And Development of Thin Film Release of GaN using AlN and AlGaN Buffer Layers for MEMS Applications

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Abstract

Gallium nitride (GaN) is an emerging material for power electronics, high frequency timing, and ultra violet light emitting diodes. Metal organic chemical vapor deposition has been instrumental in the development of high electron mobility transistors (HEMTs). The HEMT is a transistor that utilizes a conductive sheet of electrons that occurs at the interface of GaN and AlGaN, known as the two-dimensional electron gas (2DEG). Interest is growing to use the transduction properties of the 2DEG for sensing. Solid state sensors based on the GaN HEMT have been used for gas, chemical, and biological sensing. Pressure sensing has been demonstrated using etched diaphragms. However, suspended GaN structures for inertial and other forms of mechanical sensing are still far from being realized. The goal of this project is to develop a platform for AlGaN/GaN based microelectro-mechanical systems (MEMS) technology by developing a method for suspending GaN structures using AlN as a sacrificial release layer. The AlGaN etch rates are characterized as a function of aluminum percentage. Additionally, the anisotropic nature of group III-nitride etch rates is characterized. The etch rates perpendicular to the substrate are shown to be two orders of magnitude slower than lateral etch rates parallel to the c-plane.

Introduction

The Stanford Nanofabrication Facility (SNF) recently installed an Axitron metalorganic chemical vapor deposition system (MOCVD) for the growth of group III-nitrides (i.e. GaN, InN, AlN). MOCVD has been instrumental in the development of high electron mobility transistors (HEMTs), transistors fabricated on GaN heterostructures. Since GaN and many III-nitrides are polar semiconductors, the abrupt shift from GaN to a different III-nitride alloy (i.e. AlGaN or InAlN) causes a spontaneous polarization at the interface of the two materials. This creates a positive dipole at the interface, attracting a conductive sheet of electrons between the two materials, known as a two-dimensional gas (2DEG). Previously, GaN HEMTs have been used for power electronics, high frequency timing applications, and blue and ultra violet light emitting diodes. However, an emerging area of interest is developing GaN HEMTs for sensing applications. The 2DEG is also strain sensitive because it is based on a piezoelectric phenomena; therefore GaN HEMT structures are a good candidate for sensing in environments where silicon cannot survive.

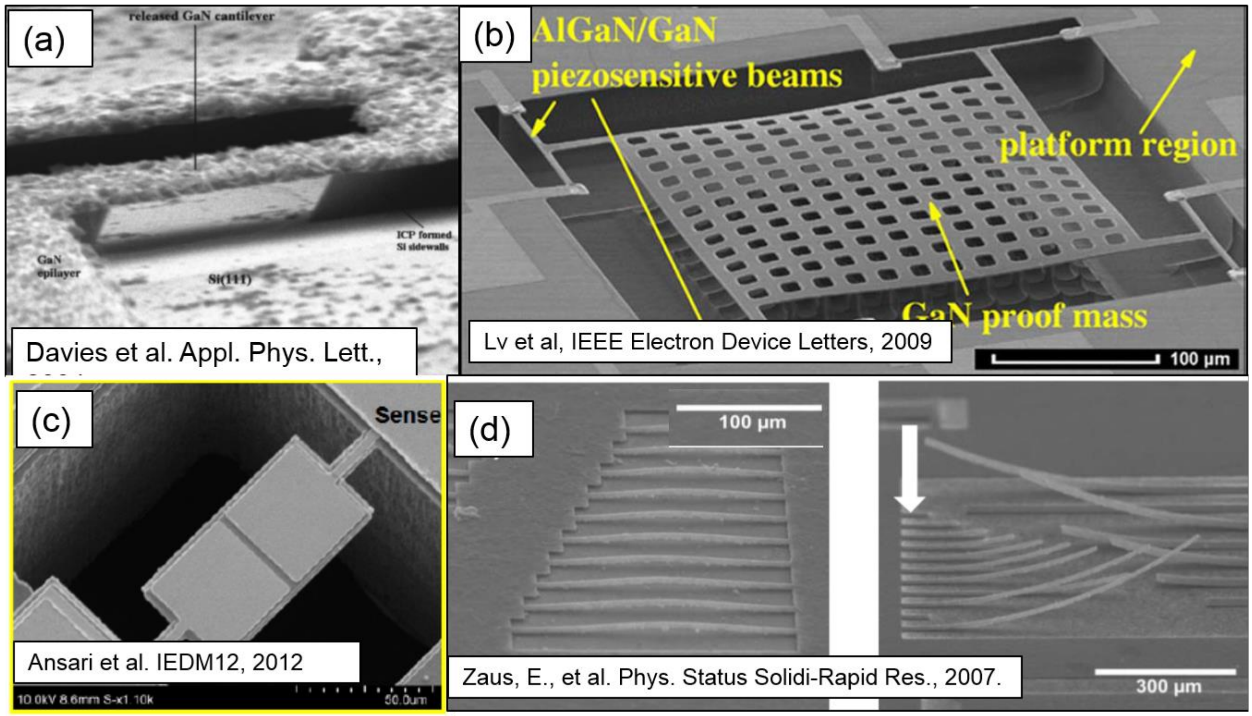

Figure 1 Previous work in the release of GaN and AlGaN/GaN films. (a) MBE GaN/AlN on Si released by Si dry etch and KOH undercut. (b) MOCVD AlGaN/GaN/AlN on Si released by SF_6 + O_2 plasma undercut. (c) MOCVD GaN/AlN on Si released by backside Si ICP etch.(d) MBE GaN/AlN on sapphire released by H_3PO_4 wet etch

The goal of this project is to develop a platform for AlGaN/GaN based microelectro-mechanical systems (MEMS) technology by developing a method for suspending GaN structures using AlN as a sacrificial release layer. The effect of aluminum concentration in AlGaN on etch rates and anisotropic etching was characterized. A literature review of GaN etch techniques is presented and vertical (perpendicular to c-plane) and lateral (perpendicular to $10\bar{1}0$ plane) etch rates of GaN, AlN, and AlGaN are presented.

Previous Work on GaN and AlGaN/GaN Suspension

Past work has been done to evaluate wet etching and dry plasma release methods for AlGaN/GaN[1–4]. Figure 1a-c summarizes a few key works in this field. The GaN layer has been released through Si releases involving KOH etches, dry plasma undercuts of Si with SF_6 and O_2, and backside deep reactive ion etching (DRIE). The AlN buffer layer has also been released under a molecular beam epitaxy (MBE) grown GaN film using a phosphoric wet etch (Figure 1d). The goal of this work is release of an AlGaN/GaN HEMT structure through the wet etching of the AlGaN and AlN buffer layers beneath it (Appendix Figure 12a). This will enable the development of suspended MEMS structures that leverage the AlGaN/GaN HEMT as a sensing layer.

Literature Review of AlN/GaN Wet Etching

Table 1 presents a summary of some of the AlN and GaN wet etch recipes previously reported in literature[5–13]. The main wet etch chemistries are phosphoric acid and

Table 1 Literature Overview of AlN and GaN wet etching. Unless otherwise stated, the etch direction report is parallel to the $10\bar{1}0$ crystal plane (perpendicular to the c plane). Any rates with a (*) next to them were measured parallel to the $11\bar{2}0$ crystal plane. A few papers do not report etch rates and are just used to characterize dislocation etching.

Material	Chemistry	Temp (°C)	Growth	Etch rate	Source
GaN	Phosphoric acid	155	MOCVD	0.4 um/min	1998, Stocker
AlN	Phosphoric acid	170	rf-MBE	7-10 nm/min	2001, Ide
GaN	Phosphoric acid	200	MOCVD, Mg Doped	1 um/min	1976, Shintani
GaN	Phosphoric & Sulfuric acid	250	MOCVD	Not reported, dislocations	2002, Wen
GaN	Molten KOH	250	MOCVD	2 um/min*, 0.4 um/min	1998, Stocker
GaN	30% KOH & ethylene glycol	185	MOCVD	1 um/min*, 0.9 um/min	1998, Stocker
GaN	Molten KOH	350-450	MOCVD	Not reported, dislocations	2002, Kamler
AlN	AZ400K(KOH)	85	MBE	33 nm/min	1997, Zavada
AlN	KOH	25	MBE	2265 nm/min	1998, Vartuli
AlN	AZ400K (KOH)	25	MBE	6-1000 nm/min	1998, Vartuli
AlN	AZ400K (KOH)	20-80	Sputter	1nm - 1um/min	1996, Vartuli
GaN	PEC KOH	25	MOCVD	500 nm/min	2002, Ko
GaN	PEC phosphoric	25	MOCVD	300 nm/min	2002, Ko

potassium hydroxide (KOH). However, these chemistries require high temperatures (>150ºC) to be effective. Etch rates on the order of 1 µm/min have been demonstrated with molten KOH, but this process is not available in the SNF and poses significant safety risks. Comparable etch rates have been demonstrated with room temperature photo-enhanced chemical etching (PEC) with dilute KOH. 150 ºC phosphoric acid anisotropically etches GaN and AlN along the $10\bar{1}\bar{2}$ and $10\bar{1}3$ crystal planes. Heated phosphoric acid (>200 ºC) shows more isotropic etches, but this requires mixing of sulfuric acid to safely increase the boiling point. The GaN and AlN etch rates depend on growth method and conditions. High quality GaN and AlN MOCVD and MBE films demonstrate anisotropic etching, as seen in Figure 2[5]. Thus, it is important to characterize the

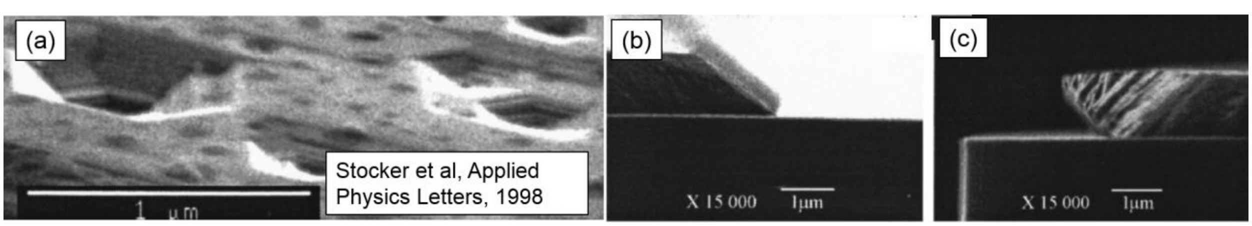

Figure 2 Previous work demonstrating anisotropic etching of MOCVD GaN. (a) GaN etched by 10% KOH in ethylene glycol. (b) GaN etched by H_3PO_4 in the $10\bar{1}3$ direction (c) H_3PO_4 in the $10\bar{1}\bar{2}$ direction.

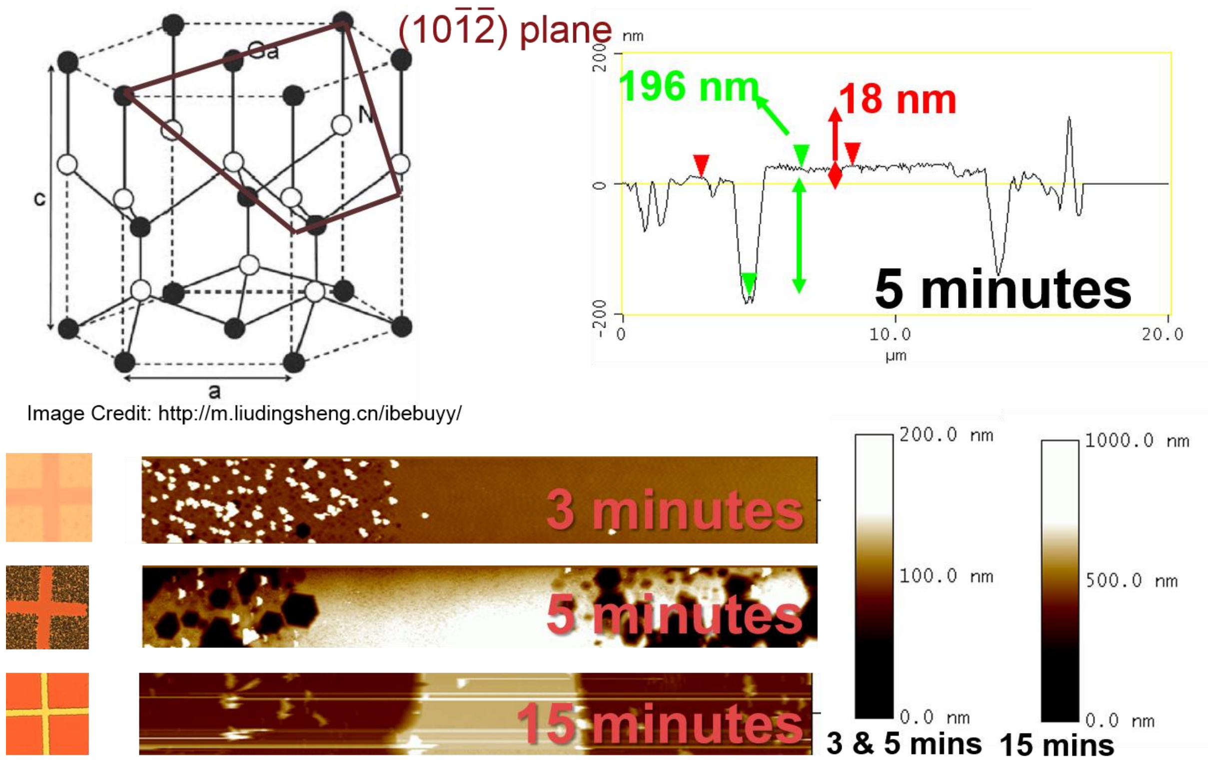

Figure 3 (Top Left) GaN Wurtzite lattice, with 1012 plane drawn in dark red. (Top Right) AFM profile of ALN sample etched in phosphoric acid at 150 ºC for 5 minutes with both C plane etching and large defects profiles. (Bottom) Optical and AFM images of AlN features etched for 3, 5, and 15 minutes from top-bottom. These show a defect-drive etch mechanism.

anisotropic etch characteristics of films grown in the SNF MOCVD III-N tool for suspending structures.

Project Overview

The following tasks were accomplished in this quarter:

1. Identified phosphoric acid (H_3PO_4) as a suitable wet etch chemistry for selective AlN etching over GaN.
2. Identified plasma enhance chemical vapor deposition (PECVD) silicon oxide as a hard mask for the wet etch chemistry.
3. Grew an AlGaN/GaN HEMT wafer using the MOCVD tool.
4. Anisotropic etch rates were characterized, and atomic force microscopy (AFM) was identified as the best tool for measurements of the vertical step heights. 4-50 nm vertical step height was observed. A scanning electron microscope (SEM) was identified as the best tool for in plane etch rate measurements.
5. A PROM committee process was developed to mix 3:1 sulfuric to phosphoric acid by volume to increase the boiling point to 200ºC with preliminary results that show promise.
6. Achieved selective etching of Al(Ga)N versus GaN, and established a ready-to-go process for suspending HEMT!

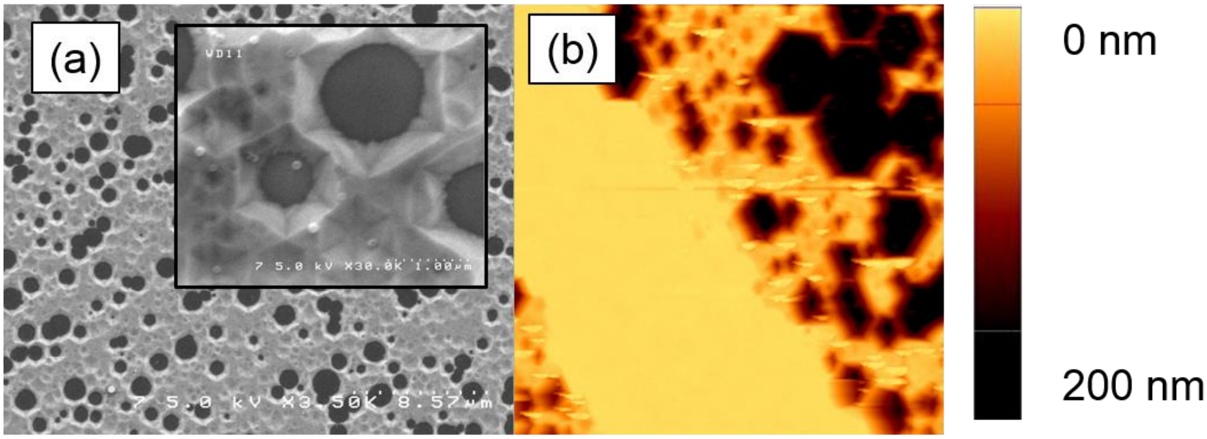

Figure 4 SEM of AlN sample etched for 5 minutes in 150 ºC in phosphoric acid with inset of higher magnification, revaling hexagonal etch pits. (b) AFM image if the same AlN sample.

Wet Etch Characterizations of AlN and AlGaN

Phosphoric acid was selected to study the etch rates of the AlN and (Al)GaN layers on Si substrates. Samples were grown by Dr. Xiaoqing Xu during early MOCVD growth characterizations. PECVD silicon dioxide was patterned using an 6:1 an buffered oxide etch (BOE) on Al(Ga)N samples. Next these samples were dipped in 150ºC phosphoric acid (85%) for varied times, depending on measurable step height. Several dips were required to identify appropriate etch times for each aluminum (Al) concentration. AFM (afm2) was used to measure the step of the samples once the oxide was removed using a 6:1 BOE dip for 5 minutes. Figure 3 shows and AFM profile for the AlN sample etched for 5 minutes in this heated phosphoric acid. There are two drastically different measurements observed: a small step height of 18 nm and a large step height of 196 nm. The large step heights occur at dislocations in the nitride film where faster crystal plane etches are exposed. Figure 3 shows AFM images of AlN samples etched at 3, 5, and 15 minutes. The first sample shows the start of defects forming hexagonal structures. The 5 min sample shows drastic increase in amount and size of these hexagonal defect pits. The 15 min sample shows a relatively smoother surface, which indicates the etch is near complete and the Si substrate serves as an etch stop. The 5 minute etched AlN sample was further characterized by SEM, as shown in Figure 4. These hexagonal etch pits were expected to occur according to our literature review.

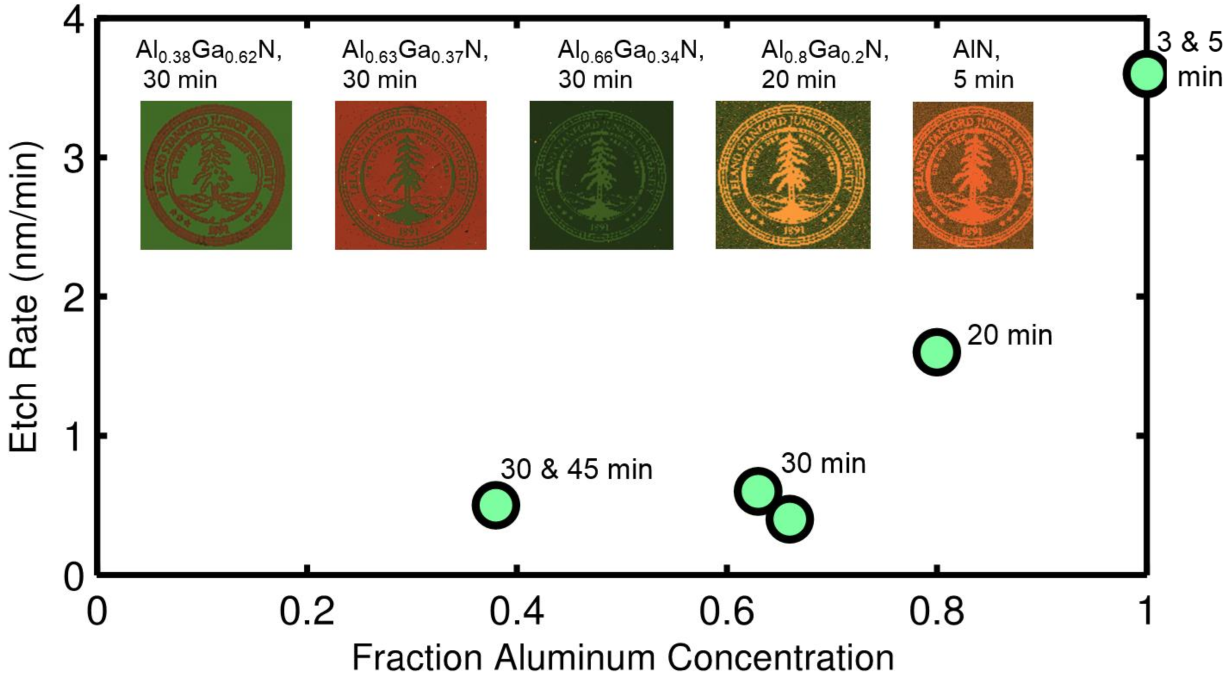

Figure 5 C-plane (vertical) etch rates of AlGaN sampled with varied Al concentration. Insets show optical images of AlGaN sampled etched with Stanford logo pattern. The data points are annotated with the etch time for each sample measurement – the window of time varies.

Vertical Etch Rate Characterization

The etch rates perpendicular to the c-plane (0001) were measured for varied Al% in different AlGaN/AlN/Si samples. The Al% value was determined through PL measurements done previous to the start of this project (except the 80% Al sample). The etch rates are reported in Figure 5. This data suggests that the increase in Al content leads to a higher etch rate of the AlGaN films.

Lateral Etch Rate Characterization

In order to characterize the lateral etch rates of the group III-nitride films, the phosphoric etches were done on samples where the plane perpendicular to the basal plane was exposed. The experimental methodology is illustrated in Figure 6. The etch rates in the

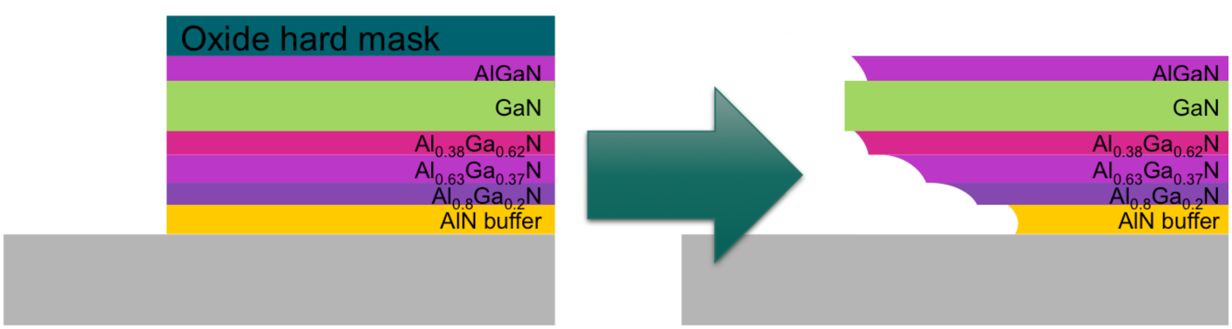

Figure 6 Schematic illustration of measurement method used to characterize lateral etch. The AlGaN/GaN HEMT layer was plasma etched in Ox III-V and then wet etched in a wet phosphoric etchant, revealing the anisotropic etch rate of the III-nitride films. The AlN buffer was hypothesized to etch faster in plane than the (Al)GaN layers.

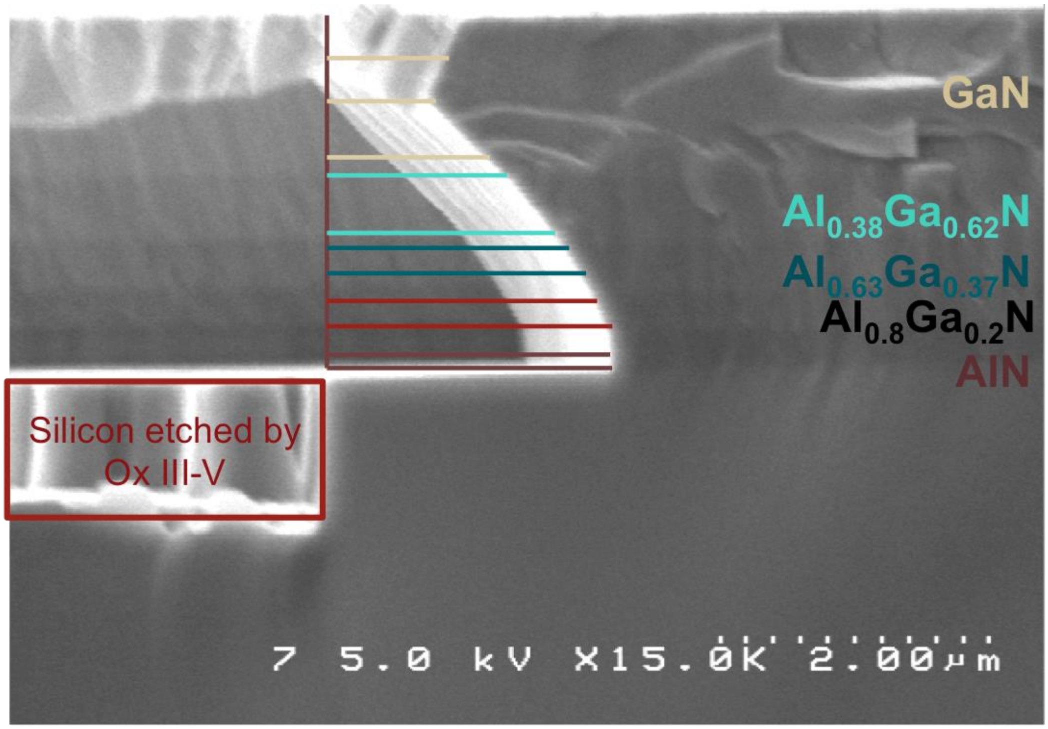

Figure 7 Cross section of the AlGaN/GaN HEMT structure used for lateral etching characterization. This cross section is from the sample that was etch in 3:1 sulfuric/phosphoric acid. The dips into the silicon substrate on the bottom left are artifacts from the plasma etch step, and can be used as a reference line to measure lateral etch rates of each film.

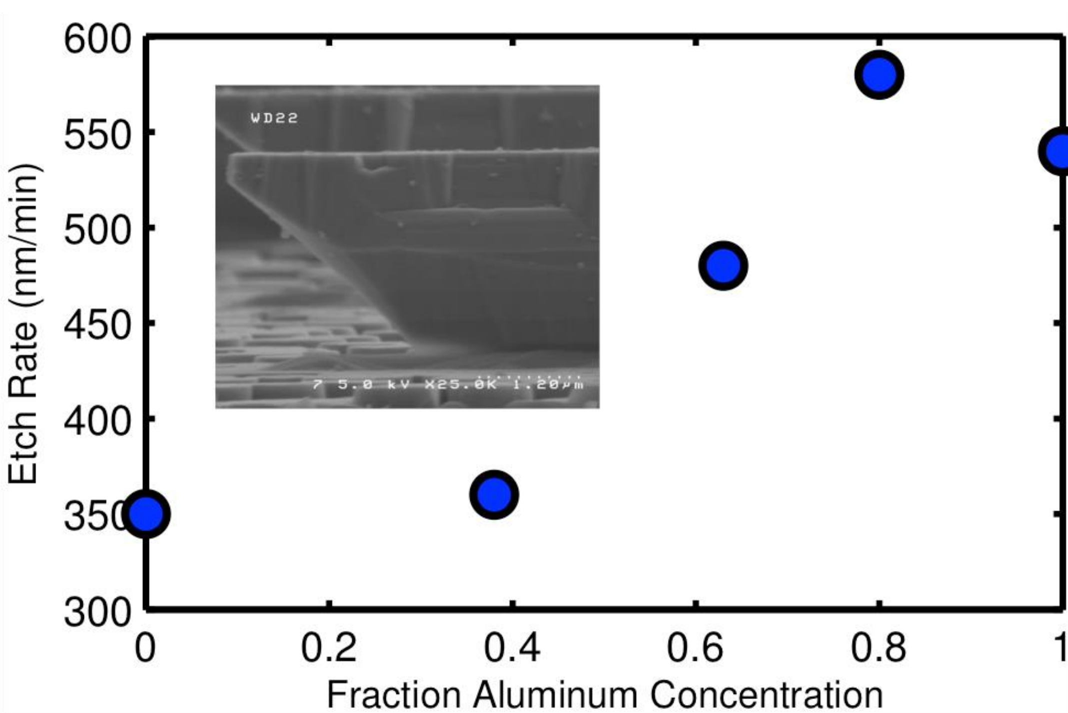

Figure 8 Lateral etch rates (parallel to 0001 crystal plane) in 150ºC phosphoric acid for the AlGaN/GaN HEMT layers varied with Al%. Inset is an SEM image of sample used for measurements.

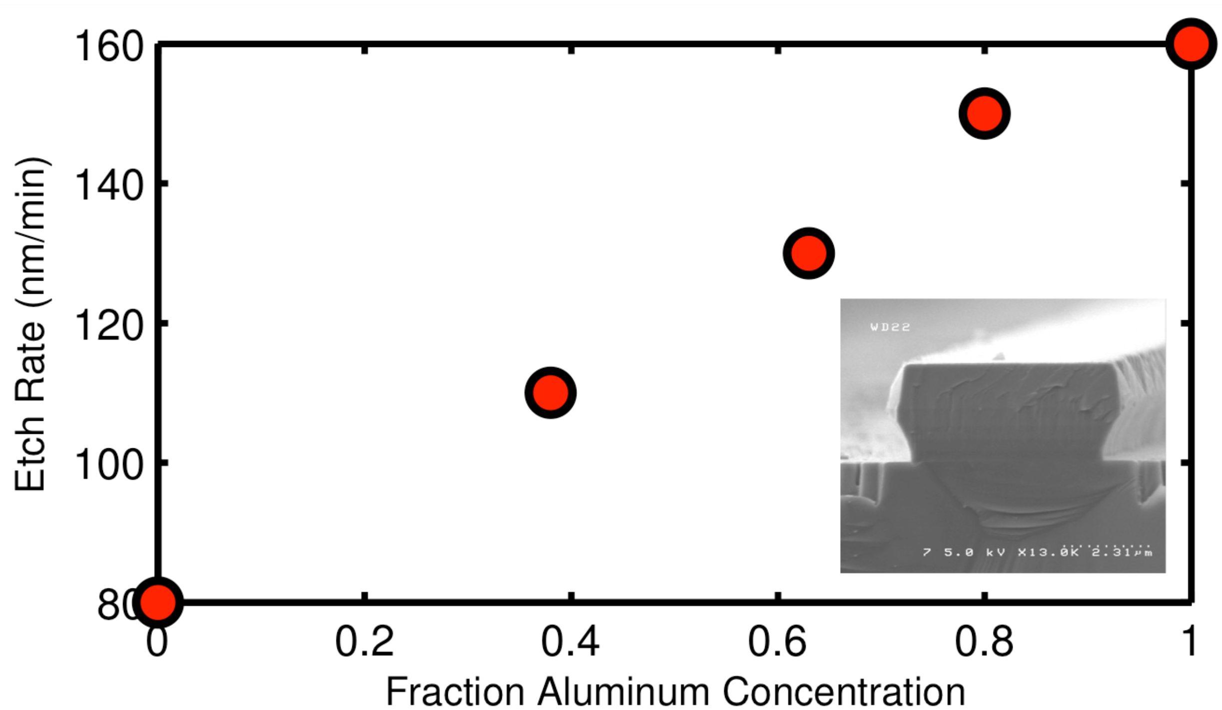

Figure 9 Lateral etch rates (parallel to 0001 crystal plane) in 200ºC 3:1 sulfuric/phosphoric acid for the AlGaN/GaN HEMT layers varied with Al%. Inset is an SEM image of sample used for measurements.

lateral direction were measured for AlN, GaN, and AlGaN films using a wafer that was grown using the 000_HEMT_on_Si recipe on the Axitron-CCS MOCVD tool (see Appendix). A 2 µm-thick oxide hard mask was deposited on pieces of HEMT wafer with the CCP-PECVD tool. The oxide was patterned with standard lithography techniques and a 5 minute 6:1 BOE. After stripping the resist, the Oxford III-V etcher was used to anisotropically etch the HEMT stack. The recipe used is described in the Table 3 in the appendix. The samples were then etched in 150ºC phosphoric acid for 5 minutes, 15 minutes, and 45 minutes and in 200ºC 3:1 sulfuric acid to phosphoric acid for 10 minutes. The oxide was then striped in 6:1 BOE for 5 minutes.

To measure the lateral etches rates, the samples were cleaved and the cross sections were images with the Hitachi SEM. The etch rates of the III-nitride films was measured perpendicular to the $(10\bar{1}0)$ direction, i.e. measured along the horizontal direction. Figure 7 exemplifies the measurements made of the etch distance using a cross-sectional SEM image. The different GaN, AlN, and AlGaN layers can be discerned in the SEM. The silicon was anisotropically etched by the Oxford III-V. Since the hard mask was removed before imaging these structures, the silicon etched during the dry etch was used as the initial point of the III-nitride films location.

Figures 8 and 9 plot etch rate perpendicular to the $(10\bar{1}0)$ plane as a function of Al concentration in 150°C phosphoric acid and 200°C 3:1 sulfuric to phosphoric acid. The

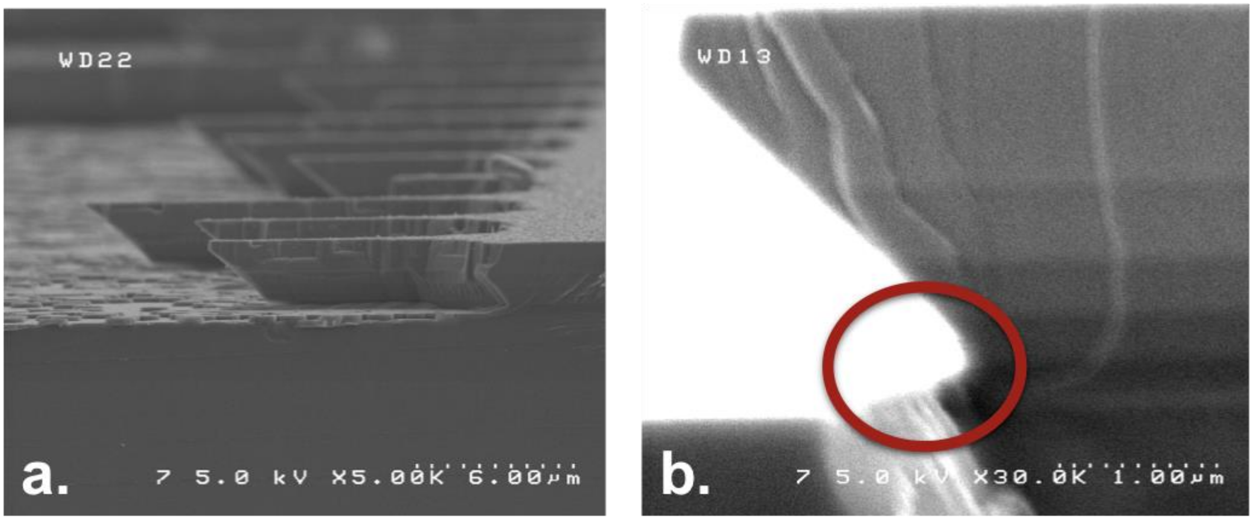

Figure 10 (a) SEM image of a pre-released cantilever array etched in 150 ºC phosphoric acid for 5 minutes. (b) SEM image of a HEMT structure with undercutting also etched in 150ºC phosphoric acid for 45 minutes, revealing an AlN crystal plane with different dominant etch plane(~21º).

etch rate of the films in 150°C phosphoric acid are not montonically increasing with aluminum concentration. The AlN appears to etch slightly slower than the $Al_{0.8}Ga_{0.2}N$ film. It can be seen in Figure 10b that the AlN appears to be dominantly etched on a different plane. This is seen in the samples dipped in 150°C phosphoric acid for 5 minutes and 45 minutes but not in the 200°C acid mixture. This could explain why the AlN etch rate is slower than the GaN etch rates. The angle between the horizontal and the exposed plane is about 46º, which indicates that $(10\bar{1}\bar{2})$ is the dominant etch plane.

Figure 10a is a SEM image of narrow cantilever structures etched in 150°C phosphoric acid. These images demonstrate potential for fully released AlGaN/GaN structures based on the anisotropic nature of the etch.

Conclusions

The vertical and lateral GaN, AlN, and AlGaN etch rates are summarized in Figure 11. The lateral etch rates (perpendicular to $(10\bar{1}0)$) are higher than the vertical etch rates (perpendicular to c-axis), as predicted in literature. In addition, the increase in Al% generally leads to higher etch rates in phosphoric acid. Increased phosphoric acid temperature by using 3:1 sulfuric to phosphoric results in a monotonically increasing linear trend of etch rate to Al%, shown in Figure 9. It is believed this work demonstrates heated sulfuric and phosphoric acid mixtures will lead to a suspended AlGaN/GaN structure.

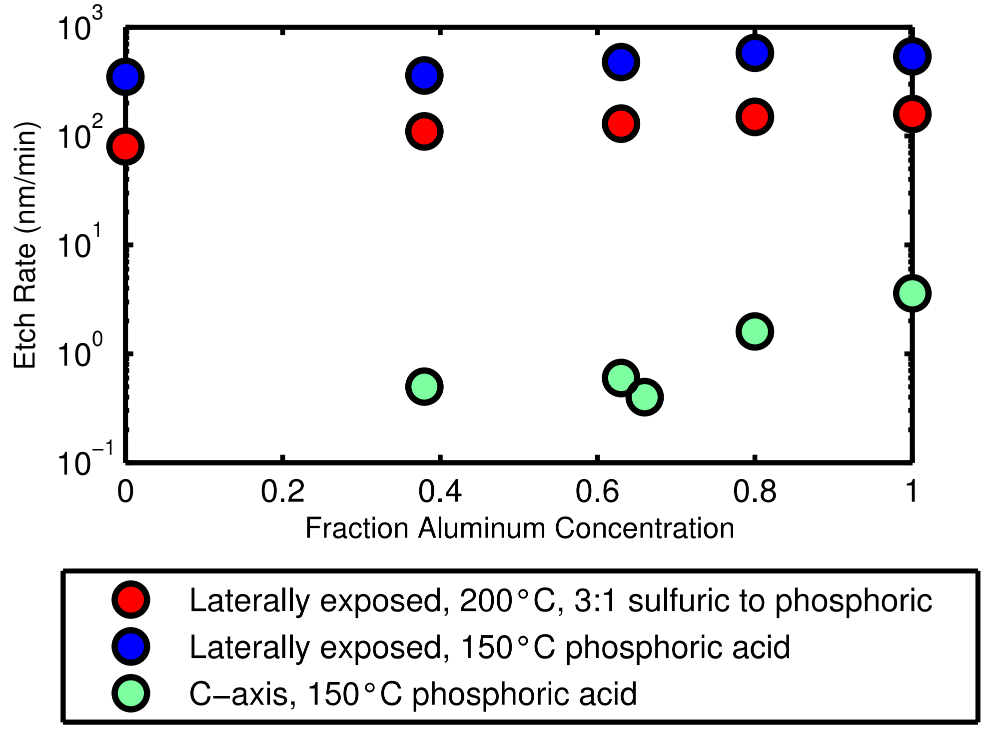

Figure11 Summary of the vertical and lateral etch rates of GaN, AlGaN, and AlN with respect to aluminum concentration for phosphoric acid and sulfuric/phosphoric acid.

Appendix

The following section covers processing details that were not directly related to the work presented, but necessary steps. These include the MOCVD growth of the HEMT wafer and the dry etch recipe in the oxford III-V.

MOCVD growth of HEMT

The recipe 000_HEMTonSi was used to grow the HEMT wafer on a <111> p type Si wafer that was 750 µm thick. Table 3 summarizes the flow rates of the precursors (trimethylaluminum(TmAl) and trimethylgallium(TmGa)), ammonia, and silane flow rates.

Figure 12 (a) Cross section of HEMT wafer films when grown on Si. (b) Image of the AAxitron metalorganic chemical vapor deposition system (MOCVD) (c) Image of the grown HEMT wafer.

Table 2 Summary of the growth process for the HEMT wafer

Step	Precursors and Gases Flow Rates (sccm)				Temperature (ºC)	Pressure (mbarr)	Time (sec)
	TmAl1	**TmGa1**	**NH3**	**SiH4**			
Bake					1230	300	300
Silane			134/100	80	1230	300	600
Low Temp AlN	25/175		134/100		1270	50	720
AlN	25/175		1341/100		1310	50	1800
Al80GaN	45/155	4/196	1341/100		1330	100	1430
Al50GaN	25/175	8/192	1341/100		1330	100	2309
Al20GaN	13.4/186.6	14.1/185.9	1341/100		1330	100	3239
GaN pre		40.5/159.5	6000/100		1270	200	500
GaN bulk		101.25/98.75	6000/100		1295	400	1320
2DEG AlN		7.6/182.4	670/100		1280	100	40
2DEG AlGaN			670/100		1280	100	360
GaN Cap		7.6/182.4	670/100		1280	100	30

A silane baking step is required to protect the surface when growing on a Si substrate, and hydrogen push gas is used to maintain constant flow rates from each source.

Oxford III-V Etch Recipe for GaN and AlGaN

The Oxford III-V was used to isotropically etch the GaN, AlN and AlGaN films of the HEMT. Minmin Hou and Caitlin Chapin previously developed the recipe for etching thin AlGaN films with boron trichloride and chlorine. The etch recipe is detailed in Table 3. The etch rate is 150 nm/min. The samples were etched for 25 minutes. The etch time includes 5 minutes of over etching because variations in dry etch rates between GaN, AlN, and AlGaN are unknown.

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Table 3 Oxford III-V Etch recipe used for AlGaN/GaN stack etch

BCl_3 flow rate	**25 sccm**
Cl_2 flow rate	10 sccm
Pressure	10 mTorr
Forward power	160 W
ICP power	500 W
Etch rate (GaN)	150 nm/min

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