MRS Internet Journal Nitride Semiconductor Research

Selective Etching of GaN from AlGaN/GaN and AlN/GaN Structures

JA. Grenko[1], CL. Reynolds Jr[1], R. Schlesser[1], K. Bachmann[1], Z. Rietmeier[1], Robert F. Davis[1] and Z. Sitar[1]

[1]*Department of Materials Science and Engineering, North Carolina State University,*

(Received Wednesday, April 7, 2004; accepted Wednesday, July 14, 2004)

Thick GaN layers as well as AlGaN/GaN and AlN/GaN heterostructures grown by metalorganic vapor phase epitaxy have been photoelectrochemically (PEC) etched in various dilute electrolytes, and bandgap-selective etching has been demonstrated in heterostructures. This result is a significant step forward in the fabrication of group III-nitride devices and one-dimensional photonic bandgap (PBG) structures in the deep UV. Based on initial results from thick GaN layers, a method was developed to achieve self-stopping selective etching of thin GaN layers in AlGaN/GaN and AlN/GaN heterostructures. Selective PEC etching requires the use of a suitable light source with photon energies larger than the bandgap of GaN, but smaller than that of AlGaN or AlN, thus enabling selective hole generation in the GaN layers to be etched. Additionally, it is imperative to use an electrolyte that supports PEC etching of GaN without chemically etching AlGaN or AlN.

1 Introduction

Motivation for the work reported here was to develop a suitable processing technique for nanoscale patterning of multiple-period heterostructures , thus enabling the fabrication of AlN-based one-dimensional photonic bandgap structures (1D-PBGs). Potential applications include nanophotonic devices, UV photonic integrated circuits, and in particular, 1D-PBG-based non-linear optical frequency converters. The same processing technique is suitable for the fabrication of integrated, passive optical elements, including Bragg reflectors, interference filter structures, and for electronic devices.

For these applications, the ability to fabricate well defined, flat and plane-parallel interfaces with ultimate tolerances better than 0.1% is essential. The lack of chemical reactivity of group III nitrides to wet chemical etching has been well documented. [1] Porbaix [2] diagrams of AlN and GaN overlap significantly and therefore, selective etching by means of wet chemical methods is not sufficiently selective. Alternatively, Wang et al. [3] have demonstrated selective etching of GaN from InGaN to create high reflectivity semiconductor/air distributed Bragg reflectors using chlorine-based reactive ion etching (RIE). However, their etching process did not consider high aspect ratios and resulted in distinct inclination of the sidewalls of their Bragg reflectors.

In PEC etching, electron-hole pairs are photogenerated in a semiconductor placed in an electrolytic solution and illuminated with photons of energy greater than its bandgap. Stonas et al. [4] demonstrated bandgap-selectivity by etching a thin layer of lower bandgap InGaN sandwiched between thick n-GaN layers. PEC etching has become a valuable tool for the fabrication of high power devices such as AlGaN/GaN high electron mobility transistors (HEMTs) and heterojunction bipolar transistors (HBTs) because it enables selective lateral etching of material by virtue of its bandgap selectivity. Improved I-V characteristics in current aperture vertical electron transistors (CAVET) have been demonstrated [5] by using a PEC process to remove the insulating layer of conventional CAVET structures [6] thereby eliminating a path for leakage current. Khare and Hu [7] examined the etch selectivity of n^+ GaAs on p-GaAs and NID GaAs substrates and found significant etch rate differences in n^+ and p^+ GaAs homostructures. Flynn [8] extended the utility of this dopant-selectivity in the fabrication of 1.3mm LEDs when he demonstrated improved coupling efficiency to optical fibers by PEC-etching n-InGaAsP into curved lenses. Thus, PEC etching has been demonstrated to be an important fabrication technique for electronic and photonic devices.

© 2004 The Materials Research Society

https://doi.org/10.1557/S1092578300000405 Published online by Cambridge University Press

Since PEC etching requires the generation of holes to form oxides with the semiconductor and subsequent dissolution of those oxides in the electrolyte, selection of an appropriate electrolyte is a primary concern. Minsky et al. [9] demonstrated that PEC etching of non-intentionally doped (NID) GaN could be achieved in solutions of HCl:H_2O (1:10) and solutions of 45% KOH:H_2O (1:3). Additionally, Peng showed the solubility of GaN in electrolytes of H_3PO_4 and KOH in the pH regime from –1 to 2 and 11 to 15, respectively. [10] A further refinement of PEC-etching using dilute electrolyte solutions of 0.04M KOH to generate smooth GaN surfaces when etched in the diffusion-controlled regime has been reported. [11] Selective PEC etching of heterostructures requires the use of light with energy higher than the bandgap of the material to be etched, yet lower than the bandgap of material to be preserved. The photons are absorbed in the material to be etched and electron-hole pairs are generated. The holes are transported to the semiconductor-electrolyte interface for bond-breaking reactions with the semiconductor. Meanwhile, the electrons are swept to the cathode to reduce the probability of unwanted electron-hole recombination. In addition to adequate illumination, a good electrical contact to the semiconductor (anode), as well as a sufficiently large cathode for effective carrier sweep-out are required.

2 Experimental

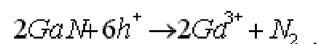
Initial etching experiments were performed on GaN samples grown by metalorganic vapor phase epitaxy onto sapphire substrates. GaN layers were typically 5 µm thick, and either not intentionally doped (NID) with a carrier concentration of ~5 x 10^{17} cm^{-3}, or, alternatively highly-doped with a carrier concentration of ~1 x 10^{19} cm^{-3}. 300 nm thick Ti contacts were deposited either as square pads with 10 x 10 $µm^2$ to 50 x 50 $µm^2$ openings or 10 µm parallel lines with 10 µm openings. The material was then cleaved into approximately 5 mm x 5 mm samples.

In order to investigate wet etching properties without illumination, films of AlN and GaN were placed in separate beakers of 1:10 HCl:H_2O, 1M KOH and 1:25 H_3PO_4:H_2O covered with aluminum foil for a 24 hr time period at room temperature. Bright-field optical microscopy revealed no evidence of etch pits. Although we used these molarities and concentrations of the electrolytes as upper limits, we did investigate and will report on other electrolytes investigated in the course of this study.

An Oriel high-pressure mercury arc lamp, Model 66021 (1000 Watt), with spectral emission lines at 297, 313 and 365 nm provided photon energies near and above the bandgap of GaN. A one meter long optical light guide fiber was used to couple the light to the sample and a lens reduced the spot size to 1.3 cm^2. A cold mirror was also used to eliminate infrared illumination thereby reducing unwanted heating of samples. After spectral and transmission loss corrections, the estimated illumination intensity at 365nm was $30 mW \cdot cm^{-2}$. The experimental apparatus was similar to that described in the literature. [9] Since the electrolytes used were highly acidic or basic, samples were mounted on a Teflon block. A stainless steel washer was used to increase the contact area to the sample (anode). A gold wire was wound around the screw securing the GaN sample to the Teflon block, and a 6” long 1 mm Pt wire wound to a coil of 8 mm diameter served as the cathode.

3 Results

The photocurrent, which is proportional to the etch rate at the semiconductor-electrolyte interface, was measured with a digital multimeter and varied from 30 to 600 µA for the dilute electrolytes H_3PO_4, KOH, and HCl, while the dark current for all electrolytes was <2 µA. The photocurrent is a measure of the oxidation reactions being induced by holes (h^+) in the valence band. The presence of holes at the semiconductor-electrolyte interface allows ionic dissolution of the semiconductor. Youtsey [11] proposed that the following oxidation reaction is responsible for the decomposition of GaN,



$$2GaN + 6h^+ \rightarrow 2Ga^{3+} + N_2 \ .$$

Bubble formation was observed in these experiments. The formation of bubbles on the sample surface during etching had been previously suggested [11] as evidence for the release of N_2.

The resultant photocurrent data for our initial choice of chemistries and geometries are shown in Figure 1. Note the stability of the photocurrent with etch time. It is evident from inspection of the data that the magnitude of the photocurrent is specific to the choice of the electrolyte. But more importantly, the data suggest that the magnitude of the photocurrent in solutions of the same electrolyte is a function of the ratio between the masked and unmasked illuminated area for the geometries used in these studies. Integration of the photocurrent vs. time curve estimates that the total charge through the cell was 0.2 – 0.5 C, depending on the etch time and chemistry.

After PEC etching, samples were examined with a field emission scanning electron microscope (FESEM) to verify that GaN etching did indeed occur, and if so, to determine the resultant etch depth. For the specific example of a 1 hr etch using 1:25 H_3PO_4:H_2O we observed an average photocurrent of 40 µA. The result-

© 2004 The Materials Research Society
https://doi.org/10.1557/S1092578300000405 Published online by Cambridge University Press

ant etch depth was 1.25μm for an effective etch rate of 21 nm·min^{-1}. The observed average photocurrent, I_{ph}, for each of the electrolytes gave a reasonable prediction of the etch rates based on Faraday's Law, from which the etch rate can be expressed as

$$\frac{h}{t} = \frac{\alpha \cdot J \cdot M_w}{n \cdot F \cdot \rho} \quad (1)$$

where h is the etch depth, t the etch time, α the collection efficiency at the cathode, J the current density, M_w the molecular weight, F Faraday's constant, and ρ the density of GaN. However, since we have no accurate determination for the illuminated area and the current density can be written as $J=I_{ph}/A$, where A is the illuminated area, Equation (1) can be written as,

$$\frac{h}{t} = \frac{\alpha' \cdot I_{ph} \cdot M_w}{n \cdot F \cdot \rho} \quad (2)$$

where α' is defined as α/A. Using the etch rate for 1:25 H_3PO_4:H_2O to determine α' in Equation (2), we can then use the measured photocurrents of 60 and 150μA to predict the PEC-etch rates for 2:25 H_3PO_4:H_20 and 0.04 M KOH electrolytes without any adjustable parameters. The calculated etch rates of 31 and 72 nm·min^{-1} are in reasonable agreement with the etch depths per unit time (33 and 51 nm·min^{-1}) as measured by FESEM and recorded in Table 1. The difference in the KOH results suggest that there may be slightly different cathode efficiencies based on the selection of the electrolyte.

Table 1 summarizes all the electrolytes that were investigated. Although the measured photocurrent for 1:10 HCl:H_2O was high, there was no evidence of etching. In general and with the exception of the 1:10 HCl:H_2O sample, FESEM inspection of the samples etched in electrolytes showing no evidence of etching revealed extensive patches of oxide across the semiconductor surface. These data suggested that excessive oxide formation most likely inhibited PEC etching of the GaN for these electrolytes.

Figure 2 shows a plot of photocurrent vs. illumination intensity for GaN etched in KOH. In the region of low illumination intensities, the photocurrent behavior is linear which is indicative of a carrier-limited regime, which is below 650W for our experiments. Here, the reaction rate is limited only by electron-hole pair generation. As the illumination is further increased, the measured photocurrent becomes sublinear as it approaches the diffusion-limited etch regime. Due to the intensity limitations of our experimental apparatus, saturation, which is indicative of a diffusion-limited process, was never reached. However, it must be noted that the ability to generate holes at the semiconductor-electrolyte interface appears to be correlated to the n-carrier concentration of the material as is indicated by the 2.5-fold increase in etch rate for the material with a donor concentration of ~$1x10^{19}$ cm^{-3}, as seen in Table I. In contrast to NID GaN and for nearly identical photocurrents, the PEC etching of this material resulted in whisker-free surfaces. These observations are consistent with the decrease in Debye length of the semiconductor as the doping density increases. A higher donor concentration confines the holes closer to the semiconductor surface thereby enabling more efficient etching.

While both KOH and H_3PO_4 chemistries resulted in well-defined patterns with vertical sidewalls in the thick film GaN material, GaN whiskers typically remained within the etched area. This observation is consistent with earlier reports that free-standing GaN whiskers remain on the surface for carrier-limited etch conditions. [12] Whiskers have been observed previously for a narrow range of KOH concentrations near 0.02M [11] and for H_3PO_4 at pH=3. [10] It has also been reported that whisker-free surfaces can be achieved for PEC etching under diffusion-controlled etch conditions in KOH. [13] The ability to deliver the electrolyte to the surface for dissolution of the GaN can be assisted by stirring the solution. However, in all cases stirring the solution caused an increase in the surface roughness due to highly localized etch rates at the semiconductor surface unless the concentration of the electrolyte was significantly reduced. Since the fabrication of PBG structures requires smooth interfaces, the electrolyte solutions were not stirred in this work. With the exception of the high carrier concentration (~$1x10^{19}$ cm^{-3}) GaN, whisker-free GaN surfaces could not be achieved by simply PEC etching in an appropriate electrolyte. In order to remove the whiskers after completion of the PEC etch, a wet chemical etch was performed for 15 to 30 min in 2M KOH. Although some whiskers remained after 15 min (Figure 3a), a 30 min clean-up etch resulted in a whisker-free surface with no deleterious effect on the vertical sidewalls (Figure 3b). Note the lack of inclination the sidewall, which is key feature for the fabrication of nanophotonic devices. Another alternative is to use highly doped, ~10^{19} cm-^{3}, GaN, in which no whiskers were observed for our etch conditions.

The heterostructure materials used in this study were grown by MOVPE on sapphire and 6H SiC (0001) substrates. These structures consisted of alternating stacks

© 2004 The Materials Research Society
https://doi.org/10.1557/S1092578300000405 Published online by Cambridge University Press

of AlN and GaN or AlGaN and GaN, comprising 5 layers, each of 100-200 nm thickness. In order to establish an electrical contact to the GaN layers, a shallow-angle, 5 mm wide wedge was polished off each sample, and a 300 nm thick Ti contact was deposited. This approach was more effective in the AlGaN/GaN heterostructures than the AlN/GaN heterostructures since the insulating layers of AlN diminish the effective cross-sectional contact to the GaN material.

AlN/GaN and AlGaN/GaN heterostructures prepared in this manner required no further photolithographic patterning. The metallized edge of the sample was fastened to the Teflon block using a stainless steel washer. We used electrolytes of KOH and H_3PO_4 and illuminated the samples with 750W of illumination. For the AlN/GaN heterostructures etched in KOH, the appearance of cones below each of the GaN layers was evidence that the AlN layers were being selectively etched with respect to the GaN layers. Switching electrolytes from KOH:H_2O to H_3PO_4:H_2O circumvented the solubility issues. PEC etching the AlGaN/GaN heterostructures resulted in the desired effect of etching the 200nm GaN layers preferentially while leaving the AlGaN layers intact, as shown in Figure 4. There is evidence of whisker formation in the GaN layers; in order to provide whisker-free surfaces, longer PEC-etching or the use of more highly doped GaN yielding accelerated etch rates would be required.

Although it is clear by examination of the Pourbaix [2] diagrams of AlN and GaN that etching an AlN/GaN heterostructure in KOH should result in solubility of the AlN in preference to GaN, low photocurrent was observed for the AlN/GaN samples. To address this issue, a simple AlN/GaN heterostructure having 200 nm GaN sandwiched between 100 nm AlN grown on a sapphire substrate was designed and an alternative means of establishing contact to the GaN layers was employed. The first step was a full surface metallization of 300 nm Ti onto the AlN/GaN substrate followed by a photolithographically generated metal mask in order to selectively wet-etch channels into the top AlN layer. Afterward, the sample was etched in dilute buffered-HF to remove the Ti mask. The full surface metallization with 300 nm Ti was then repeated. This processing generated areas where the GaN layers were in direct contact with the Ti mask. By employing backside illumination through the sapphire substrate, GaN in the heterostructure was selectively etched in 2:25 H_3PO_4:H_20. Figure 5 shows that this fabrication sequence and the selection of the appropriate electrolyte result in the desired selective etching of 200 nm GaN layer from the 100 nm AlN layers. Additional effort is required to ensure smooth interfaces.

4 Conclusions

To our knowledge, this is the first demonstration of selective etching of GaN from AlN and AlGaN layers. Significant differences in etch rate between the high and low carrier concentration material investigated in this study suggest that it will be beneficial to increase the n-carrier concentration in the GaN material to further improve selectivity. Additionally, it should be investigated whether thin p-type layers are indeed resistant to PEC etching. This work could be confirmed using thin GaN homostructures of alternating p- and n- type material. And finally, p-doping the thin AlN and AlGaN layers within the AlN/GaN and AlGaN/GaN heterostructures while keeping the n-carrier concentration of the GaN high may provide even greater selectivity. To our knowledge, successful p-doping of these layers has not be achieved to date.

REFERENCES

[1] C. B. Vartuli, S. J. Pearton, C. R. Abernathy, J. D. MacKenzie, *Sol. St. Electr.* ***41***, 1947 (1997).

[2] Pourbaix, M. Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd edition, 1974. pp 171 and 431

[3] H. Wang, M. Kumagai, T. Tawara, T. Nishida, T. Akasaka, N. Kobayashi, T. Saitoh, *Appl. Phys. Lett.* ***81***, 4703 (2002).

[4] A. R. Stonas, T. Marglith, S. P. Denbaars, L. A. Coldren, E. L. Hu, *Appl. Phys. Lett.* ***78***, 1945 (2001).

[5] Y. Gao, Ar. R. Stonas, I. Ben-Yaacov, U. Mishra, S. P. DenBaars, E. L. Hu, *Electron. Lett.* ***39***, 1 (2003).

[6] I. Ben-Yaacov, Y.K. Seck, S.P. DenBaars, E.L. Hu, and U.K. Mishra, Mat. Res. Soc. Symp. Proc. 764,C4.8.1(2003)

[7] R. Khare, E. Hu, *J. Electrochem. Soc.* ***138***, 1516 (1991).

[8] E. J. Flynn, unpublished

[9] M. S. Minsky, M. White, E. L. Hu , *Appl. Phys. Lett.* ***68***, 1531-1533 (1996).

[10] L. -H. Peng, C. -W. Peng, J. -K. Ho, C. -N. Huang, C. -Y. Chen, *Appl. Phys. Lett.* ***72***, 939 (1998).

[11] C. Youtsey, I. Adesida, G. Bulman, *Appl. Phys. Lett.* ***71***, 2151 (1997).

[12] C. Youtsey, L. T. Romano, I. Adesida, *Appl. Phys. Lett.* ***73***, 797 (1998).

[13] C. Youtsey, I. Adesida, L. T. Romano, G. Bulman, *Appl. Phys. Lett.* ***72***, 560 (1998).

© 2004 The Materials Research Society

https://doi.org/10.1557/S1092578300000405 Published online by Cambridge University Press

FIGURES

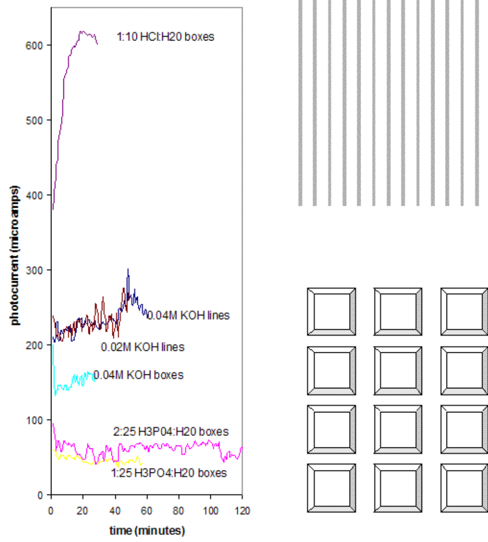


Figure 1. Photocurrent vs. etch time for electrolytes of KOH, H_3PO_4, and HCl (left) and two types of mask geometry used in this study.

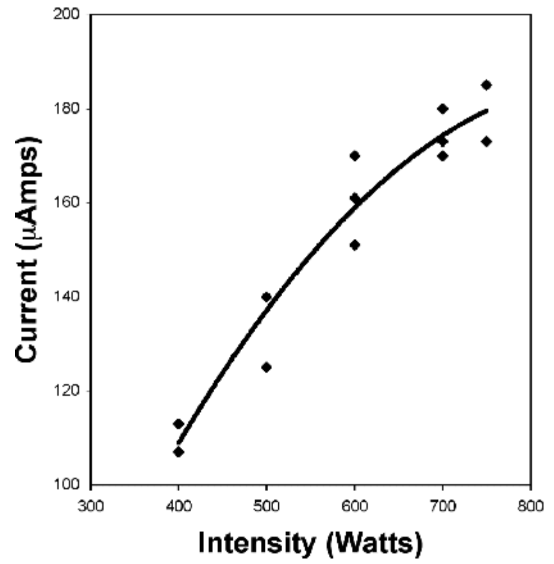


Figure 2. Photocurrent behavior in the carrier-limited regime.

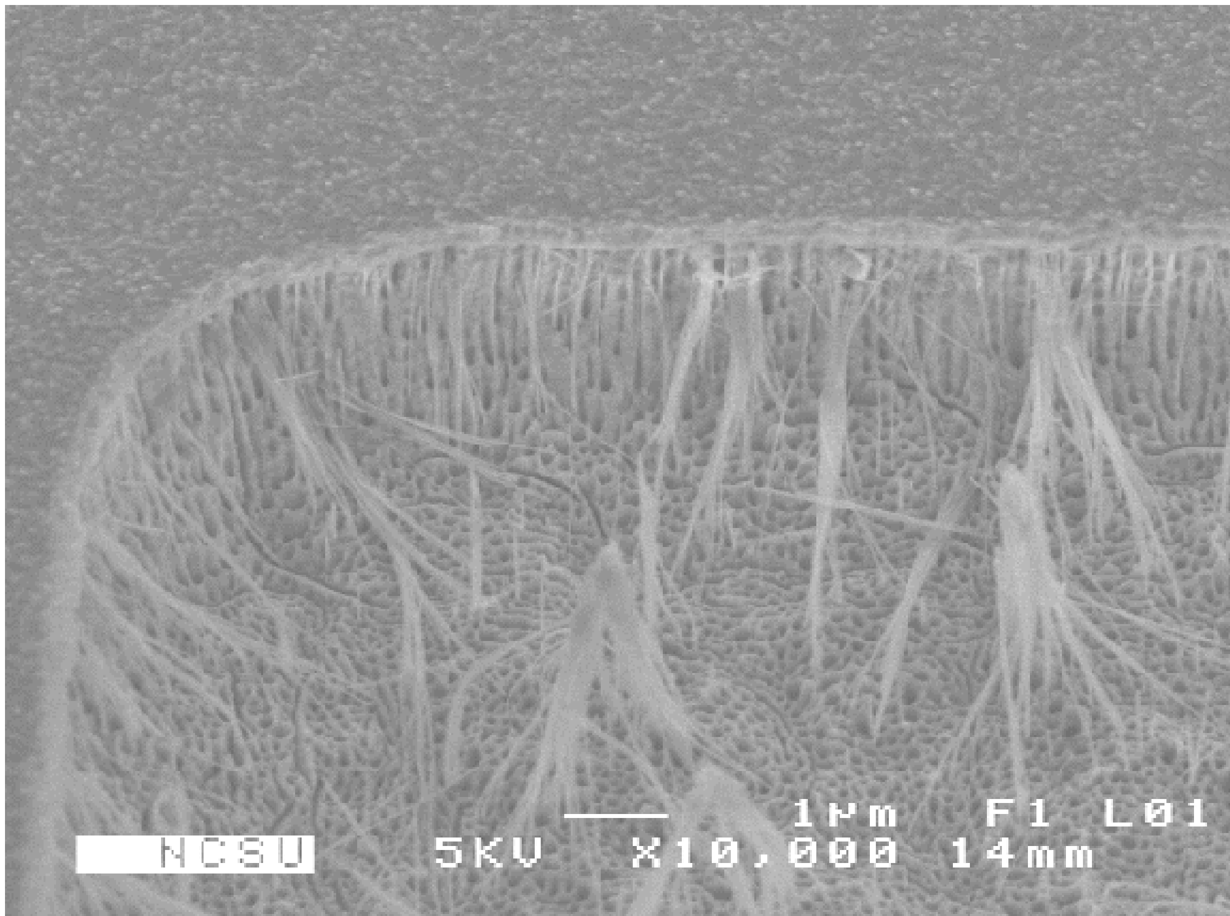


Figure 3a. Whiskers remaining after 15 min. clean-up etch.

© 2004 The Materials Research Society

https://doi.org/10.1557/S1092578300000405 Published online by Cambridge University Press

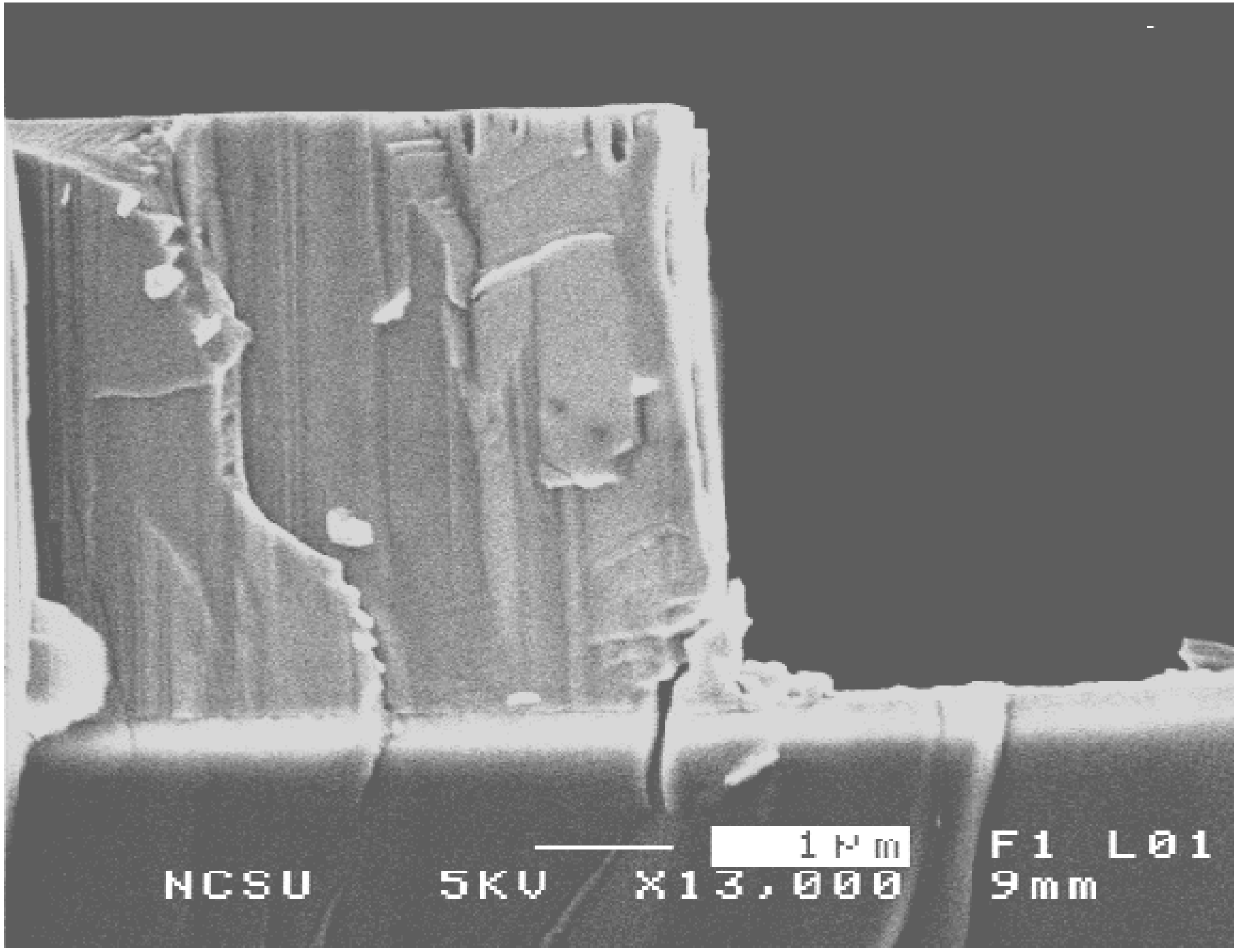


Figure 3b. Line-patterned GaN after 3 hr. PEC etch in H_3PO_4:H_2O at pH=3 followed by 30 min. clean-up etch in 2M KOH.

© 2004 The Materials Research Society

https://doi.org/10.1557/S1092578300000405 Published online by Cambridge University Press

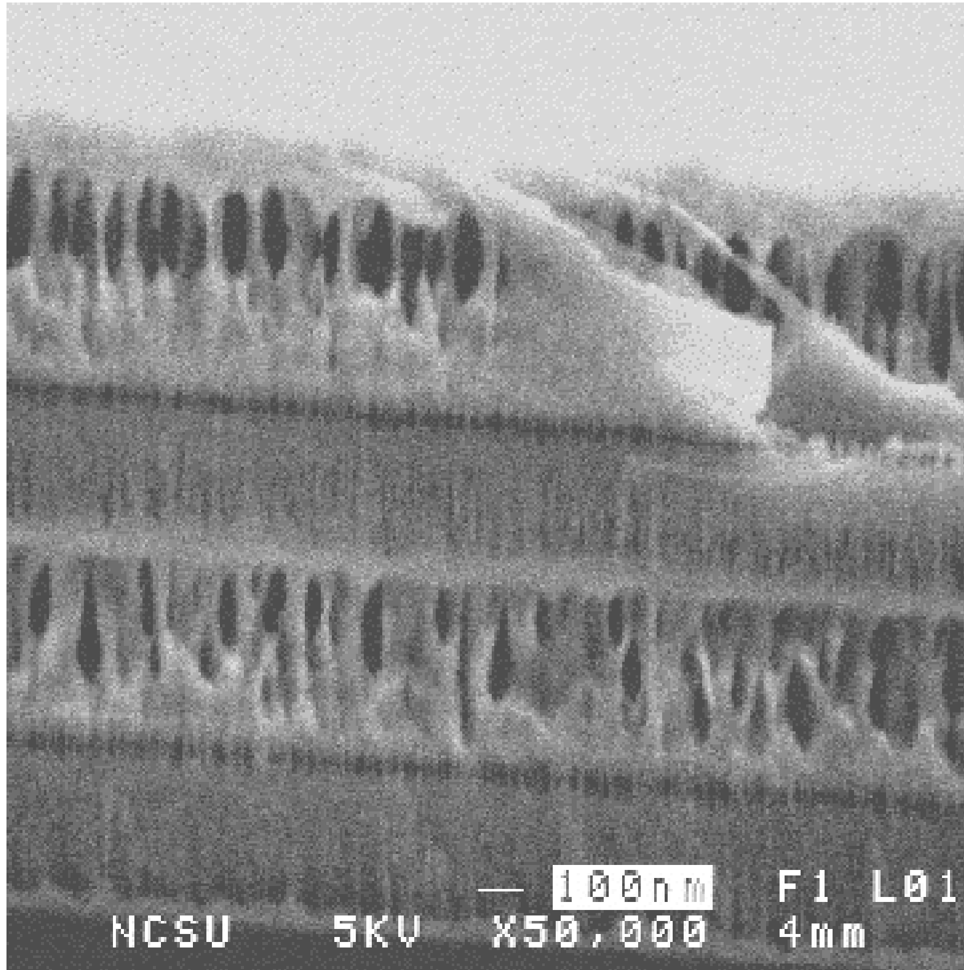


Figure 4. PEC-etched AlGaN/GaN heterostructure showing good selectivity between the AlGaN and the GaN layers.

© 2004 The Materials Research Society

https://doi.org/10.1557/S1092578300000405 Published online by Cambridge University Press

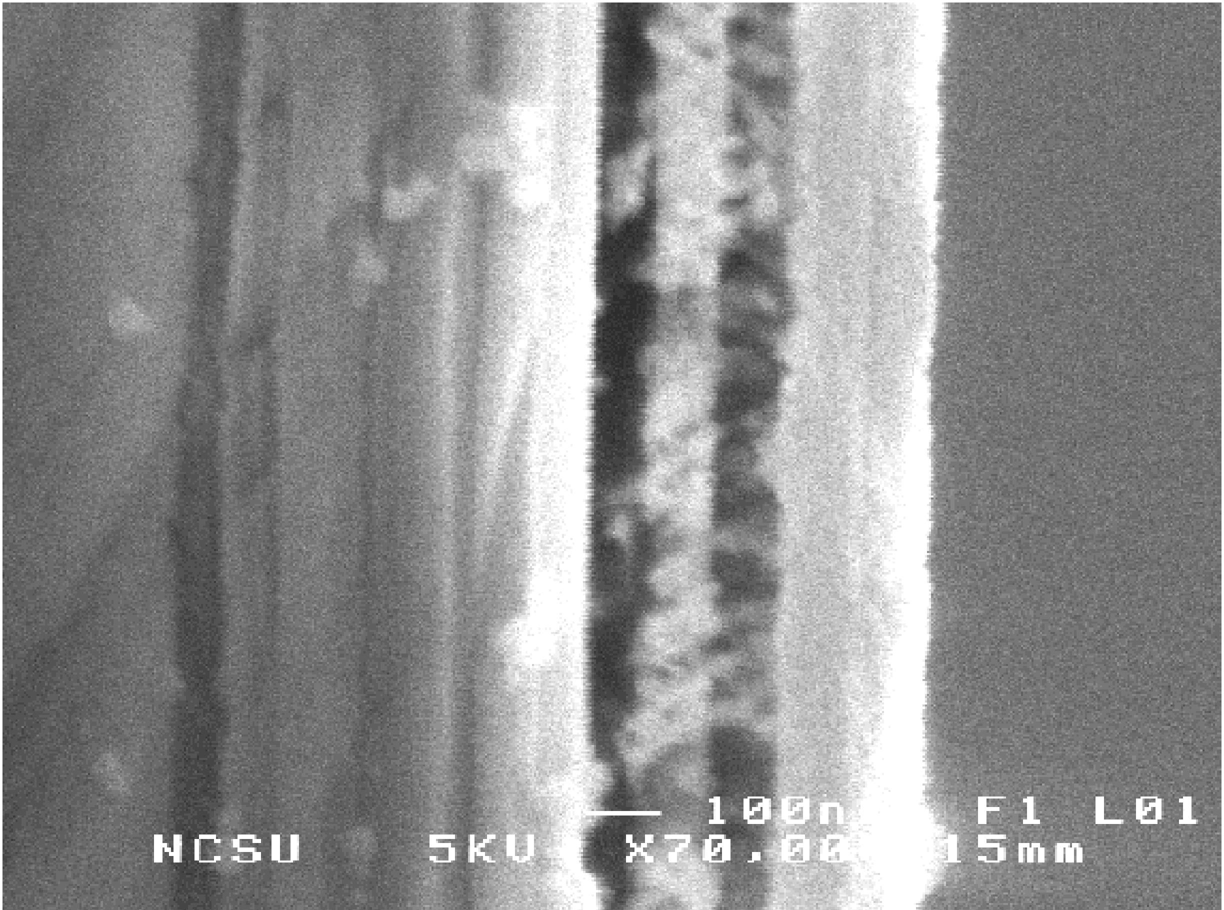


Figure 5. PEC-etched AlN/GaN/AlN sample after 3 hr. etch in 2:25 H_3PO_4:H_2O.

TABLES

Table 1. Comparison of room temperature PEC etch rates for GaN and AlN under Hg arc illumination.

Electrolyte	Concen.	I_{ph} [μA]	GaN etch rate [nm/min]	AlN etch rate [nm/min]
KOH	0.02 M	150	42	0
KOH	0.04 M	150	51	0
H_3PO_4:H_2O	1:25	40	21	0
H_3PO_4:H_2O (NID GaN)	2:25	60	33	0
H_3PO_4:H_2O (~1E19 cm^{-2} GaN)	2:25	60	83	0
HCl:H_2O	1:10	600	0	0
H_2SO_4:H_2O	1:25	20	0	0
$B_4K_2O_7$	0.1 M	175	0	-
$B_4Na_2O_7$	0.1 M	175	0	-
$C_4H_6O_6$:NaOH):H_2O	2:100	30	0	-
HBrpH=0.67):H_2O	2:100	45	0	-

© 2004 The Materials Research Society

https://doi.org/10.1557/S1092578300000405 Published online by Cambridge University Press