng, C.-W. Chuang, J.-K. Ho, C.N. Huang and C.-Y. Chen, *Appl. Phys. Lett.* 72 939 (1998).
17. J. O, P.S. Zory and D.P. Bour, *SPIE Proc.* 3002 117 (1997).

18. C.B. Vartuli, S.J. Pearton, C.R. Abernathy, J.D. MacKenzie, F. Ren, J.C. Zolper and R.J. Shul, *Solid-State Electron.* 41 1944 (1997).
19. A. Shintani and S. Minagawa, *J. Electrochem. Soc.* 123 707 (1976).
20. T. Kozawa, T. Kachi, T. Ohwaki, Y. Tager, N. Koide and M. Koike, *J. Electrochem. Soc.* 143 L17 (1996).
21. D.A. Stocker, E.F. Schubert and J.M. Redwing, *Appl. Phys. Lett.* (in press).
22. B.J. Kim, J.W. Lee, H.S. Park, Y. Park and T.I. Kim, *J. Electron. Mater.* 27 L32 (1998).

## Figure Captions

Figure 1. Optical micrographs of GaN surfaces after PEC etching at low illumination powers, magnification  $\times 50$  (top) and  $\times 1000$  (bottom).

Figure 2. Etch rate of  $n^+$  and non-intentionally-doped (NID) GaN, either with or without 1.5V bias, in KOH solutions at 25°C as a function of solution molarity.

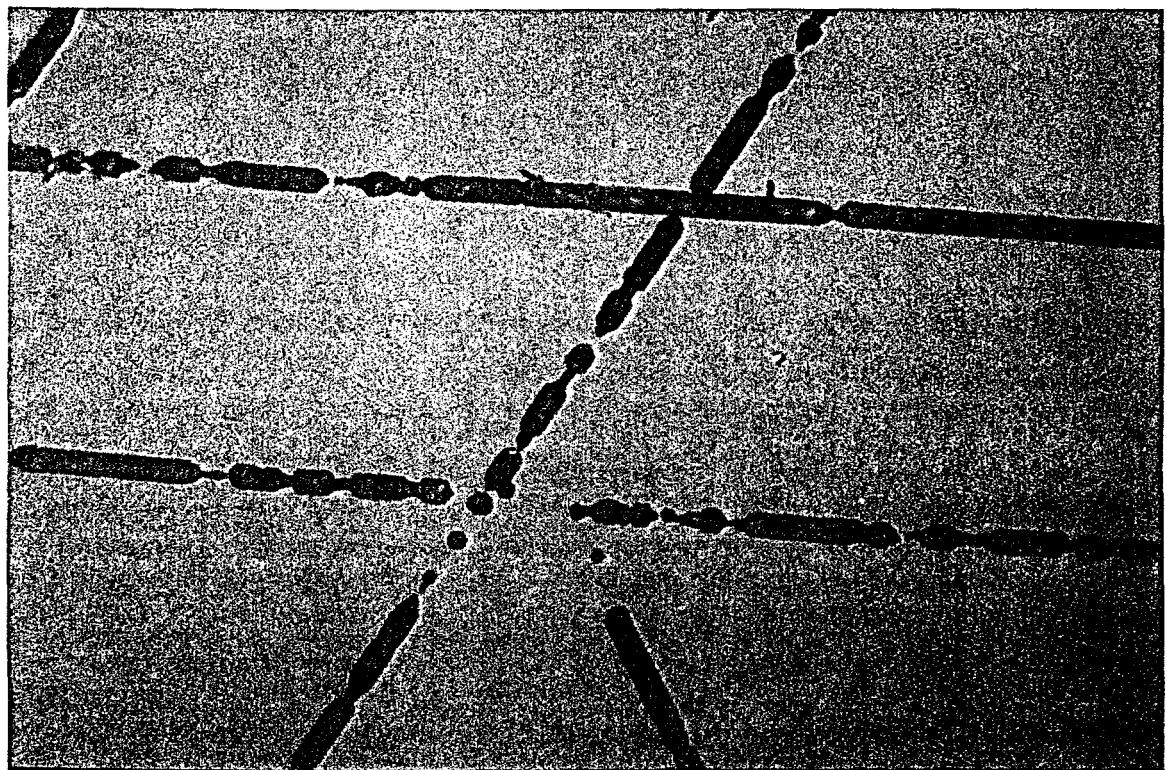
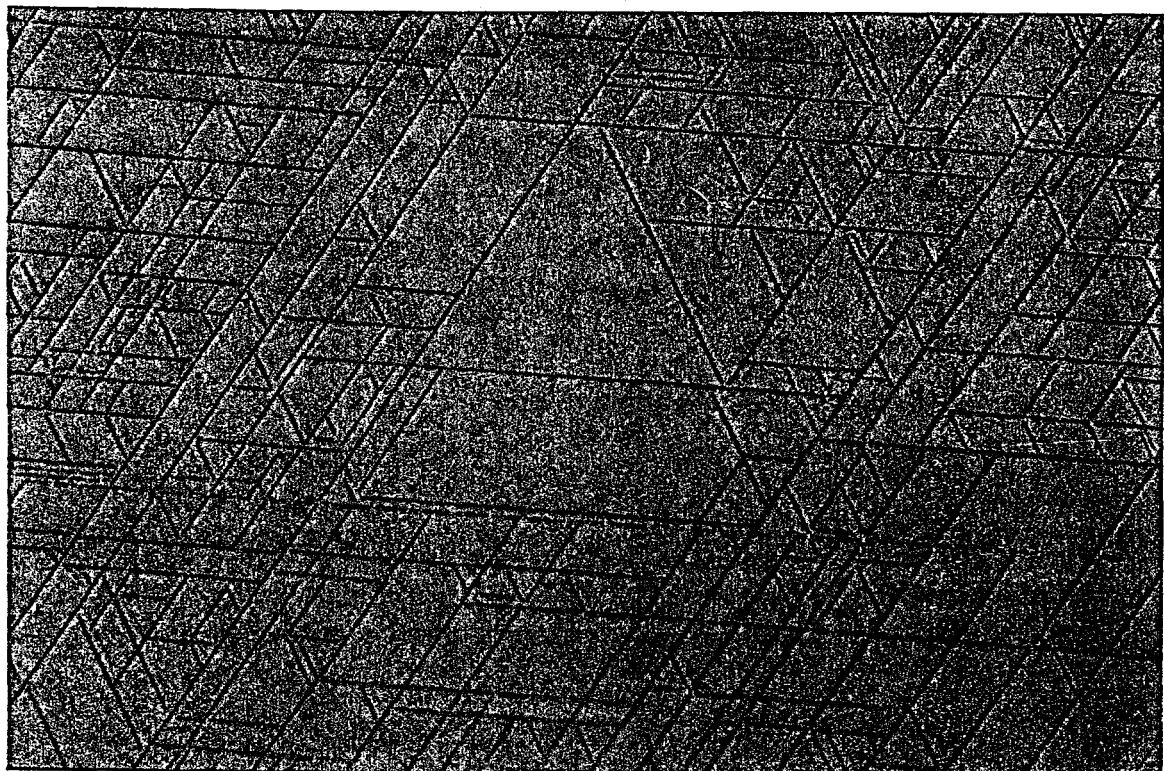
Figure 3. Temperature dependence (top) and Arrhenius plot (bottom) of GaN PEC etch rate in 0.05M KOH solutions without biasing of the sample.

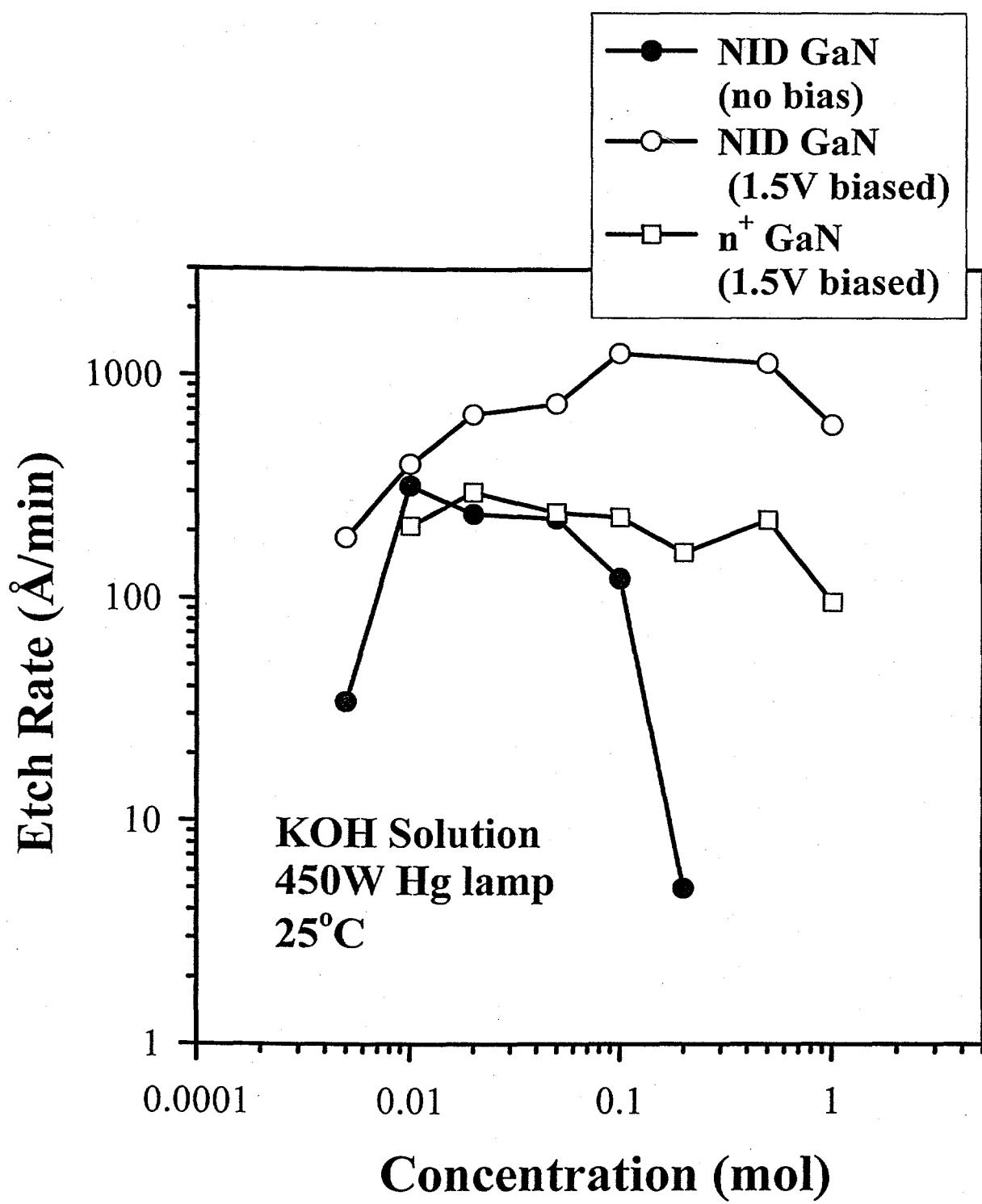
Figure 4. AFM scans of GaN before and after PEC etching without bias in KOH solutions of different molarities.

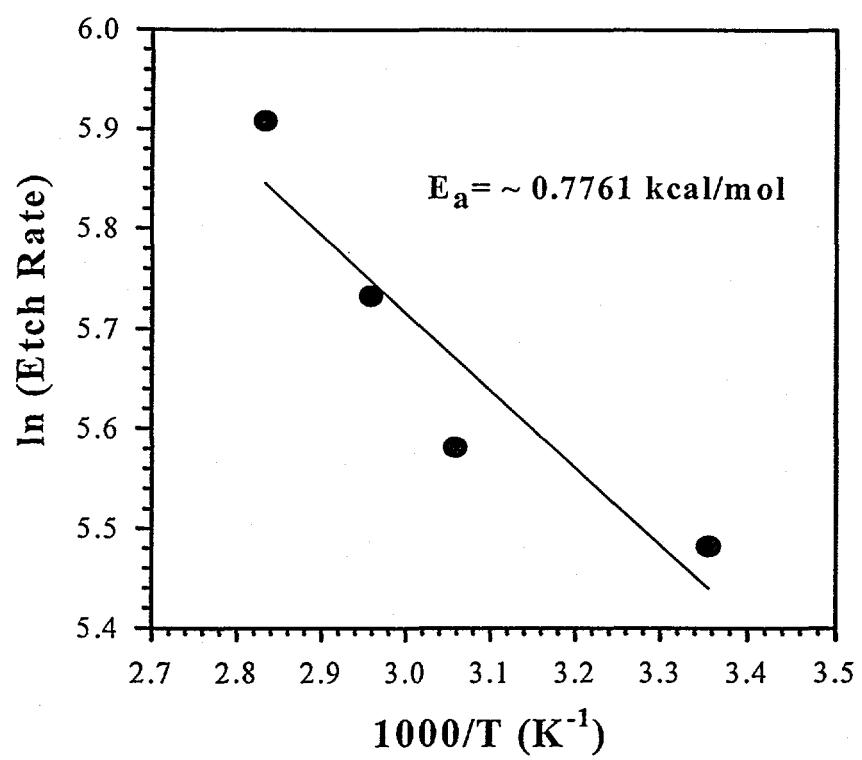
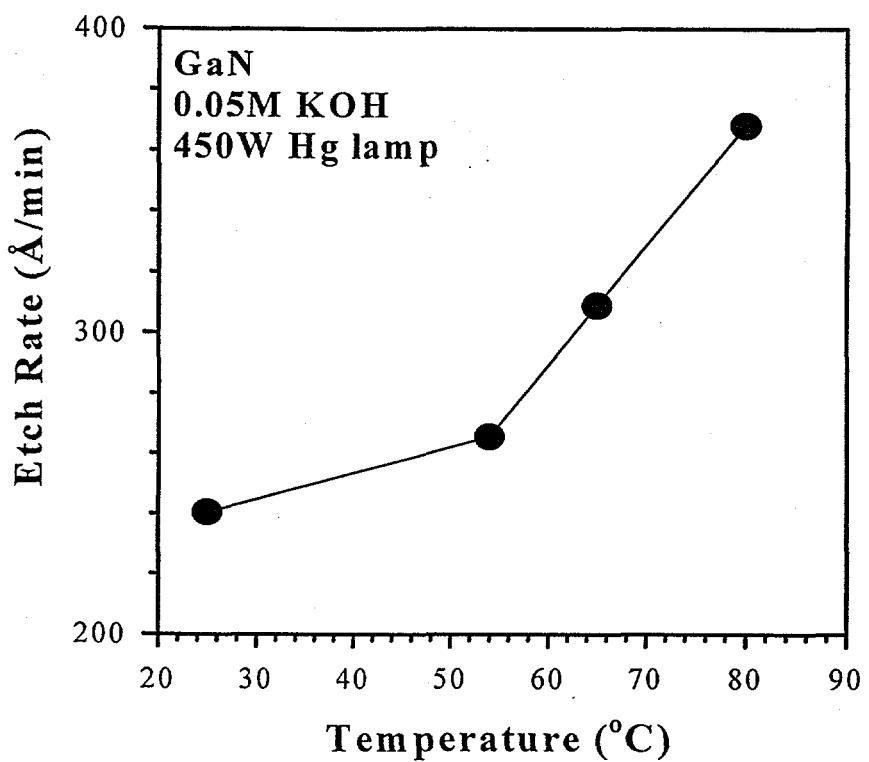
Figure 5. Normalized surface roughness (control sample has a value of 1) of PEC etched GaN as a function of KOH solution molarity.

Figure 6. Features etched into  $n^+$  GaN using 0.01M KOH solution at 25°C.

Figure 7. AES surface scans of GaN before (top) and after PEC etching in 0.01M KOH solution at 25°C.







**GaN**  
**450W Hg lamp, 25°C**

