



# Photo-electrochemical etching of free-standing GaN wafer surfaces grown by hydride vapor phase epitaxy



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## ABSTRACT

An investigation into the photo-electrochemical (PEC) etching of free-standing GaN wafers produced by hydride vapor phase epitaxial growth (HVPE) has found that etching is only possible with UV illumination in an acidic or basic electrolyte. Through photo-current measurement and X-ray analysis it was determined that lack of etching in a neutral electrolyte can be attributed to the formation of an oxide film on the GaN surface. Surface damage was also found to be a significant factor, with the etching rate and photo current density of surfaces treated by grinding and mechanical polishing being markedly less compared to a finely polished surface. Subsequent investigation of the luminescence and the etching characteristics of the intentionally-introduced scratches indicated that subsurface damage is difficult to remove from GaN by PEC etching due to the trapping of photo-excited carriers. A peculiar surface feature of concentric ring structures made up of alternating small and large pores was observed on the GaN surface along with small island regions, which is attributed to variations in the electronic properties of the GaN crystal that is created during HVPE growth.

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## 1. Introduction

Gallium nitride (GaN) and other Group III–V materials have attracted significant attention due to their suitability for use in short-wavelength emitters or detectors, as well as in high-power and high-frequency electronic devices. Achieving the full potential of such devices, however, requires a suitable method for removing selected portions of the GaN surface. Although wet chemical etching techniques are extensively used with conventional semiconductor technology for removing subsurface damage, surface cleaning and nano-structure fabrication, such methods are far less effective in etching GaN due to its inherently high thermal and chemical stability [1]. Indeed, only high temperature treatments involving molten KOH [2] and hot phosphoric acid [3,4] have proven to be capable of etching GaN surfaces, but this creates a high cost and energy consumption.

Extensive investigation into the photo-electrochemical (PEC) etching of semiconductors has led to the development of a suitable method for use at room temperature. In this, the surface of a semiconductor immersed in an electrolyte is irradiated by

ultraviolet (UV) light with an optical energy greater than the band gap of the materials. This generates electron-hole pairs, which then initiate a redox reaction at the semiconductor/electrolyte interface. This method has been used for the chemical lift off of GaN layers [5] and in light-emitting diode (LED) fabrications [6] with a practical etching efficiency, but has so far only been used with epitaxial GaN thin films [7–10] applied to a substrate by metal organic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE). However, free-standing GaN bulk wafers have been produced quite recently by hydride vapor phase epitaxy (HVPE) [11–14], and the demand for these has significantly increased due to the fact that they represent high-quality GaN crystals with a low dislocation density. This paper therefore looks at the PEC etching of a free-standing HVPE GaN surface. The effect of the electrolyte composition and presence of subsurface damage on the etching rate is evaluated along with the morphology of the etched GaN surface.

## 2. Experimental

The samples used in this study were commercially available free-standing GaN wafers (*n*-type doped, 300 μm thick) that were produced by hydride vapor phase epitaxial (HVPE) growth, and which had a carrier concentration of  $(1-3) \times 10^{18} \text{ cm}^{-3}$ . Unless

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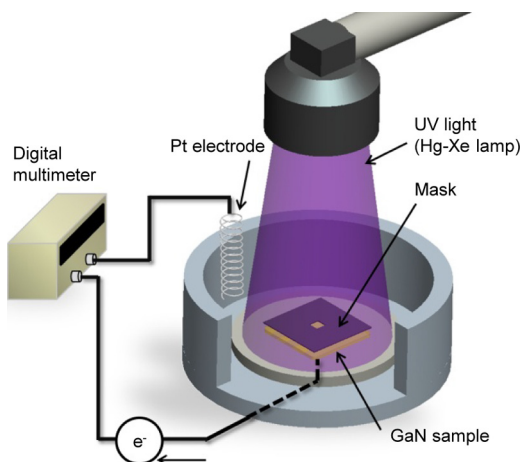


Fig. 1. Schematic view of the experimental setup used.

otherwise noted, all samples were treated prior to testing by fine polishing [15,16] to obtain a damage-free surface with a typical root-mean-square surface roughness of just 0.1 nm.

As shown in Fig. 1, GaN samples immersed in an electrolyte were illuminated to a controlled intensity using a Hg-Xe lamp (LIGHTNING CURE L9588, Hamamatsu photonics). In order to determine the etching depth, part of the sample surface was masked with a polyimide film and the step formed was measured using a stylus profiler. The pH of the electrolyte was controlled to 1.0, 6.86 or 13.0 by adding  $\text{H}_3\text{PO}_4$ , phosphate buffered solution (PBS) or KOH, respectively. To provide an electrical contact, a Pt/Cr bilayer was applied to the back of the GaN wafer by electron-beam evaporation. The photo-induced current flow between the sample and a Pt counter electrode was measured using a digital multimeter, with no bias being applied between the two electrodes. All etching experiments were conducted at room temperature.

The surface morphology of the etched samples was observed using confocal laser scanning microscopy (LEXT OLS3100, Olympus), optical interferometric microscopy (NewView 200CHR, Zygo), and scanning electron microscopy (SEM; S-4800, Hitachi). A chemical analysis of the sample surface was also conducted using X-ray photoelectron spectroscopy (XPS; Quantum 2000, ULVAC PHI) with an Al  $K\alpha$  X-ray source.

### 3. Results and discussion

#### 3.1. Effect of electrolytes

Figs. 2 (a)–(c) show cross-sectional profiles of GaN surfaces subjected to UV illumination for 20 min in various electrolytes, which reveals that the etching depths in acidic (pH=1) and basic (pH=13) electrolytes are both approximately 1.5–2.0  $\mu\text{m}$ . As shown in Fig. 3, these two electrolytes also produced concentric

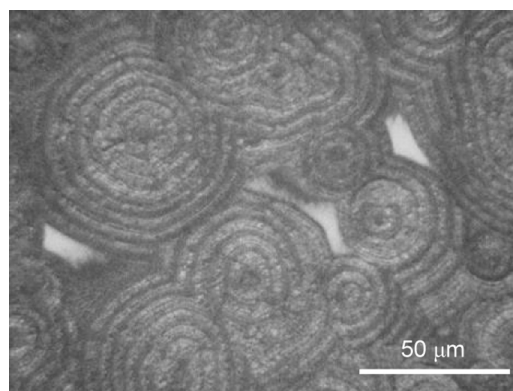


Fig. 3. Optical micrograph of the surface of GaN PEC etched in  $\text{H}_3\text{PO}_4$  (pH = 1.0).

ring structures with some islands structure that is believed to originate from the non-uniformity of the electronic properties of GaN crystals produced by HVPE, which is discussed in more detail further on. In contrast, there was no step evident between the illuminated and masked region in the case of the neutral (pH=6.8) solution, suggesting that this failed to produce any significant etching of the GaN surface.

As shown in Fig. 4, the current density flowing from the Pt electrode to the GaN samples varies depending on the pH of the electrolyte. That is, in an acidic or basic electrolyte the current density remains almost constant during UV illumination, while in a neutral electrolyte the current density decreases rapidly with time. As shown in Fig. 5, PEC etching is initiated by the generation of

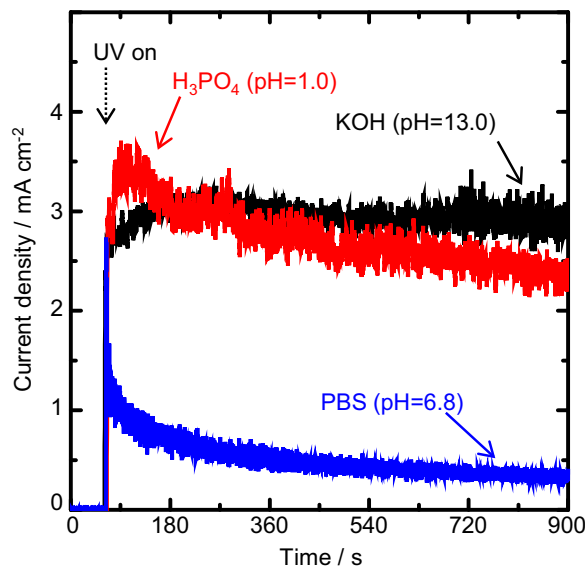


Fig. 4. Photo-current density between a GaN wafer and Pt cathode as a function of time. UV illumination started from 1 min under all electrolyte conditions.

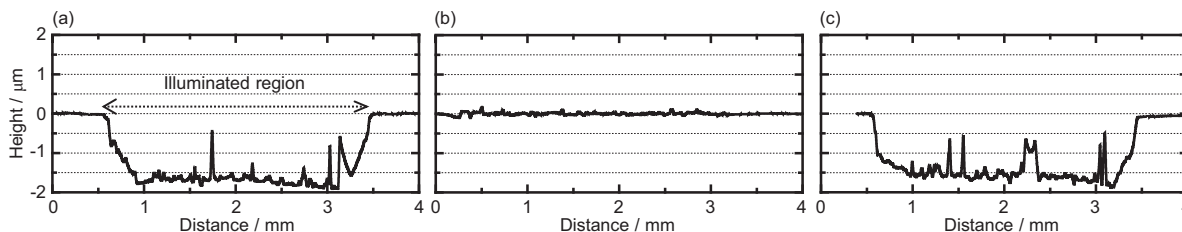


Fig. 2. Cross-sectional profiles of GaN surfaces treated in (a)  $\text{H}_3\text{PO}_4$  (pH = 1.0), (b) phosphate buffered solution (pH = 6.8) or (c) KOH (pH = 13.0) electrolytes under a UV intensity of  $5.2 \text{ mW}/\text{cm}^2$  for 20 min.

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