PHOTOELECTROCHEMICAL ETCHING OF $In_xGa_{1-x}N$

Hyun Cho[1], S.M. Donovan[1], C.R. Abernathy[1], S.J. Pearton[1], F. Ren[2], J. Han[3] and R.J. Shul[3]

[1] Department of Materials Science and Engineering, University of Florida, Gainesville FL 32611
[2] Department of Chemical Engineering, University of Florida, Gainesville FL 32611
[3] Sandia National Laboratories, Albuquerque NM 87185

Abstract

A comparison of KOH, NaOH and AZ400K solutions for UV photo-assisted etching of undoped and n^+ GaN is discussed. The etching is diffusion-limited ($E_a < 6 kCal \cdot mol^{-1}$) under all conditions and is significantly faster with bias applied to the sample during light exposure. No etching of InN was observed, due to the very high n-type background doping ($> 10^{20} cm^{-3}$) in the material.

Introduction

To date relatively little success has been achieved with wet chemical etching of GaN with room temperature solutions [1]. Molten KOH and elevated temperature H_3PO_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 H_3PO_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, H_3PO_4, NaOH or KOH solutions have been found to remove the 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 above bandgap light [10-14]. The basic mechanism for their photo-enhanced etching is oxidative dissociation of the semiconductor into its component elements (thereby consuming the photogenerated holes) and the subsequent reduction of the oxidizing agent in the solution by reaction with the photogenerated electrons. In most cases, n-type material is readily etched, in contrast to p-type samples where the inability to confine photogenerated holes at the semiconductor electrolyte interface prevents etching. The first photoenhanced wet etching of GaN at room temperature was reported using HCl/H_2O and KOH/H_2O 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 H_3PO_4 or tartaric acid/ethylene glycol to achieve maximum room-temperature etch rates typically in the range 1000-2000Å·min^{-1}. In some cases the etched surfaces are smooth, but a more general result is the appearance of very rough microstructure. The etch mechanism appears to be creation of Ga_2O_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 photoelectrochemical (PEC) etching of undoped and 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 PEC etching of thin film InN. Since this material is degenerately doped n-type (> 5×10^{20}cm^{-3}) due to the presence of residual shallow donors (possibly nitrogen vacancies), it appears that we are unable to create enough photogenerated carriers to enhance the oxidative dissociation of the InN and no etching was observed in any of our experiments.

Experimental

The GaN layers were ~ 2μm thick and were grown on Al$_2$O$_3$ substrates at 1040ºC by Metal Organic Chemical Vapor Deposition. Both n$^+$ (n ~ 3×10^{18}cm^{-3}) and unintentionally doped (n ~ 3×10^{16}cm^{-3}) layers were used in these experiments. InN layers ~ 1μm thick were grown on Al$_2$O$_3$ at ~ 650°C by Metal Organic Molecular Beam Epitaxy. These films are degenerately n-type (~ 10^{20}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 450W Hg arc lamp ~ 15cm from the sample provided illumination of the samples, which were immersed in unstirred KOH, NaOH or H$_2$O/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 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 n$^+$ 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.
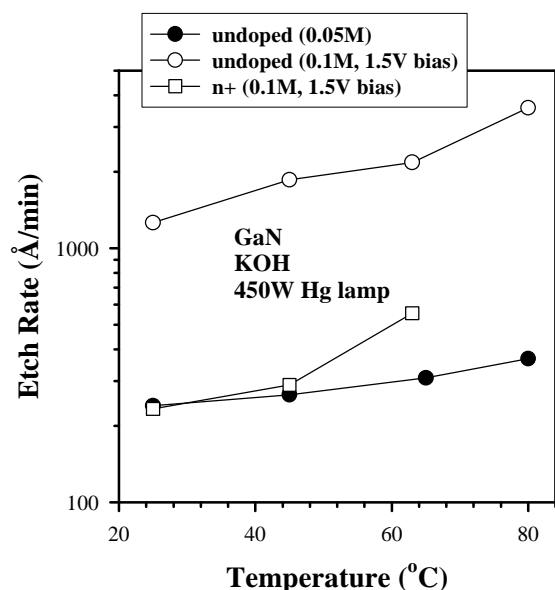

Figure 1. Temperature dependence of GaN PEC etch rate either with or without 1.5V bias in different molarity (0.05 or 0.1M) KOH solutions.
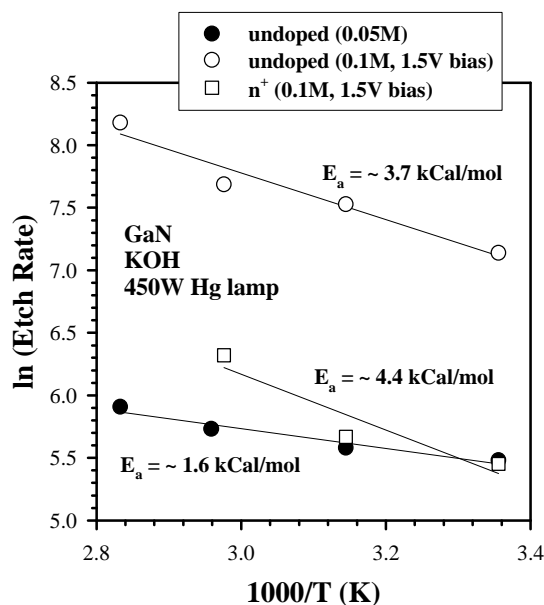
Figure 2. Arrhenius plot of GaN PEC etch rate either with or without 1.5V bias in different molarity (0.05 or 0.1M) KOH solutions.

The data is plotted in Arrhenius form in Figure 2. In all cases the activation energies are < 6kCal·mol^{-1}, consistent with 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. [16-18, 20]

There was also a strong dependence of etched surface morphology on doping level and presence of bias, as shown in Figure 3. Note that in the case of 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 photogenerated carriers with a resultant improvement in uniformity of the surface oxidation reactions.

Little 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 n$^+$ GaN at 25ºC. The rates fall-off dramatically at high molarities ($\geq$ 0.1M), most likely due to excessive oxidation of the surface. This effect is also seen with KOH solutions under the same conditions [21-23].
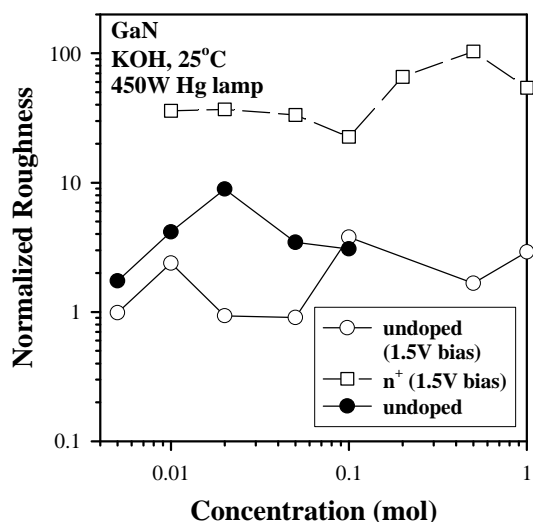
Figure 3. Normalized surface roughness (control has a value of 1) of PEC etched undoped or n$^+$ GaN in KOH solutions at 25ºC as a function of solution molarity.
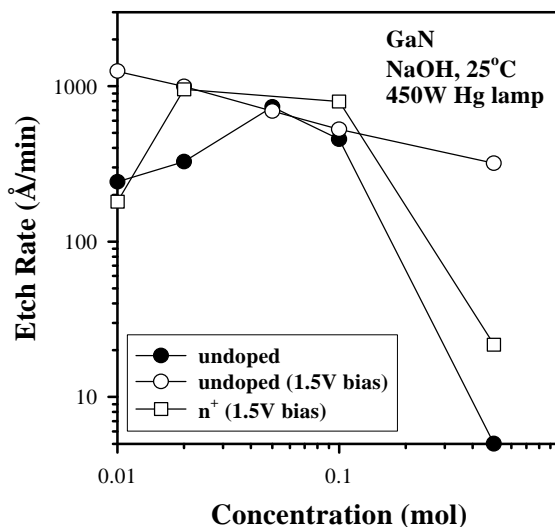
Figure 4. Etch rate of undoped or n$^+$ GaN either with or without 1.5V bias in NaOH solutions at 25ºC as a function of solution molarity.

The temperature dependence of PEC etch rates in NaOH solutions is shown in Figure 5. The application of 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 (Figure 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 a 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 lithography. We found that a 5H$_2$O:1AZ400K mixture provided similar PEC etch rates to KOH or NaOH solutions with low (0.01-0.1M) molarities, as shown in Figure 8 for both undoped and n$^+$ GaN. There was no discernible difference between the surface morphologies with KOH, NaOH and AZ400K. The etching is again diffusion-limited with latter solution as shown in the Arrhenius data of Figure 9. Auger Electron Spectroscopy of etched surfaces generally showed that the average Ga-to-N ratio in the top 100Å of the surface remained similar to that of unetched control samples.
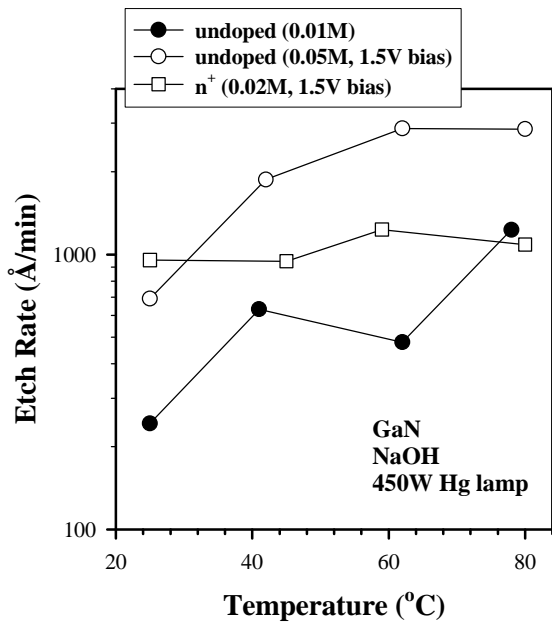
Figure 5. Temperature dependence of GaN PEC etch rate either with or without 1.5V bias in different molarity (0.05 or 0.1M) NaOH solutions.
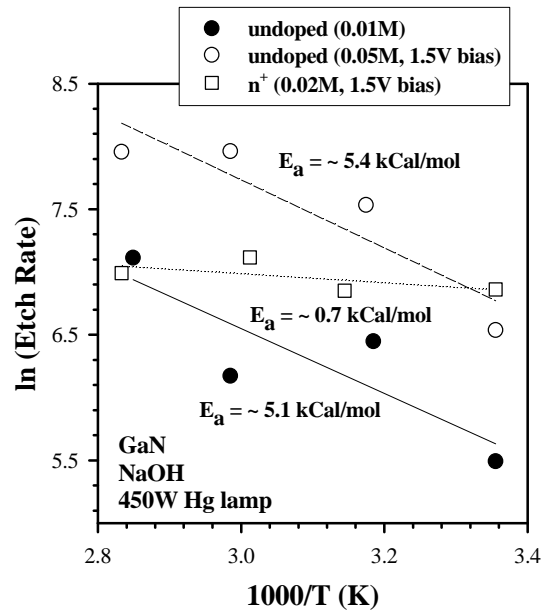

Figure 6. Arrhenius plot of GaN PEC etch rate either with or without 1.5V bias in different molarity (0.05 or 0.1M) KOH solutions.
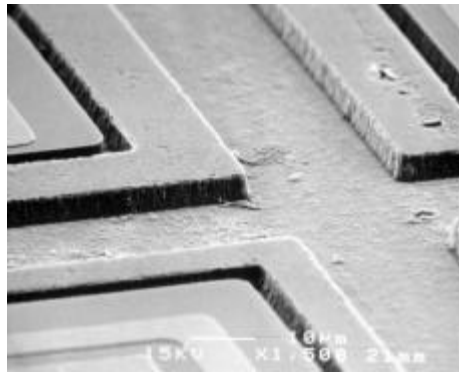

Figure 7. SEM micrograph of features etched into GaN with 1.5V bias using a Ti mask and 0.02M NaOH solution.
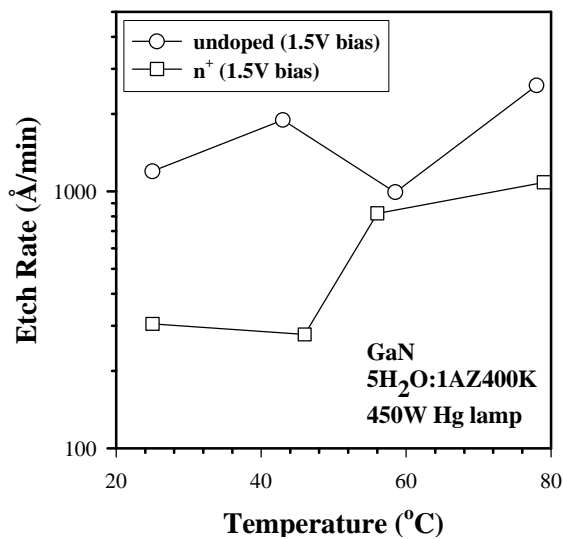

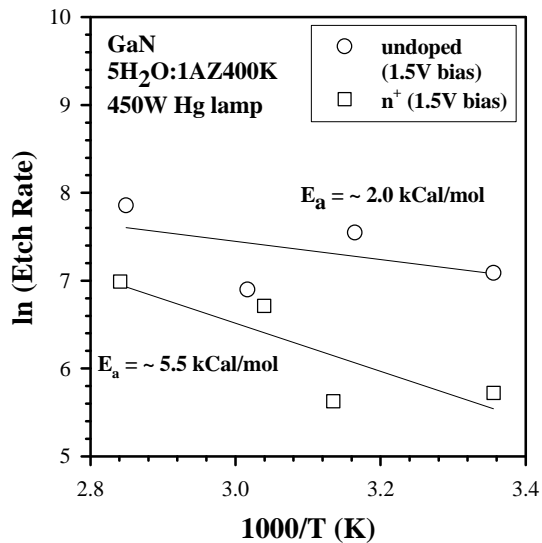Figure 8. Temperature dependence of GaN PEC etch rate either with or without 1.5V bias in H_2O:AZ400K solutions.

Figure 9. Arrhenius plot of GaN PEC etch rate either with or without 1.5V bias in H_2O:AZ400K solutions.

Summary and conclusions

The etch rate of GaN under UV-assisted photoelectrochemical 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 ~ 3×10^{16} cm^{-3}) GaN are ≥ 1000Å·min^{-1}. The etching is diffusion-limited under our conditions with an activation energy of < 6kCal·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 p$^+$ base layer is necessary in order to make an ohmic contact.

Acknowledgements

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