**Supporting Information:**

# Enhanced piezoelectricity and electromechanical efficiency in semiconducting GaN due to nanoscale porosity

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## S1. GaN layer growth, etching, and porosity assessment

GaN epitaxy was performed onto a 2-inch sapphire wafer substrate (sample C7030A) using the metal-organic chemical vapour deposition (MOCVD) technique in a close-coupled showerhead Thomas Swan reactor equipped with a 6x2-inch susceptor. A GaN template with a low dislocation density was grown first, followed by an unintentionally doped (UID) GaN buffer region similar to that of LED structures, and a superficial n-type highly-doped (n+) GaN layer, with $N_D$ in the region of $5\times10^{18}$ $cm^{-3}$ and 1.5μm thickness.

The grown wafer was cleaved into several samples for observing the influence of the etch voltage on the resulting device characteristics. For each cleaved sample, the peripheral region of the conductive n-type layer was connected to the electrical circuit by an indium contact deposited onto the surface by manual soldering. The superficial n-type doped GaN layer was electrochemically etched in a potentiostatic configuration at various bias voltages, using a bath of 0.25M oxalic acid and a platinum counter-electrode. Since the region surrounding the indium contact was not submerged into the etching bath, no etching occurred in its proximity and the same indium structure was later used as the substrate contact. The etching was performed at 20°C under laboratory ambient illumination. Figure S1 shows the etch current progression

over time for two doped layers of different thicknesses. In the first case, the etch was stopped by the operator before affecting the entire thickness of the doped layer, while the second case shows the drop in etch current associated with the self-limiting nature of the process. Finally, the etched samples were afterwards cleaned with ethanol and blow-dried with $N_2$. Notably, the two samples and conditions are different, and the second sample reaches full etching in a shorter period of time.

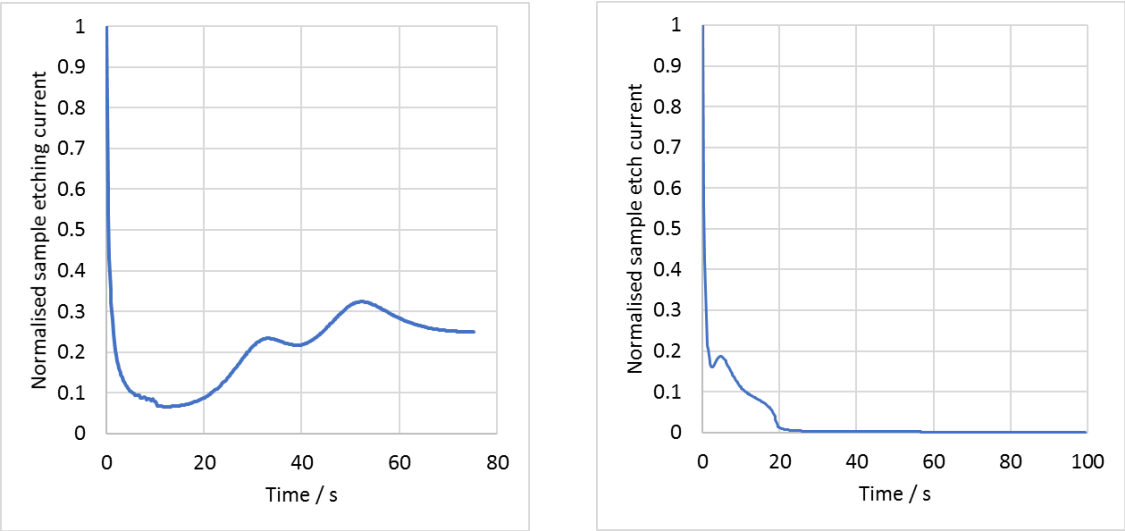
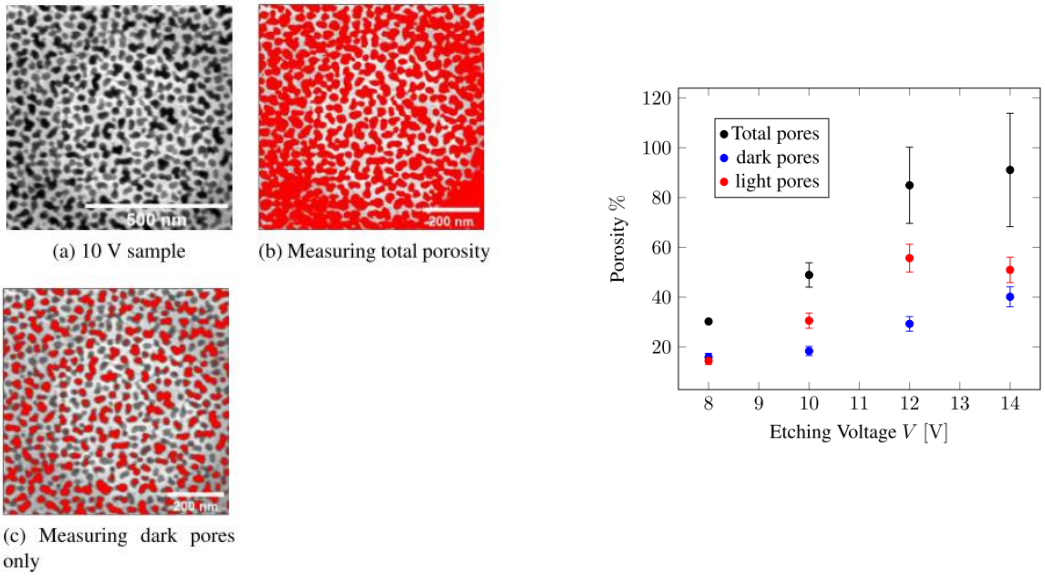



Figure S1 (a) The electrochemical etching current profile of the sample used for piezoelectric characterization (14 V applied); (b) an etching current profile of a sample etched throughout the doped thickness. The sharp drop around 20 s is when etching has gone through the thickness. The exact characteristics may vary with doping, crystal defects and applied voltage.

The porosity level was assessed by analysing the contrast using ImageJ software.[1] The contrast level of SEM images of porous media (both top and cross sections) were examined, to reveal the porosity level (Figure S2 a-c). In this case the samples used were porous to a level corresponding to about 40%.




(a) 10 V sample

(b) Measuring total porosity

(c) Measuring dark pores only

Figure S2 (a) Top SEM view of an etched sample with: (b) low threshold – including all pores; (c) higher threshold, including only the darkest pores – probably those that reach the surface. (d) Porosity as a function of etching voltage

S2. Atomic force microscopy –

*Nanomechanical mapping*

Quantitative mechanical characterization of porous GaN using the AFM is complicated due to two reasons. Firstly, non-porous GaN is a very stiff material (Y ~ 300 GPa), therefore using the QNM feature requires a very hard tip. A suitable tip was not available to us, and subsequent issues regarding calibrations then arise. Secondly, as will be shown below both experimentally and theoretically, porosification has a strong effect on the material stiffness and so characterizing the complete range of porous samples is challenging. Therefore, we include here the results of samples etched using 10, 12, 14 V (thus increasing porosity as mentioned above), which yielded measurable results in our experimental system – using a tip with nominal force constant of 0.4 N/m (*scanasyst-air, Bruker*) and a peak force of

80-90 nN. These results qualitatively show how the material becomes more compliant with increased etching voltage / increased porosity.

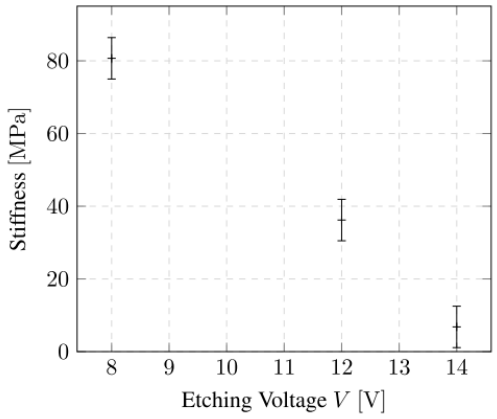



Figure S3 Decline of measured stiffness with etching voltage – hence porosity. These results should be treated as qualitative.

*PFM Calibration*

In order to calibrate the Piezoelectric signal a known sample needs to be measured. In this work a 100 nm thick film of PVDF-TrFE was first poled using -10V, then measured and attributed the value of 22 pm/V. As with any PFM measurement reported here, KPFM measurements were carried out and used as bias prior to the PFM measurement.

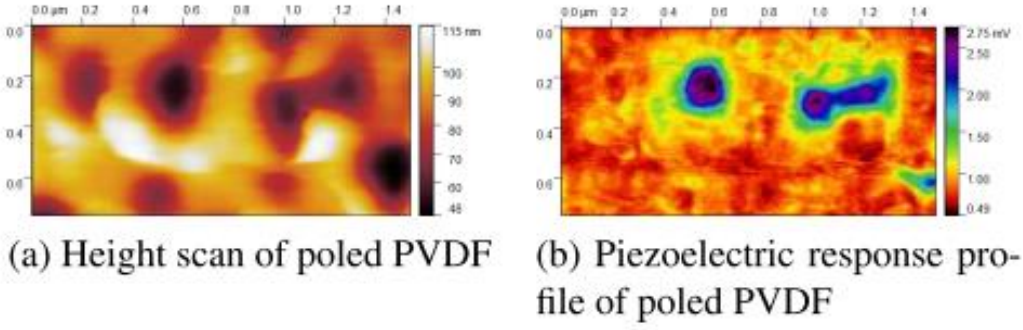



Figure S4 (a) A region of PVDF-TRFE sample after poling; (b) PFM signal of that region. The thinner areas are poled more efficiently and are considered at 22 pm/V.

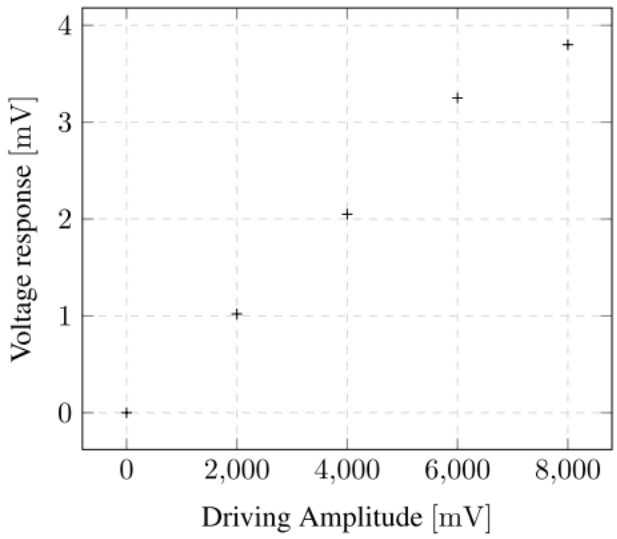



Figure S5 Raw PFM signal as a function of AC drive amplitude, providing the basis for PFM signal calibration.

In order to account for the background noise, the sample was measured prior to etching. Since the sample is conductive, it is not expected to exhibit piezoelectricity. Any signal measured, was treated as a background signal, and subtracted from the measured signal of the porous sample. In any case, this signal was 4-5 times smaller compared to the raw measured signal of the post-porosification layer. This is evident by Figure S6. The left hand side shows the PFM signal (at 2 and 8 V AC amplitude) for two scales. The top is directly comparable to the raw measurement of the porosified layer (on the right hand side). The bottom, at a smaller scale, shows the increase of the background signal with the AC voltage.

Furthermore, PFM was conducted under a deflection set-point of ~ 0.12 V, corresponding to less than 10 nm of deflection (according to the deflection sensitivity of about 50-60 nm/V for the tips used). As the tips used here were MESP-RC-V2, with a nominal force constant of 5 N/m, this corresponds to an application of less than 50 nN. The scanning was non-destructive for both GaN and PVDF-TrFE, for several consecutive scans. This indicates that the tip/substrate systems is stable, and the applied force is not expected to be large enough to alter the piezoelectric response – overall indicating the PFM is “well-behaved”, such that the tip follows the surface deflection in both GaN and PVDF-TrFE.

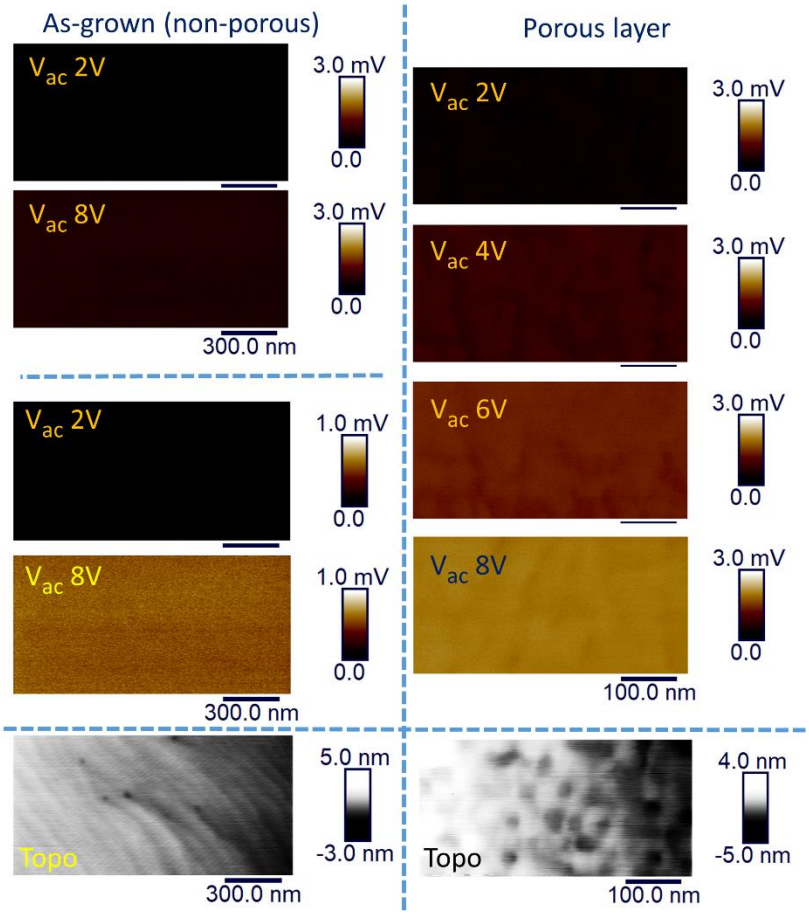



Figure S6 Raw PFM for the examined sample before (left) and after (right) etching. The signal is clearly stronger after etching and moreover, the unetched signal is used as background and subtracted from the measured signal. The unetched signal is shown here in two different scales, one identical to the etched signal for comparison, and one smaller, for resolving the signal. The bottom section shows the topography channel. Noticeably, the PFM signal is quite uniform, without considerable crosstalk with the pores.

References

(1) Rueden, C. T.; Schindelin, J.; Hiner, M. C.; DeZonia, B. E.; Walter, A. E.; Arena, E. T.; Eliceiri, K. W. ImageJ2: ImageJ for the next generation of scientific image data. *Bmc Bioinformatics* **2017,** *18*, DOI: 10.1186/s12859-017-1934-z.