A Study of the Photoelectrochemical Etching of n-GaN in H₃PO₄ and KOH Electrolytes

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We investigated the photoelectrochemical etching of n-GaN in H₃PO₄ and KOH as a function of electrolyte concentration, potential and light intensity. Etch rates measured by stylus profilometry were compared with coulometric and amperometric values. In both electrolytes, etch rates increased with concentration, reaching a maximum at 3.0 mol dm⁻³ and decreasing at higher concentrations. The increase in etch rate with concentration of either H₃PO₄ or KOH reflects the amphoteric nature of gallium and the decrease above 3.0 mol dm⁻³ is attributed to common-ion effects. Profilometric etch rates were lower than coulometric and amperometric etch rates reflecting formation of a surface film. SEM and profilometry demonstrated that thick surface films are formed at lower concentrations. Etch rates increased linearly with light intensity indicating a carrier-limited etching regime: a quantum efficiency of 57.6% was obtained. At light intensities greater than ~35 mW cm⁻² the etch rates showed evidence of saturation. AFM and SEM images of the etched GaN surfaces showed a distinctive ridge-trench structure with a hexagonal appearance. Photoluminescence spectra of the etched GaN show a significant increase in the defect-related yellow luminescence peak suggesting correlation to the formation of the ridge structures, which may represent dislocations terminating at the surface.

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Since the pioneering work of Akahashi, Amani and Nakamura,1–3 the development of GaN-based semiconductor technology has revolutionized the lighting industry.4 GaN-based high-efficiency light-emitting diodes (LEDs) have become the dominant illumination technology, rapidly replacing incandescent bulbs. There has also been remarkable progress in the development of GaN-based laser diodes (LDs) and in particular there has been considerable recent work on vertical-cavity surface-emitting lasers (VCSELs).5–9 GaN is an attractive candidate material for high-voltage and high-power devices10 because of its high electric field strength and electron mobility. It is also a promising semiconductor for solar energy conversion by photoelectrochemical water splitting or photovoltaic power generation.11,12 Because of their strong bonding, Group III nitrides are generally more difficult to etch than other III-V semiconductors.13–17 Plasma etching is most commonly used in processing GaN-based devices.18 However, wet etching19,20 has advantages such as avoiding the ion damage associated with reactive ion etching (RIE) and has the potential for selective etching and faster etch rates. It is thus an important complementary technology to plasma etching for use in certain applications.8,10,23–26

The most common method of wet etching for n-type Group-III nitrides is photoelectrochemical (PEC) etching.15,20,22,23–40 There have been several fundamental investigations of this process35,36,40 using techniques such as linear sweep voltammetry, rotating disk voltammetry, electrochemical impedance and Mott-Schottky analysis. Photogenerated holes lead to electrochemical etching of the semiconductor while the corresponding electrons are involved in a reduction process at the cathode. The species being reduced can be dissolved oxygen, normally present in the electrolyte, or an electron acceptor such as peroxydisulfate may be added.41,42 As a practical etching method, the technique typically utilizes a cathode which consists of metal deposited directly on the semiconductor surface, which is illuminated with above-bandgap light, and sometimes connected to a platinum wire in contact with the electrolyte.29 There have been several studies20,22,27–34,37–39 of etching conditions, etch rate and etch morphology. Various electrolytes have been studied and it has been shown that significant etching can occur under both acidic and basic conditions but not in pH neutral solutions. However, in most of these investigations of etch rate, the actual potential of the semiconductor during etching could not be measured because no reference electrode was used. In many cases, the metal contact to the semiconductor was simply connected directly to a platinum electrode in contact with the electrolyte and, in the cases where an external bias was applied, it was referenced only to a counter electrode of uncertain potential. Previous studies using potentiostatic control generally focused on fundamental mechanistic aspects.

In this paper, we report a photoelectrochemical investigation of the etching of n-GaN using a conventional three-electrode cell in which all experiments were carried out under careful potentiostatic control. Both H₃PO₄ and KOH electrolytes were studied as a function of concentration, applied potential and illumination intensity. We thus provide quantitative data independent of any complications due to processes at the counter electrode and show that the previous observations can be unambiguously attributed to the PEC process at the GaN itself. We also report measurements of the quantum efficiency for the process, which to our knowledge have not been previously reported.

Experimental

GaN samples consisted of a 2-μm epitaxial layer of Ga-terminated n-GaN grown by MOVCD on a sapphire substrate. The layer was silicon-doped with a carrier concentration of ~3 × 10¹⁸ cm⁻³. Assuming an electron mobility of 150 cm V⁻¹ s⁻¹, we estimate a resistivity of 1.4 × 10⁻² Ω cm for the GaN. Working electrodes were fabricated by alloying indium to the GaN to form an ohmic contact which was then masked from the electrolyte by means of epoxy or varnish. The electrode area was typically 0.3 – 0.8 cm². Experiments were carried out at room temperature in a standard three-electrode configuration using a platinum counter electrode and a saturated calomel reference electrode (SCE) to which all potentials were referenced. No correction was made for any ohmic drop across the GaN. The electrolytes consisted of aqueous H₃PO₄ and KOH solutions ranging in concentration from 1.0 × 10⁻¹ mol dm⁻³ to 5.0 mol dm⁻³ bubbled with nitrogen to purge dissolved oxygen. Unless otherwise stated, the solution was unstirred. The working electrode was illuminated by an expanded 5 mW HeCd laser beam. For illumination intensity related experiments the intensity was varied by use of neutral density filters, which gave an illumination intensity range of 5 mW cm⁻² – 50 mW cm⁻². Etch depths were measured using a Sloan Dektak stylus profilometer at a scan rate.
Figure 1. Linear sweep voltammograms for an n-GaN electrode in H₃PO₄ of various concentrations, as indicated: (a) 0.001–3 mol dm⁻³; (b) 3–5 mol dm⁻³. The scan rate was 10 mV s⁻¹ and the illumination intensity was 26 mW cm⁻².

Anodization in H₃PO₄ Solutions

Fig. 1 shows linear sweep voltammograms of n-GaN in various concentrations of H₃PO₄ ranging from 1.0 × 10⁻³ to 5.0 mol dm⁻³ under an illumination intensity of 26 mW cm⁻². It can be seen that in all cases the onset of etching occurs at potentials more positive than about –0.4 V. From Fig. 1 it can be seen that, at the lowest concentration (0.001 mol dm⁻³ H₃PO₄), the current is small at potentials more negative than about 0.3 V. At higher potentials the current increases significantly and eventually levels off to an approximately steady-state value. At intermediate concentrations (0.1 to 2.0 mol dm⁻³) the current initially increases sharply with potential and a peak or peaks appear in the voltammogram. The appearance of such peaks is probably related to the formation of a surface film which is partly passivating: the formation of such films is discussed in detail later. At higher concentrations (3.0–5.0 mol dm⁻³), the current initially increases sharply with potential and a peak or peaks appear in the voltammogram. The appearance of such peaks is probably related to the formation of a surface film which is partly passivating: the formation of such films is discussed in detail later. At higher potentials the current increases significantly and eventually levels off to an approximately steady-state value. At intermediate concentrations (0.1 to 2.0 mol dm⁻³) the current initially increases sharply with potential and a peak or peaks appear in the voltammogram.

Figure 2. Current-time (I-t) curves for an n-GaN electrode in various concentrations of H₃PO₄ from 0.1 to 3 mol dm⁻³ as indicated, following a step from open-circuit to (a) the half-peak potential \(E_h\) and (b) 2.0 V (SCE). The illumination intensity was 30 mW cm⁻².

Current versus time (I-t) curves were also measured for H₃PO₄ concentrations ranging from 0.1 to 5.0 mol dm⁻³ at an illumination intensity of 30 mW cm⁻². The potential was stepped from open-circuit to the “half-peak potential” \(E_h\), i.e., the potential at which the current reaches half of the peak value in the I-V curves in Fig. 1: the value of \(E_h\) depended on the concentration (see Figs. 1a and 1b). Fig. 2a shows the resulting I-t curves. In all cases, a high current density is initially observed when the potential is stepped from open-circuit to \(E_h\) and this decreases rapidly with time. In the case of 1.0, 3.0 and 5.0 mol dm⁻³, following the initial decrease the current density reaches a minimum and subsequently increases relatively slowly to an approximately constant value. This increase in current may be attributed to surface roughening effects increasing the surface area of the electrode. In the case of 0.1 mol dm⁻³, a relatively slow decrease in current density is observed throughout the experiment. The current density dependence on the H₃PO₄ concentration shows a similar trend to current densities observed in Fig. 1 at \(E_h\). The highest current density is observed in a H₃PO₄ concentration of 3.0 mol dm⁻³ with a value of \(\sim 8.0\) mA cm⁻² at 100 s. Similar potential-step measurements were carried out at 2.0 V; the corresponding current-time curves are shown in Fig. 2b. The behavior at shorter times is somewhat different and the currents at longer times are somewhat higher than in Fig. 2a; the current density dependence on the H₃PO₄ concentration shows a similar trend to that observed in Fig. 1 at 2.0 V.

The charge corresponding to the I-t curves in Fig. 2 was determined by numerical integration of the current with respect to time. From this coulometric data, the etch rate \(r_Q\) was estimated from Faraday’s Law of 0.1 cm/min. Etch profiles were analyzed using scanning electron microscopy (SEM).
The amount of etching was also measured by stylus profilometry as shown in Fig. 5. The values of both coulometric (average over 100 s) and profilometric etch rates were plotted against H3PO4 concentration reaching peak values at 3.0 mol dm$^{-3}$ and then decrease at higher concentrations. Qualitatively similar results have been reported by others in experiments in which the potential was not externally controlled. In general, since the profilometric etch rate does not take into account the thickness of any solid film formed on the etched surface, it will be an underestimate of the etch rate if any such film is present. In fact, as can be seen from Fig. 3, the profilometric etch rates are lower than both the coulometric and amperometric etch rates for all H3PO4 concentrations. This implies that the charge consumed in the PEC etching process is partitioned between the formation of solution species and a surface film. The presence of such a film is consistent with the proposal that the PEC etching process for n-GaN involves the initial formation of an oxide on the surface, which then dissolves into electrolytes of suitable pH.

**Effect of Light Intensity**

Fig. 5 shows current-time curves for n-GaN anodized in 1.0 mol dm$^{-3}$ H3PO4 under various illumination intensities ranging from 6.0 mW cm$^{-2}$ to 46 mW cm$^{-2}$. The potential was stepped from open-circuit to 0.15 V (the half-peak potential, $E_0$). It can be seen that the curves are generally similar to the corresponding curve (1.0 mol dm$^{-3}$, 30 mW cm$^{-2}$) in Fig 2a, discussed earlier. In each case, following an initial decrease to a minimum, the current again increases to a broad maximum followed by a slight further decrease. These effects are much less pronounced at the lowest light intensity and at higher concentrations. Qualitatively similar results have been reported by others in experiments in which the potential was not externally controlled. In general, since the profilometric etch rate does not take into account the thickness of any solid film formed on the etched surface, it will be an underestimate of the etch rate if any such film is present. In fact, as can be seen from Fig. 3, the profilometric etch rates are lower than both the coulometric and amperometric etch rates for all H3PO4 concentrations. This implies that the charge consumed in the PEC etching process is partitioned between the formation of solution species and a surface film. The presence of such a film is consistent with the proposal that the PEC etching process for n-GaN involves the initial formation of an oxide on the surface, which then dissolves into electrolytes of suitable pH.
Figure 5. Current-time (I-t) curves for an n-GaN electrode in 1.0 mol dm$^{-3}$ H$_3$PO$_4$ following a step from open-circuit to the half-peak potential $E_h = 0.15$ V (SCE) under various illumination intensities.

tions, implying that the charge consumed is partitioned between the formation of solution species and a surface film.

When photons of wavelength $\lambda$ are incident with an illumination intensity $L$ on an electrode, the number of photons per unit area is

$$N = \frac{L \lambda}{hc}$$

where $h$ is plank’s constant and $c$ is the speed of light. If the photons generate electron-hole pairs with quantum efficiency $\eta$ the limiting photocurrent density is therefore

$$I = \eta N e = \frac{\eta L \lambda e}{hc}$$

where $e$ is the charge on an electron. Thus the limiting photoetching rate is

$$r_{lim} = \frac{IV_{M,GaN}}{nF} = \frac{\eta L \lambda e V_{M,GaN}}{nFhc}$$

Plots of $r_{lim}$ versus $L$ are shown in Fig. 6 at several values of quantum efficiency for comparison with the experimentally determined etch rates.

It can be seen that over most of the range shown in Fig. 6, the coulometric etch rate increases with light intensity in a roughly linear manner, similar to the theoretical plots of $r_{lim}$. This indicates a carrier-limited regime where the etch process is limited by the rate at which carriers are photogenerated. At light intensities greater than $\sim 35$ mW cm$^{-2}$ the etch rates show evidence of saturation. This indicates a diffusion-limited etching regime where the etch process is limited by the rate at which reactant species in solution can diffuse to and react with the semiconductor surface. Similar results have been reported by other investigators.$^{30,31,49}$ The linear least-squares best fit line through the origin for the first four points (i.e., the linear region) in the coulometric etch rate plot has a slope $m = 7.16 \times 10^{-6}$ cm$^3$ s$^{-1}$ W$^{-1}$.

Using Equation 4, this gives a value of quantum efficiency

$$\eta = \frac{mnFhc}{\lambda eV_{M,GaN}} = 0.576$$

i.e., the quantum efficiency for the photoelectrochemical etching of n-GaN in 1.0 mol dm$^{-3}$ H$_3$PO$_4$ is estimated to be 57.6%.

Figure 6. Etch rate of n-GaN electrodes plotted against illumination intensity. The coulometric (average over time) and profilometric (apparent) etch rates are shown. In each case the potential was held constant for 500 s at the half-peak potential $E_h = 0.15$ V (SCE) in 1.0 mol dm$^{-3}$ H$_3$PO$_4$. The solid black line through the first four coulometric data points is the linear least-squares best fit line and its slope corresponds to a quantum efficiency $\eta = 0.576$. Theoretical etch rates corresponding to quantum efficiencies of 1.0 and 0.8 are also shown.

Figure 7. (a) AFM image of the surface of n-GaN anodized at the half-peak potential $E_h$ in 1.0 mol dm$^{-3}$ H$_3$PO$_4$ for 500 s under an illumination intensity of 10 mW cm$^{-2}$; and (b) typical line scan through the image.

Morphology of Etched Surface

The morphology of the etched GaN surfaces was investigated using atomic force microscopy (AFM). Fig. 7a shows an AFM image of GaN etched in 1.0 mol dm$^{-3}$ H$_3$PO$_4$ at a potential $E_h = 0.15$ V for 500 s under an illumination intensity of 10 mW cm$^{-2}$. A rough surface morphology is apparent with no particularly distinctive pattern. A line scan through the image is shown in Fig. 7b and from this an average root-mean-square (rms) roughness of 64 nm is obtained. This suggests that the average peak-to-trough height difference is roughly...
Figure 8. (a) Three-dimensional and (b) plan-view AFM images of the surface of n-GaN anodized at the half-peak potential $E_h$ in 1.0 mol dm$^{-3}$ H$_3$PO$_4$ for 1000 s under an illumination intensity of 10 mW cm$^{-2}$; and (c) typical line scan through the images.

$64 \times 2\sqrt{2}$ nm = 181 nm and consequently that the portion of the coulometric thickness corresponding to the roughness is approximately 90 nm. This represents approximately 25% of the Coulombic etch depth (360 nm) for these etching conditions. The profilometric etch depth is 196 nm and so the difference between the Coulombic and profilometric depths is 174 nm. This would suggest that roughly 52% of this difference is due to surface roughness and that roughly 48% (84 nm) can be attributed to a surface oxide film. Fig. 8 shows AFM images of GaN etched for 1000 s under the same conditions. The three-dimensional image of the surface in Fig. 8a shows a distinctive pattern of selective etching emerging: a ridge-trench structure with a hexagonal appearance. This can be seen from another perspective in the plan-view image in Fig. 8b. A line scan through the image is shown in Fig. 8c. The average distance separating the ridges is approximately 1.6 $\mu$m and the peak-to-trough height difference varies from approximately 400 nm to 720 nm. Taking the average peak-to-trough height difference as 560 nm, this suggests that the portion of the coulometric thickness corresponding to the roughness is $\sim$280 nm. This represents approximately 39% of the coulometric etch depth ($\sim$720 nm) for this longer etching time. The profilometric etch depth is 392 nm and so the difference between the coulometric and profilometric depths is 328 nm. This would suggest that roughly 48 nm can be attributed to a surface oxide film.

We caution that these are very rough estimates, but they serve to give some indication of the relative contributions of surface roughness and oxide films.

Fig. 9 shows an SEM micrograph of GaN etched under similar conditions to those in Fig. 8. The image observed is in good agreement with the AFM images in Fig. 8, both qualitatively in terms of the type of morphology and quantitatively in terms of the feature sizes. Similar results have been reported in experiments in which the n-GaN surface was etched by platinum-assisted electroless photoetching and also in wet photoetching experiments that relied on the addition of a suitable oxidizing agent. The three-dimensional ridge structures were attributed to dislocations or low-angle grain boundaries. This is in agreement with reports which suggest that such structures act as non-radiative recombination centres and therefore are not etched at the same rate during the PEC etching process.

Similar PEC etching experiments were performed under light intensities of 30 mW cm$^{-2}$ and 50 mW cm$^{-2}$. In all cases, the formation of ridge structures was observed after prolonged etching. Fig. 10 shows SEM micrographs of samples etched under an illumination intensity of 50 mW cm$^{-2}$ for periods of 30, 100, 300 and 500 s, respectively. The evolution of the ridge structures with etch depth is apparent. No significant change to the surface morphology is observed after 30 s of etching. After 100 s, significant roughening of the etched surface is evident: a coulometric etch depth, $d_{Q_c}$, of 280 nm was estimated. A significant transition in the etched surface morphology occurs after 300 s of etching ($d_{Q_c} = 880$ nm) when formation of ridge structures is evident; however the ridges are thin and not yet fully formed. After 500 s of etching ($d_{Q_c} = 1285$ nm), the ridges appear thicker and the ridge-to-trench height is greater as is evidenced by the fact that it is harder to focus on both the ridge and the trench area simultaneously. Finally, in many cases the etched ridge structures take on the form of a hexagon, suggesting that many of the dislocations or grain boundaries form preferentially along the wurtzite crystallographic planes.
Figure 10. SEM image of the surface of n-GaN anodized at the half-peak potential $E_h$ in 1.0 mol dm$^{-3}$ H$_3$PO$_4$ for (a) 30 s, (b) 100 s, (c) 300 s, and (d) 500 s under an illumination intensity of 50 mW cm$^{-2}$.

Figure 11. Photoluminescence spectrum of the etched GaN sample in Fig. 8, and of a corresponding unetched sample.

Fig. 11 shows a photoluminescence spectrum of the etched GaN sample in Fig. 8. No shift in the band-edge luminescence is observed following the PEC etching process. This is consistent with the fact that no blueshift has been reported for porous GaN (PGaN) structures produced by anodic etching.$^{57,58}$ A significant increase in the defect-related yellow luminescence peak centred at approximately 535 nm relative to that observed from the untreated n-GaN surface is apparent. The existence of this peak may be correlated to the formation of the ridge structures, which may represent dislocations terminating at the surface. The origin of yellow luminescence has previously been attributed to extended defects such as dislocations or point defects;$^{59}$ however Diaz et al.$^{50}$ found the ridges to be optically inactive.

Surface Films

As previously discussed, the profilometric etch rate does not take into account the thickness of any solid film formed on the etched surface and is therefore an underestimate of the etch rate if any such film is present. To analyze the etching process more accurately it is necessary to take into account any films present on the etched electrode surface.

Fig. 12 shows a schematic representation of the cross-section of a PEC-etched n-GaN electrode. It is seen that the thickness $d_f$ of any surface film formed during etching is, ideally, the difference between...
the coulometrically and profilometrically measured etch depths, i.e.,

\[ d_f = d_q - d_P \]  \[6\]

where \( d_f \) is the coulometric etch depth and \( d_P \) is the profilometric etch depth. Values of film thickness \( d_f \) were estimated using Equation 6 with values of \( d_P \) from the data in Fig. 2 (and similar experiments at the peak potential \( E_p \)) and values of \( d_P \) from the corresponding profilometric measurements. The values obtained are plotted against concentration of H\(_3\)PO\(_4\) in Fig. 13 for potentials of \( E_h \), \( E_p \), and 2.0 V. It should be noted that there may also be a contribution to the difference between the coulometric and profilometric etch depths due to the roughness of the etched surface because the trenches shown in the AFM images in Figs. 7 and 8 are too small for the stylus probe to enter. Equation 6 ignores this and so it represents a source of error.

In all cases, significantly higher values of \( d_f \) are observed at 0.1 mol dm\(^{-3}\) than at higher concentrations. This may explain the trend observed in Fig. 3 where the etch rate is reduced at lower H\(_3\)PO\(_4\) concentrations. The effect of an increase in surface film thickness would be to hinder the diffusion and migration of species in solution to and from the semiconductor surface resulting in a decrease in etch rate. At all concentrations, the values of \( d_f \) are largest at the peak potential \( E_p \). This suggests that significantly thicker surface films are formed at \( E_p \), which may explain the decrease in current observed in the potential sweep measurements (Figs. 1a and 1b) at potentials more positive than \( E_p \).

As already discussed, it appears that the surface films are thicker at low concentrations of H\(_3\)PO\(_4\). In order to investigate the process of film formation in more detail, we therefore performed a series of experiments at low concentrations of H\(_3\)PO\(_4\). Electrodes were anodized in 1.0 \times 10^{-3} mol dm\(^{-3}\) H\(_3\)PO\(_4\) for 3000 s at 0.5 V at an illumination intensity of 10 mW cm\(^{-2}\). The etched samples were also examined by stylus profilometry and by SEM.

A typical surface profile is shown in Fig. 14. It is noted that the surface of the etched area is higher than that of the masked area. The step between the masked and unmasked areas is 420 nm. Thus, the oxide film is quite thick, not only replacing the etched GaN but also extending 420 nm above the original surface.

Fig. 15 shows SEM images of cross sections of (a) the masked area and (b) the unmasked area of a typical electrode after etching as described above. Fig. 15c shows a plan-view SEM micrograph of the same sample. The transition from a smooth unetched n-GaN epilayer to a cracked porous oxide film is clearly visible. Comparing (a) and (b) it is clear that a thick anodic film has formed on the surface and that the GaN epitaxial layer is correspondingly thinner. The average thickness of the GaN layer in (a) is approximately 2.3 \( \mu \)m while the combined thickness of the GaN and the oxide film in (b) is approximately 2.8 \( \mu \)m, in general agreement with the 420-nm step measured by profilometry.

**Anodization in KOH Solutions**

The photoelectrochemical etching of n-GaN in alkaline solutions was also investigated. Fig. 16 shows linear sweep voltammograms in concentrations of KOH ranging from 1.0 \times 10^{-3} to 5.0 mol dm\(^{-3}\) under an illumination intensity of 10 mW cm\(^{-2}\). As the potential is scanned in the positive direction, an increase in current is observed. For KOH concentrations in the range 0.1–5.0 mol dm\(^{-3}\), the current reaches a peak value at approximately 2.5 V and subsequently decreases, initially rapidly and then more slowly. This qualitatively resembles somewhat the behavior observed in H\(_3\)PO\(_4\) (Fig. 1), where a decrease in current at potentials more positive than the peak was attributed to the formation of a passivating oxide film. At lower concentrations (0.01 and 0.001 mol dm\(^{-3}\)) no peak is observed, similar to observations at low concentration (0.001 mol dm\(^{-3}\)) in H\(_3\)PO\(_4\). It is also noted that, at all potentials, current increases with concentration in the range 0.001 – 3.0 mol dm\(^{-3}\) and subsequently decreases in the range 3.0 – 5.0 mol dm\(^{-3}\), again similar to observations in H\(_3\)PO\(_4\).

Current versus time (I-t) curves were also measured for KOH concentrations ranging from 0.1 to 5.0 mol dm\(^{-3}\) at an illumination intensity of 10 mW cm\(^{-2}\). The potential was stepped from open-circuit to 1.6 V, which corresponds to the plateau region in the current-potential curves in Fig. 16. Fig. 17 shows the resulting I-t curves. In all cases, the current initially increases and arrests at an approximately constant value. The current density dependence on the H\(_3\)PO\(_4\) concentration shows a similar trend to that observed in Fig. 16.

The charge corresponding to the I-t curves in Fig. 17 was determined by numerical integration of the current with respect to time and from this data coulometric etch rates were estimated. Amperometric (instantaneous) etch rates were estimated from the current density at 200 s. The amount of etching was also measured by stylus profilometry as described earlier: profilometric etch rates were measured for each of the samples in Fig. 17. The values of the coulometric, amperometric and profilometric etch rates are plotted against KOH concentration in Fig. 18. All three curves are observed to exhibit a similar dependence on KOH concentration. The etch rates increase with increasing KOH concentration reaching peak values at 3.0 mol dm\(^{-3}\) and then decrease at higher concentrations. Again, as for H\(_3\)PO\(_4\) (Figs. 3 and 7) the profilometric etch rates are lower than the coulometric etch rates for all concentrations, implying that the charge consumed is partitioned between the formation of solution species and a surface film.

The increase in etch rate with increasing concentration of either KOH or H\(_3\)PO\(_4\), at values less than 3 mol dm\(^{-3}\), reflects the amphoteric nature of gallium. In acidic solutions, gallium in the +3 oxidation state is soluble as a trivalent cation and in alkaline solutions it is soluble as an oxyanion; it is generally insoluble in neutral solutions, tending to form an insoluble hydroxide or oxide. Thus, at lower concentrations...
Figure 15. SEM images of n-GaN anodized at 0.5 V (SCE) in $1.0 \times 10^{-3}$ mol dm$^{-3}$ H$_3$PO$_4$ for 3000 s under an illumination intensity of 10 mW cm$^{-2}$: (a) cross-section of masked area, (b) cross-section of unmasked (etched) area and (c) plan view.

Figure 16. Linear sweep voltammograms for an n-GaN electrode in KOH of various concentrations, as indicated: (a) 0.001–3 mol dm$^{-3}$; (b) 3–5 mol dm$^{-3}$. The scan rate was 10 mV s$^{-1}$ and the illumination intensity was 10 mW cm$^{-2}$.

of either KOH or H$_3$PO$_4$ the etch rate decreases due to the reduced solubility of the etch product and the formation of a surface film. As we have shown above, there is direct microscopical evidence for the presence of a thick surface film at low concentrations of H$_3$PO$_4$. Surface films present a physical barrier that inhibits the transport of reactant species to and from the semiconductor surface. Additionally,

Figure 17. Current-time (I-t) curves for an n-GaN electrode in various concentrations of KOH from 0.1 to 3 mol dm$^{-3}$ as indicated, following a step from open-circuit to 1.6 V (SCE). The illumination intensity was 10 mW cm$^{-2}$.
they may have the effect of reducing the amount of incident light that can penetrate to the n-GaN surface and generate carriers that are essential for the PEC etching process.

The decrease in etch rate at concentrations above 3 mol dm$^{-3}$ may be due to a reduction in the solubility of the gallium species by a common-ion effect due to the high concentrations of phosphate and potassium ions, respectively. Just as the solubility of the trivalent gallium cation is decreased by the increased concentration of hydroxyl ions, respectively. Just as the solubility of the trivalent gallium cation is decreased by the increased concentration of hydroxyl ions, so also it may be decreased by the increased concentration of phosphate ions above 3 mol dm$^{-3}$. Correspondingly, just as the solubility of the gallium oxycyanide is reduced by the decreased concentration of hydroxyl ions at low concentrations of KOH, so also it may eventually be decreased by the increased concentration of potassium ions above 3 mol dm$^{-3}$. It is also noted that the increased viscosity of the more concentrated solution may play some role in decreasing the etch rate but such an effect is likely to be small.

Conclusions

We investigated the PEC etching characteristics of n-GaN in H$_3$PO$_4$ and KOH as a function of electrolyte concentration, applied potential and light intensity. In both electrolytes, linear sweep voltammograms showed peak currents, which are attributed to the formation of a passivating oxide film. I-t measurements were carried out at selected potentials and the etch rates measured by stylus profilometry: the profilometric etch rates were compared with coulometric and amperometric etch rates obtained from the I-t curves.

In both H$_3$PO$_4$ and KOH, the etch rates were found to increase with increasing concentration, reaching a maximum at 3.0 mol dm$^{-3}$ and then decreasing at higher concentrations. The increase in etch rate with concentration of either H$_3$PO$_4$ or KOH reflects the amphoteric nature of gallium and the decrease above 3.0 mol dm$^{-3}$ is believed to be due to common-ion effects. Profilometric etch rates were somewhat lower than coulometric and amperometric etch rates and it is proposed that this reflects the formation of a surface film. We demonstrated by SEM and profilometry that thick surface films are formed during PEC etching in 1.0 $\times$ 10$^{-3}$ mol dm$^{-3}$ H$_3$PO$_4$.

Etch rates measured in 1.0 mol dm$^{-3}$ H$_3$PO$_4$ increased approximately linearly with light intensity up to $\sim$35 mW cm$^{-2}$ indicating a carrier-limited etching regime: from the slope of the line a quantum efficiency of 57.6% is obtained. At light intensities greater than $\sim$35 mW cm$^{-2}$ the etch rates showed evidence of saturation, indicating a mass-transport-limited etching regime.

AFM and SEM images of the etched GaN surfaces show a rough morphology. At longer etch times a distinctive ridge-etch structure with a hexagonal appearance is observed. Photoluminescence spectra of the etched GaN show a significant increase in the defect-related yellow luminescence peak centred at $\sim$535 nm relative to the untreated GaN. This peak may be correlated to the formation of the ridge structures, which may represent dislocations terminating at the surface.

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