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Herbert Wertheim College of Engineering
UNIVERSITY of FLORIDA

POWERING THE NEW ENGINEER TO TRANSFORM THE FUTURE

MATERIALS SCIENCE AND
ENGINEERING SWAMP GROUP

Chemical Wet Etching of $Al_{(X)}Ga_{(1-X)}N$ Nanostructures

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Sandia National Laboratories

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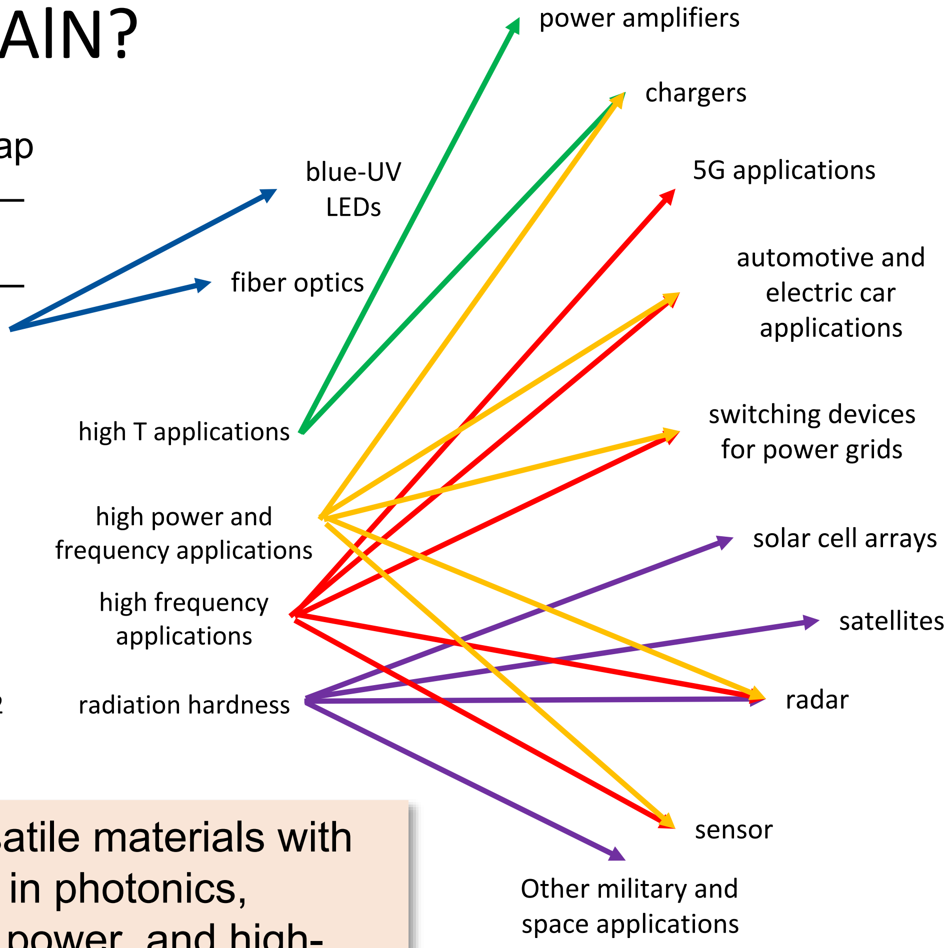
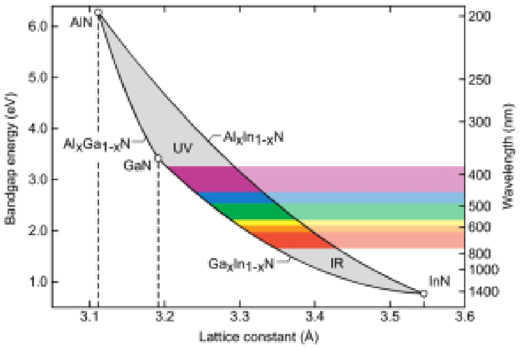
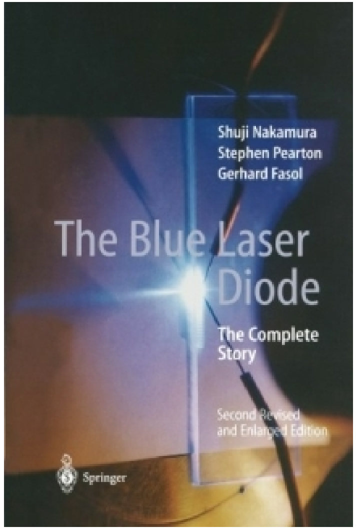
Why GaN-AlN?

- Direct, wide bandgap semiconductors

	GaN	AlN
Bandgap (eV)	3.4	6.0
Thermal conductivity (W/mK)	253	319
Breakdown voltage (MV/cm)	4.9	15.4
Electron mobility (cm^2/Vs)	1500	426
Bond strength (eV/atom)	8.92	11.52





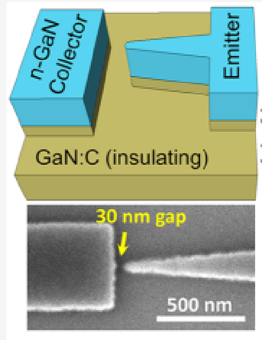


GaN-AlN are versatile materials with applications in photonics, optoelectronics, power, and high-frequency sectors

III-Nitride nanostructures for novel applications

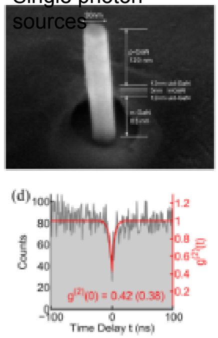
GaN

Vacuum nanoelectronic diode



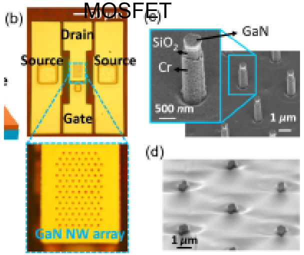
Sapkota et al., ACS Nano, (2021)

Single photon sources



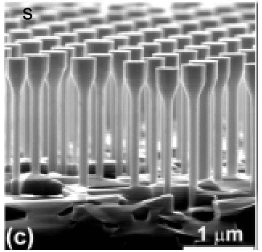
Zhang et al., APL, (2016)

Vertical MOSFET



Yu et al., IEEE Transactions (2018)

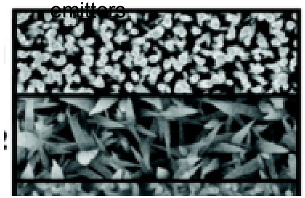
LEDs



Li et al., Optics Express (2011)

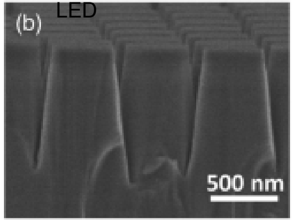
AlGaN

LEDs and field emitters



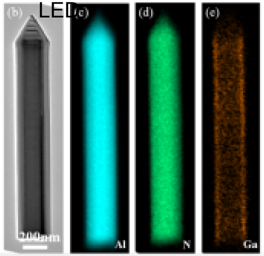
He et al., ACS Nano, (2011)

AlGaN/GaN DUV LED



Zhang et al., Photonics Research (2019)

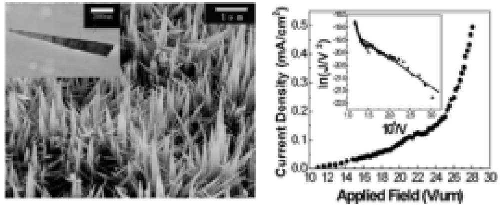
AlGaN/AlN DUV LED



Coulon et al., ACS Appl. Mater. Interfaces, (2018)

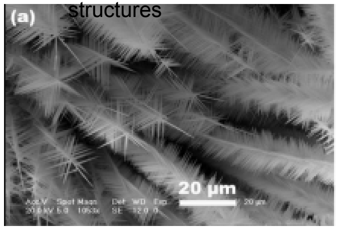
AlN

Field emitter



Liu et al., J. Am. Chem. Soc., (2005)

Ferromagnetic structures

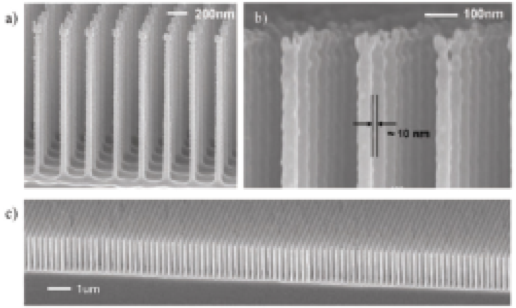


Lei et al., APL, (2009)

How do we make nanostructures?

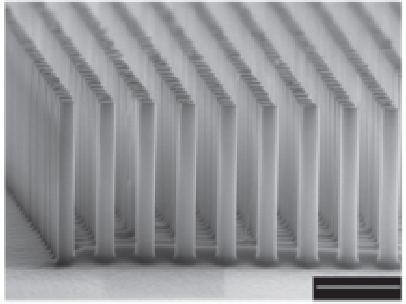
Nanowires via top-down plasma-etch alone

Silicon



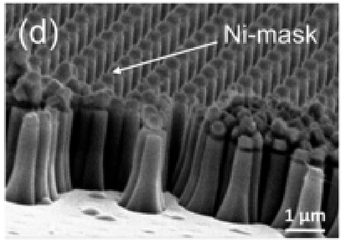
K. J. Morton et al., Nanotechnology, (2008)

GaAs

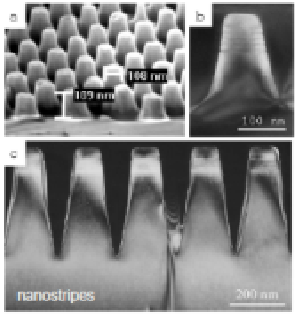


N. Dhindsa et al., Nanotechnology, 25, (2014)

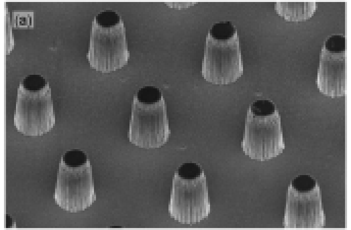
Ga



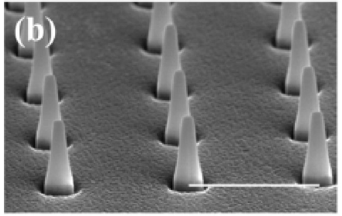
Behzadirad et al., ACS Nano, (2018)



S. Keller et al., J. Appl. Phys. (2006)



Yu et al., Nanotechnology, (2017)



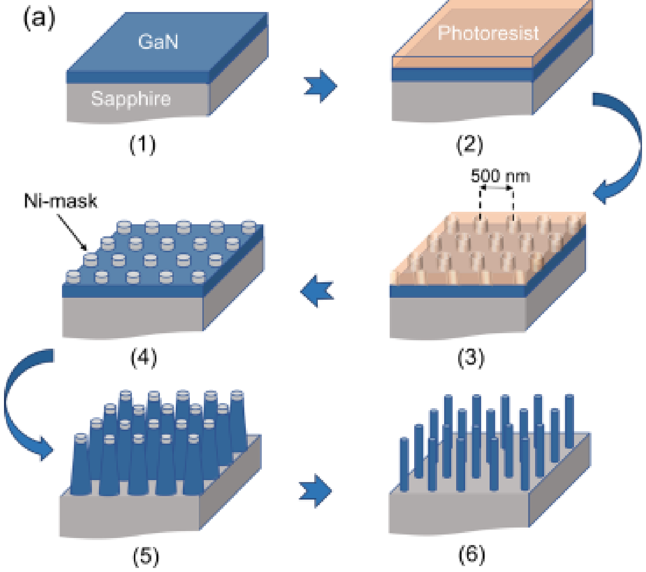
Debnath et al., J. Vac. Sci & Tech., (2014)

- Silicon and GaAs plasma etching yields high aspect ratio nanowires and vertical nanowires
- GaN plasma etching yields tapered sidewalls, base trenching
- Surface roughness and ion damage are an issue

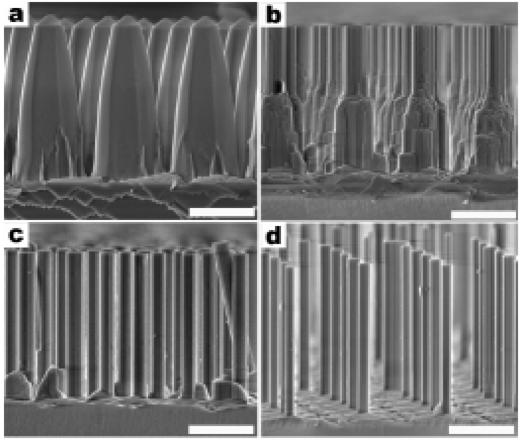
Plasma etching alone inadequate top-down fabrication method for high quality GaN nanowires

Two-step top-down method

- Pioneered by Sandia National Laboratories in 2010
- Plasma etch followed by ***anisotropic*** wet etch
    - Remove surface damage and improve upon sidewall

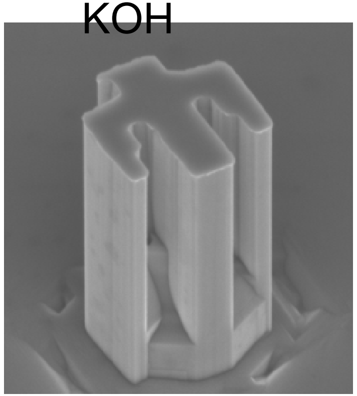


Behzadirad et al., ACS Nano, (2018)



Q. Li et al., Opt. Exp., (2012)

GaN in KOH



Leung et al., SNL, unpublished

Anisotropic etch?

Chemical etching of III-Nitrides: thought to be inert?

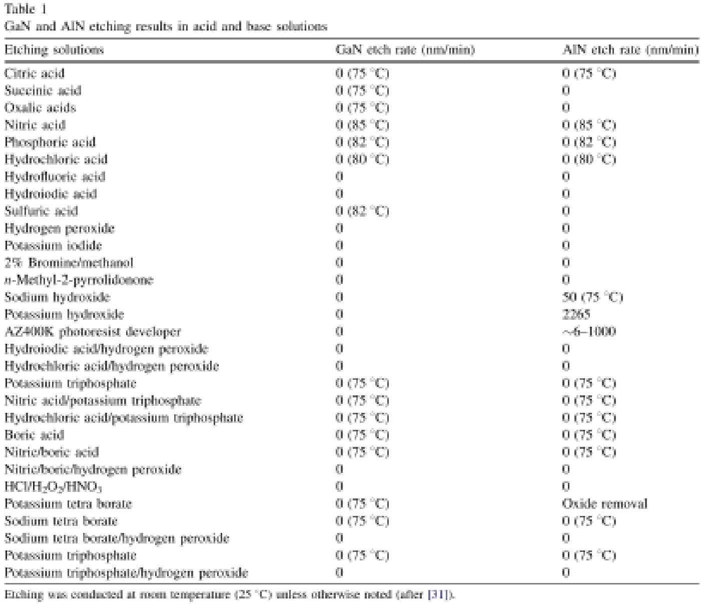
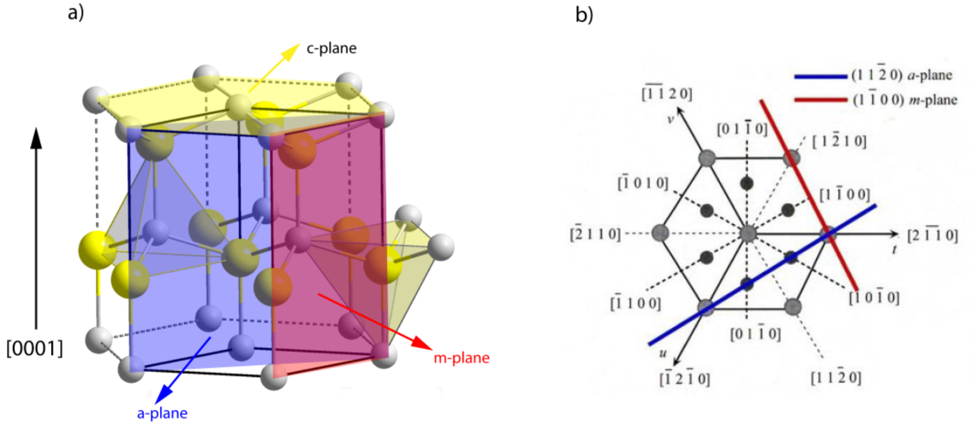


Table 1
GaN and AlN etching results in acid and base solutions

Etching solutions	GaN etch rate (nm/min)	AlN etch rate (nm/min)
Citric acid	0 (75 °C)	0 (75 °C)
Succinic acid	0 (75 °C)	0
Oxalic acids	0 (75 °C)	0
Nitric acid	0 (85 °C)	0 (85 °C)
Phosphoric acid	0 (82 °C)	0 (82 °C)
Hydrochloric acid	0 (80 °C)	0 (80 °C)
Hydrofluoric acid	0	0
Hydroiodic acid	0	0
Sulfuric acid	0 (82 °C)	0
Hydrogen peroxide	0	0
Potassium iodide	0	0
2% Bromine/methanol	0	0
n-Methyl-2-pyrrolidonone	0	0
Sodium hydroxide	0	50 (75 °C)
Potassium hydroxide	0	2265
AZ400K photoresist developer	0	~6–1000
Hydroiodic acid/hydrogen peroxide	0	0
Hydrochloric acid/hydrogen peroxide	0	0
Potassium triphosphate	0 (75 °C)	0 (75 °C)
Nitric acid/potassium triphosphate	0 (75 °C)	0 (75 °C)
Hydrochloric acid/potassium triphosphate	0 (75 °C)	0 (75 °C)
Boric acid	0 (75 °C)	0 (75 °C)
Nitric/boric acid	0 (75 °C)	0 (75 °C)
Nitric/boric/hydrogen peroxide	0	0
$HCl/H_2O_2/HNO_3$	0	0
Potassium tetra borate	0 (75 °C)	Oxide removal
Sodium tetra borate	0 (75 °C)	0 (75 °C)
Sodium tetra borate/hydrogen peroxide	0	0
Potassium triphosphate	0 (75 °C)	0 (75 °C)
Potassium triphosphate/hydrogen peroxide	0	0

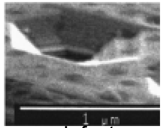
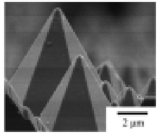
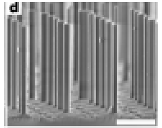
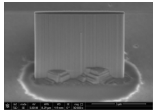
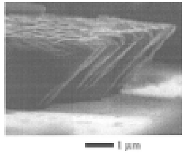
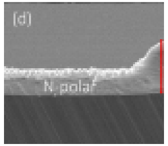
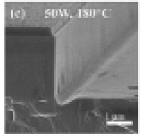
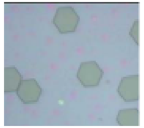
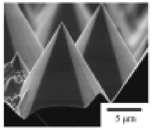
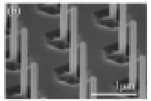
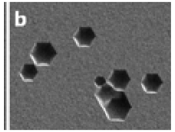
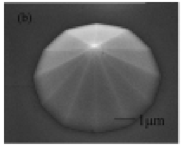
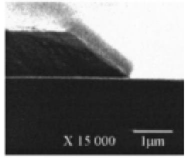
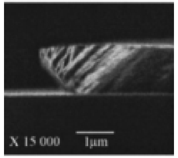
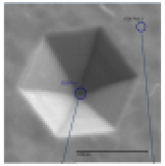
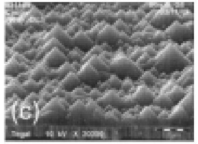
Etching was conducted at room temperature (25 °C) unless otherwise noted (after [31]).

Zhuang & Edgar
(2005)



Anisotropic etchants exploit crystalline properties to remove material in specific directions

Prior etching of crystalline $Al_{(X)}Ga_{(1-X)}N$

	GaN			**AlGaN**			**AlN**		
	polar	non-polar	semi-polar	polar	non-polar	semi-polar	polar	non-polar	semi-polar
Alkaline	 +c, defects  -c, hex. pyramids	 vertical NWs  walls	 undercut profiles	+c, defects  -c, pyramids	 m-plane wall ? Pre-defined structures?	?	 +c, defects  -c, hex. pyramids	 vertical NWs ? Walls? Etch progression?	?
Acidic	 +c, defects  -c, dodec. pyramids	? Pre-defined structures? Bulk crystal?	  tapered and undercut profiles	 +c, defects ? -c-plane etch?	? Pre-defined structures? Bulk crystal?	?	+c, defects  -c, pyramids	? Pre-defined structures? Bulk crystal?	?

Does a better understanding of etching GaN in acids/bases translate to AlGaN and AlN?

Motivation and thesis structure

Motivation: build off two-step top-down approach, explore $Al_{(X)}Ga_{(1-X)}N$ substrates and extend method to other etch chemistries

How is the alkaline etching of nanostructures affected by the substrate Al content?

Alkaline Etching of AlGaN

- Directionally resolved non-polar etch rates and energetics in KOH
- Macroscopic etch progression
- Non-polar and semi-polar geometries
- Etching Barrier Index (EBI)

Acidic Etching of GaN NWs

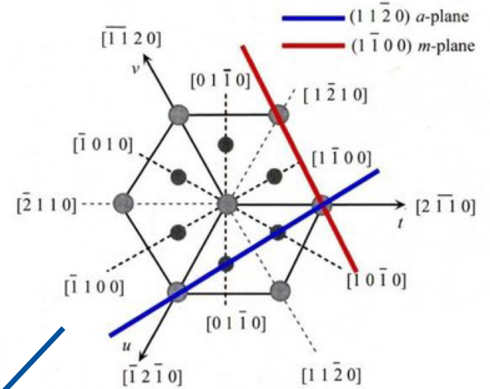
Motivated by

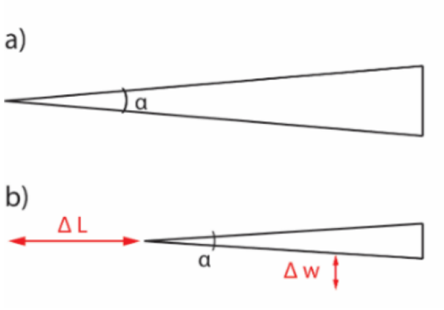
- Lack of fundamental understanding and experimental results
- Desire for vertical, atomically smooth sidewalls in AlGaN/AlN substrates

- Directionally resolved etch rates and energetics
- Macroscopic etch progression
- Previously unseen geometries
- Field emission study of GaN NWs

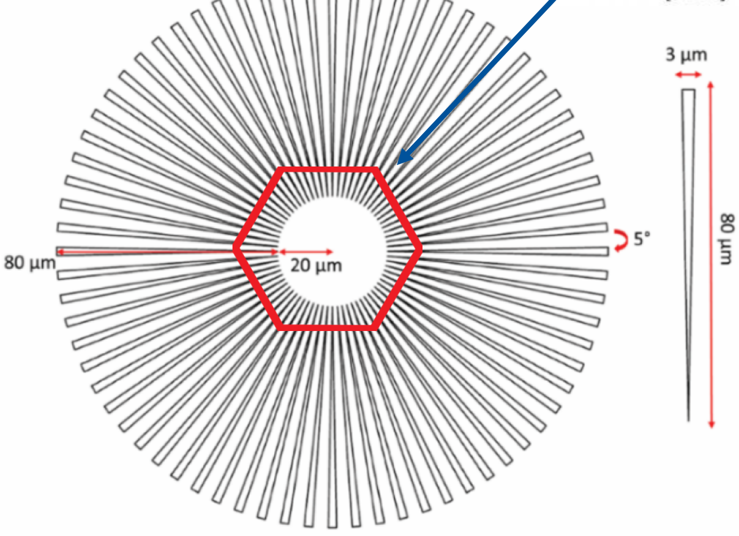
Wagon wheel: non-polar etch rate method

- Based on geometric amplification inherent to the etching of wedges
- Used previously in Si/SiGe etching experiments*
- *a*- and *m*- planes are perpendicular to each other
- Amplifies etch 53X



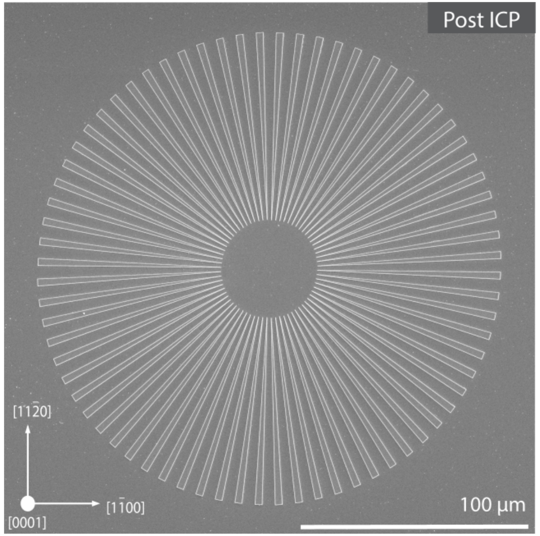


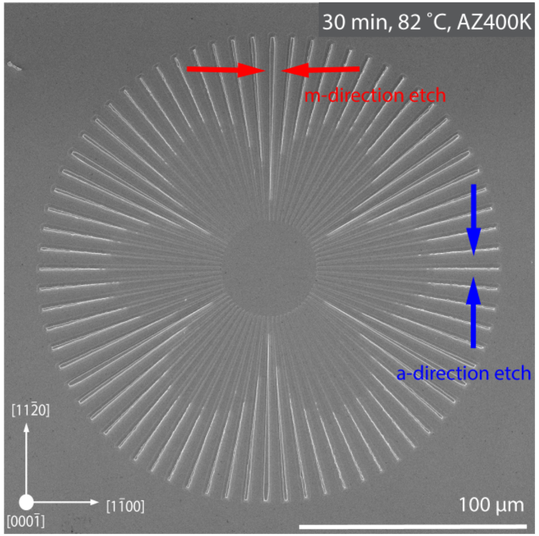
$$\Delta w = \Delta l * \sin\left(\frac{\alpha}{2}\right)$$

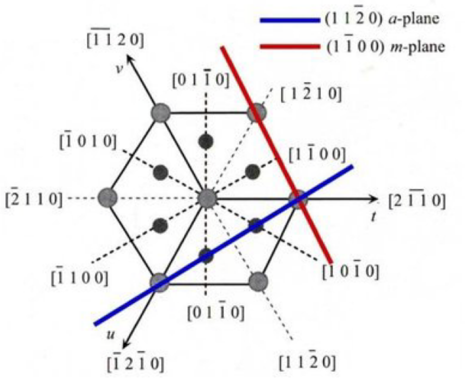


* Pacco et al., Nanoscale Research Letters, (2019)

GaN in KOH: directionally defined etch rates


Post ICP


30 min, 82 °C, AZ400K

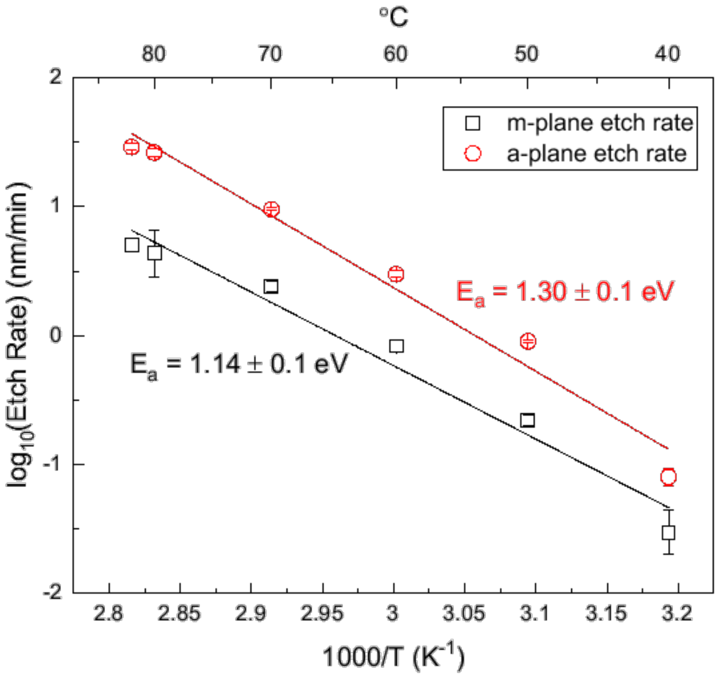


Temp (°C)	m-plane rate (nm/min)	a-plane rate (nm/min)
40	0.03 ± 0.01	0.08 ± 0.01
50	0.22 ± 0.02	0.91 ± 0.03
60	0.83 ± 0.08	3.0 ± 0.2
70	2.4 ± 0.2	9.5 ± 0.2
80	4.3 ± 1.8	26 ± 2
82	5.0 ± 0.6	29 ± 2

- Hexagonal crystal structure apparent with rosette pattern appearance
- Clear distinction between *a*- and *m*-plane etch rates
- *a*-plane etches ***faster*** than *m*-plane

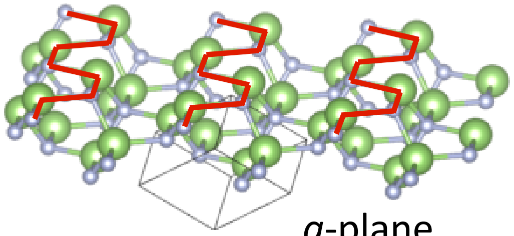
What about the activation energy?

GaN in KOH: activation energy of etching

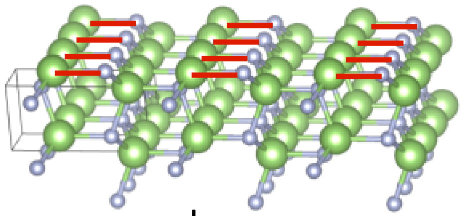


- Activation energy higher for *a*-plane than *m*-plane
- Surface energy in meV/Å^2
  - Ga-N-Ga-N chains vs. Ga-N dimers

Surface Plane	Dreyer et al.	Li et al.	Zhang et al.	Northrup and Neugebauer	Jindal and Shahedipour-Sandvik
m- $[10\bar{1}0]$	122	124	102.1	118	136.7
a- $[11\bar{2}0]$	125	132	106.0	123	158.8



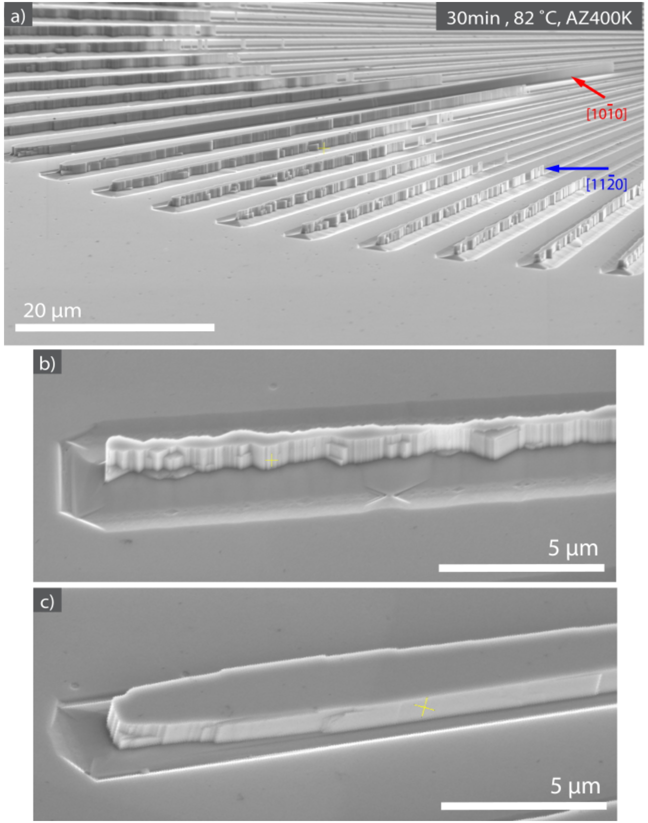
a-plane



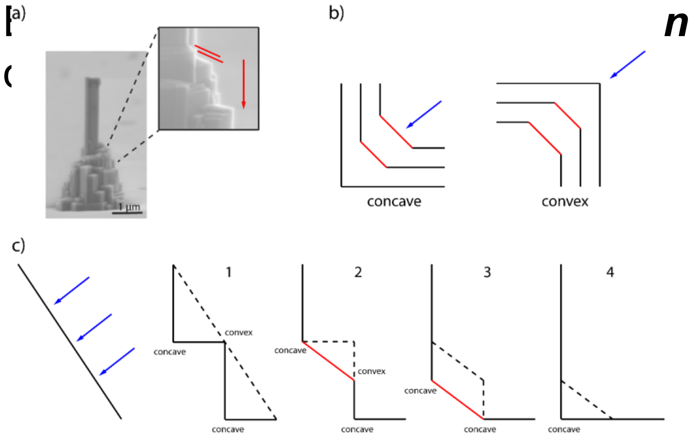
m-plane

a-plane: higher activation energy and faster etch rate

GaN in KOH: microfaceted etch evolution



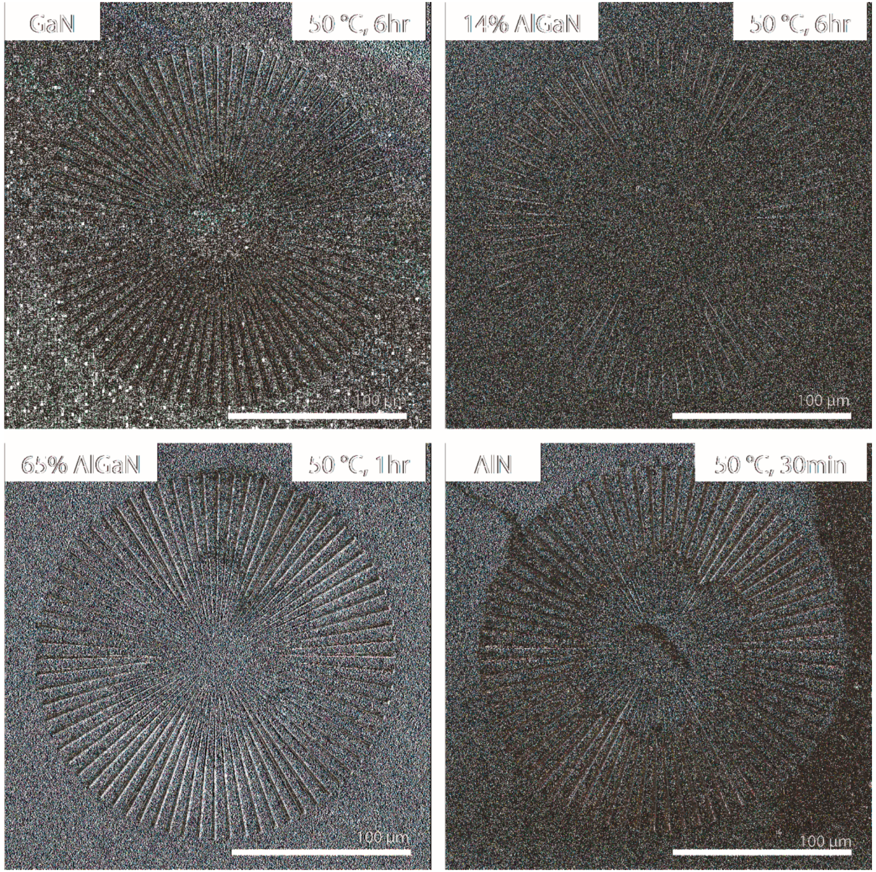
- Etches via appearance and disappearance of microfacets
  - Triangular microfacets on *a*-plane
  - Rectangular microfacets on *m*-plane
  - Macroscopic etch mechanism presented by Sandia Labs
- I **n** etch rate in *m*-
  (

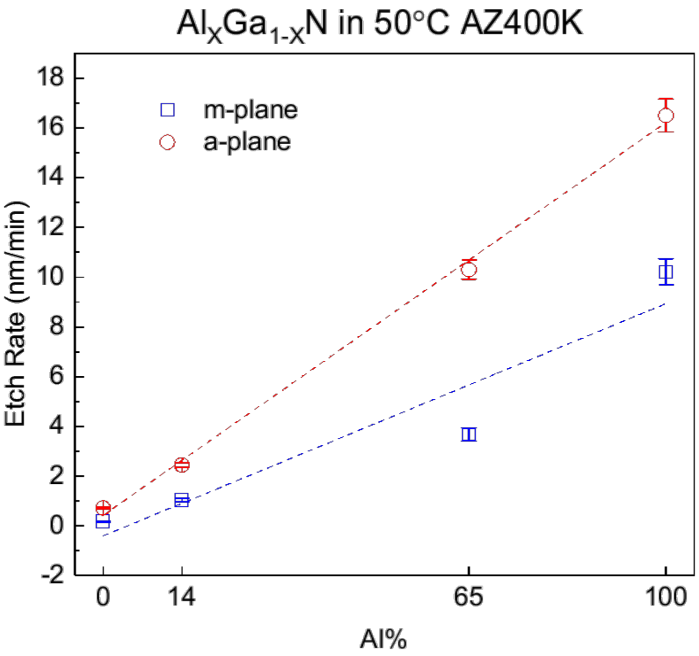


Sandia National Labs, unpublished (2016)

More etch nucleation sites on *a*-plane

Effect of Al content on etch rate at constant temp

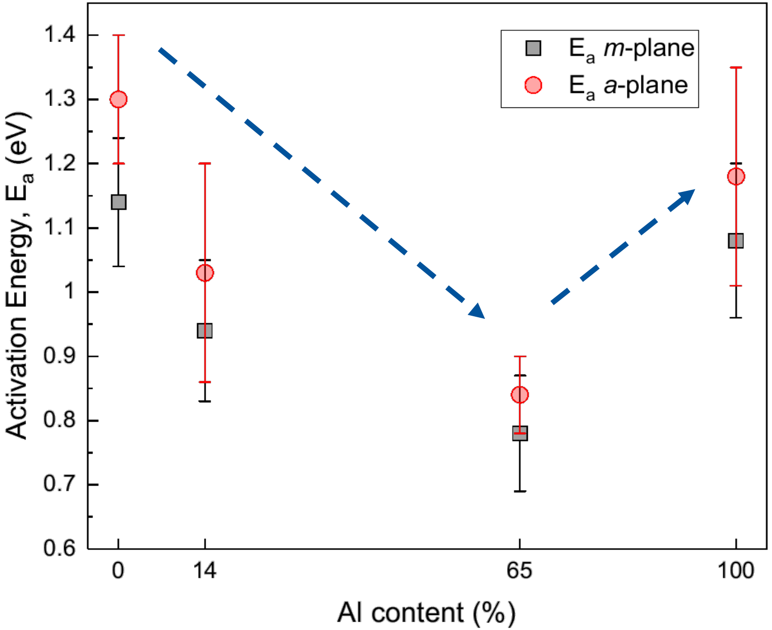




Increasing Al content increases etch rate of non-polar planes in KOH (AZ400K) at all temperatures

Effect of Al content on activation energy of etching

$$rate = A\,e^{-\frac{E_a}{k_B T}}$$



- Activation energy higher for *a*-plane than *m*-plane
- Activation energies highest for GaN, followed by AlN
- Lower activation energies for ternary alloy consistent with faster etch rates
  - Crystal quality
- Inconsistency with AlN trends?

Highest etch rate should indicate lowest activation energy?

Surface and Gibbs free energy for GaN vs AlN

- AlN
  - Bond energy: 11.52 eV/atom
  - Surface energy:
    - *a*-plane: 187 meV/Å^2
    - *m*-plane: 175 meV/Å^2
- GaN
  - Bond energy: 8.92 eV/atom
  - Recalling prior GaN surface energies:

Surface Plane	Dreyer et al.	Li et al.	Zhang et al.	Northrup and Neugebauer	Jindal and Shahedipour-Sandvik
m- $[10\bar{1}0]$	122	124	102.1	118	136.7
a- $[11\bar{2}0]$	125	132	106.0	123	158.8

$2AlN + 3H_2O \xrightarrow{KOH} Al_2O_3 + 2NH_3$ $\Delta \; = -350.1 \; /$

$AlN + 3H_2O \xrightarrow{KOH} Al(OH)_3 + NH_3$ $\Delta \; = -334.2 \; /$

$2AlN + 3H_2O \xrightarrow{KOH} Al_2O_3 + 2NH_3$ $\Delta \; = -350.1 \; /$

$\Delta \; = -334.2 \; /$

$\Delta \; = 1399.9 \; /$

$\Delta \; = 723.5 \; /$

$\Delta \; = 1399.9 \; /$

$GaN + 3H_2O \xrightarrow{KOH} Ga(OH)_3 + NH_3$ $\Delta \; = 723.5 \; /$

Guo et al. APL (2015)

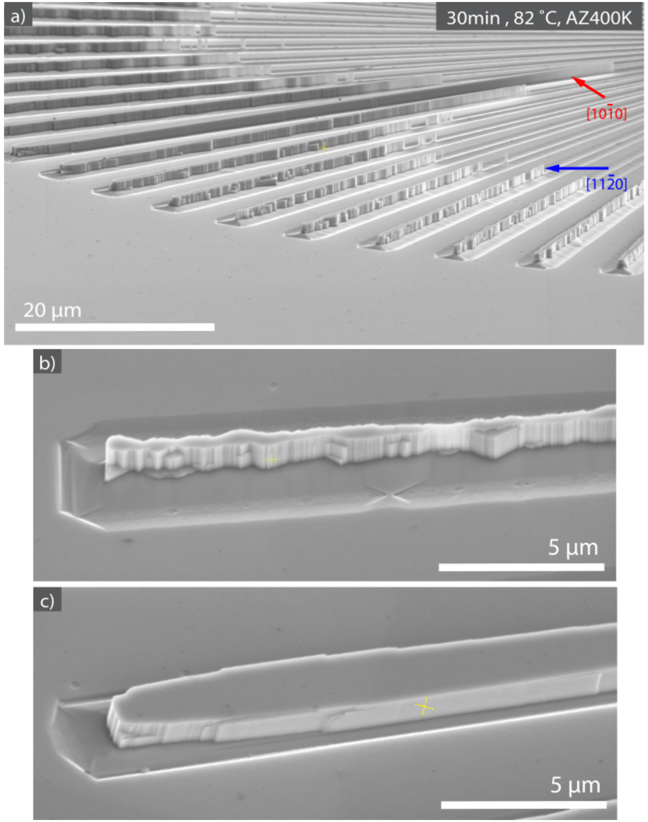
Guo et al. APL (201

Higher surface energy and bond strength leads to higher than anticipated E$_a$.

Gibbs free energy points to faster etch rates.

Higher surface energy and bond strength leads to higher than anticipated E$_a$. Gibbs free energy points to faster etch rates.

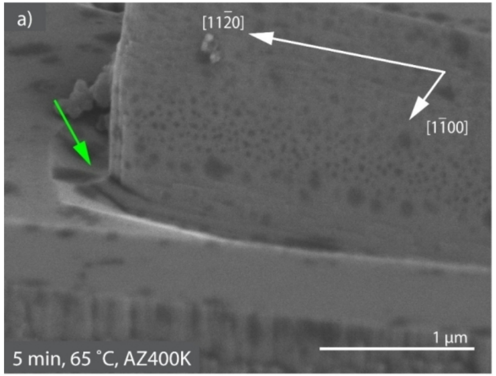
Etch evolution in KOH?

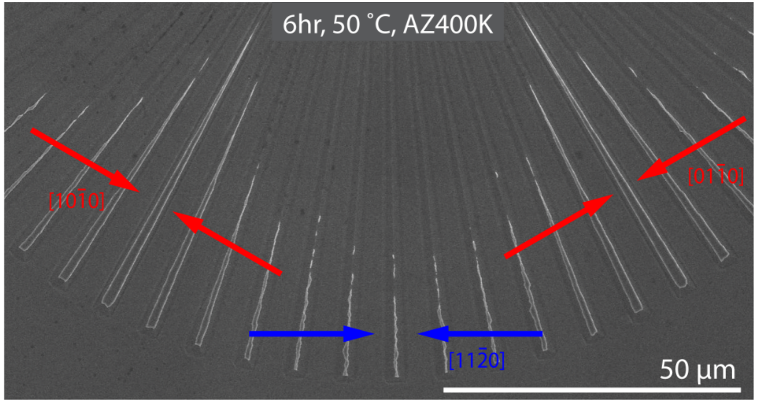


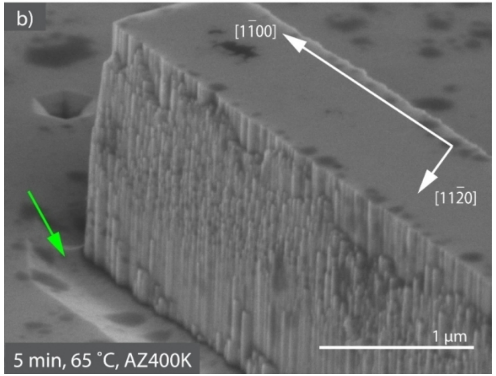
- Microfaceting observed for GaN in KOH

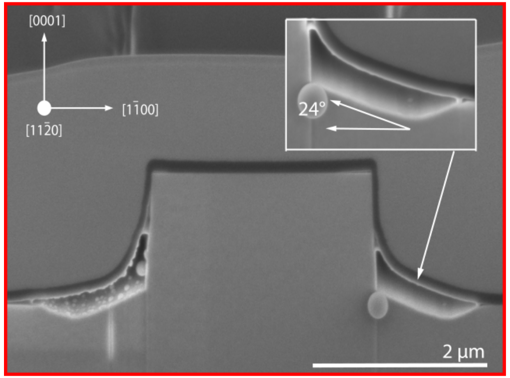
What about AlGaN and AlN?

14% AlGaN in KOH: etch evolution reveals ‘cuboid’ structure



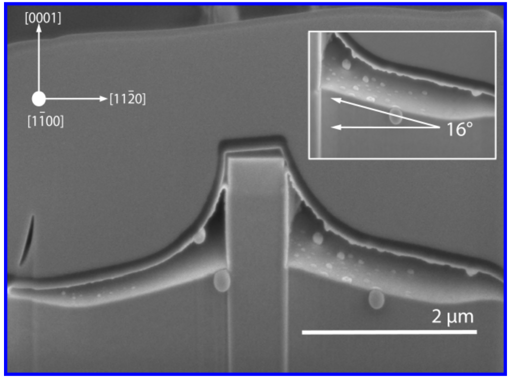






- Microfaceting similar to that of GaN in KOH!

How do we determine what this plane is?



$\{10\bar{1}4\}$ at 25.2
$\{3\ 0\ \bar{3}\ 13\}$ at 23.5

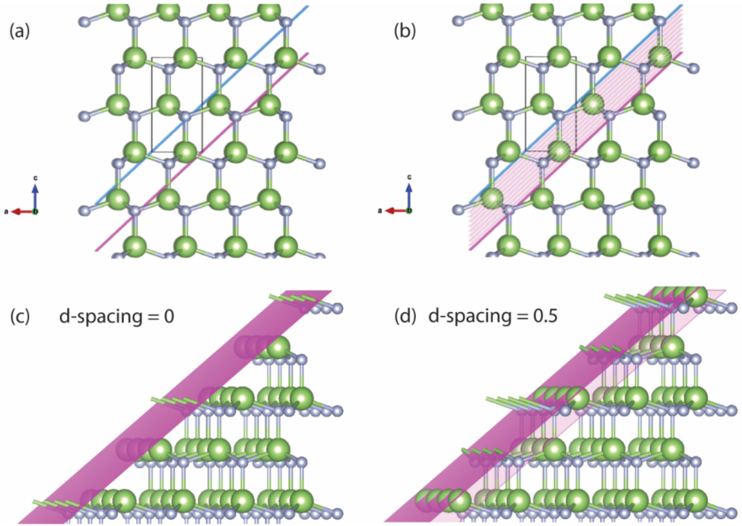
$\{1\ 1\ \bar{2}\ 10\}$ at 17.7
$\{1\ 1\ \bar{2}\ 12\}$ at 15.1

Etch Barrier Index (EBI): first step in plane assignment

- ***EBI = planar atomic density x nitrogen dangling bonds***
  - Quantitative measure of etching potential
  - Developed for GaN in KOH by Lai et al.[1]
  - N-dangling density calculated manually
- ***Lower EBI indicates exposed plane***

EBI Calculations for selected planes in 14% AlGaN

Miller index	ρ_{planar} (atom/Å^2) [2]	d(Å)	n_N (1/atom)	EBI (1/Å^2)
(0001)	0.1145	5.5170	3	0.3435
$\{10\bar{1}0\}$	0.1221	2.7507	1.27	0.1554
$\{11\bar{2}0\}$	0.1410	1.588	1	0.1410
$(000\bar{1})$	0.1145	5.5170	1	0.1145
$\{10\bar{1}4\}$	0.0259	1.1674	1.5	0.0389
$\{3\,0\,\bar{3}\,13\}$	0.0081	0.3641	1.5	0.0122
$\{1\,1\,\bar{2}\,10\}$	0.0218	0.4905	1.5	0.0327
$\{1\,1\,\bar{2}\,12\}$	0.0184	0.4148	1.5	0.0276



Kazanowska et al., ***Nanotechnology***, 2021

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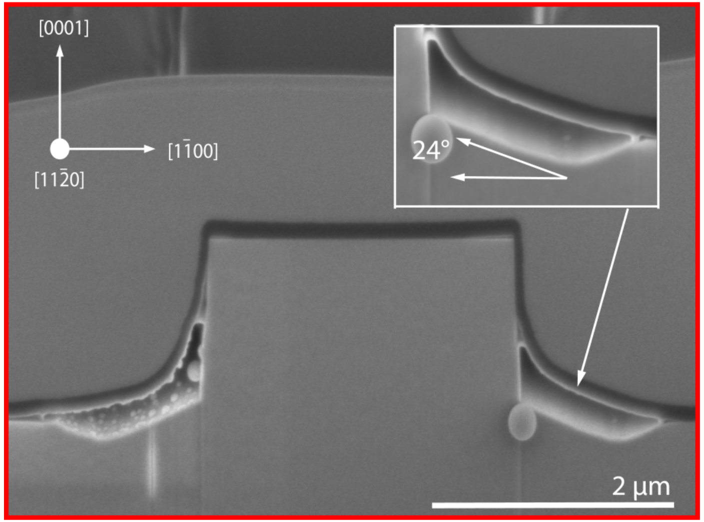
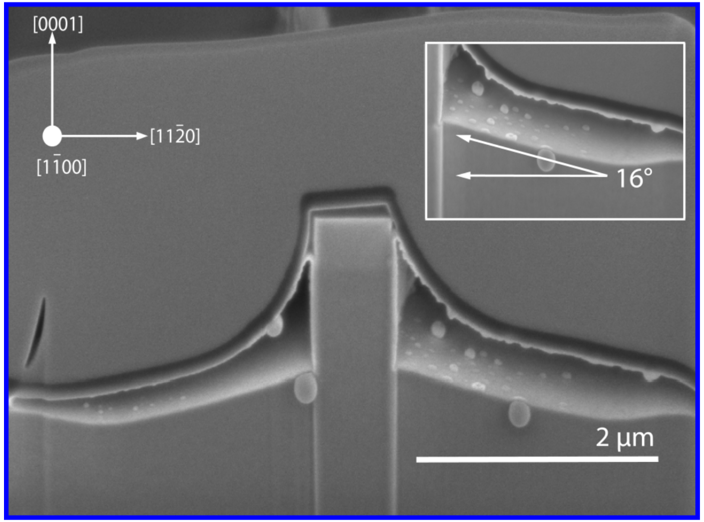
1 Lai et al., Res Chem Intermed (2017)

2 Fan et al., J. App. Crystal. (2016)

14% AlGaN in KOH: etch evolution reveals ‘cuboid’ structure



$\{3\ 0\ \bar{3}\ 13\}$ at 23.5



$\{1\ 1\ \bar{2}\ 12\}$ at 15.1

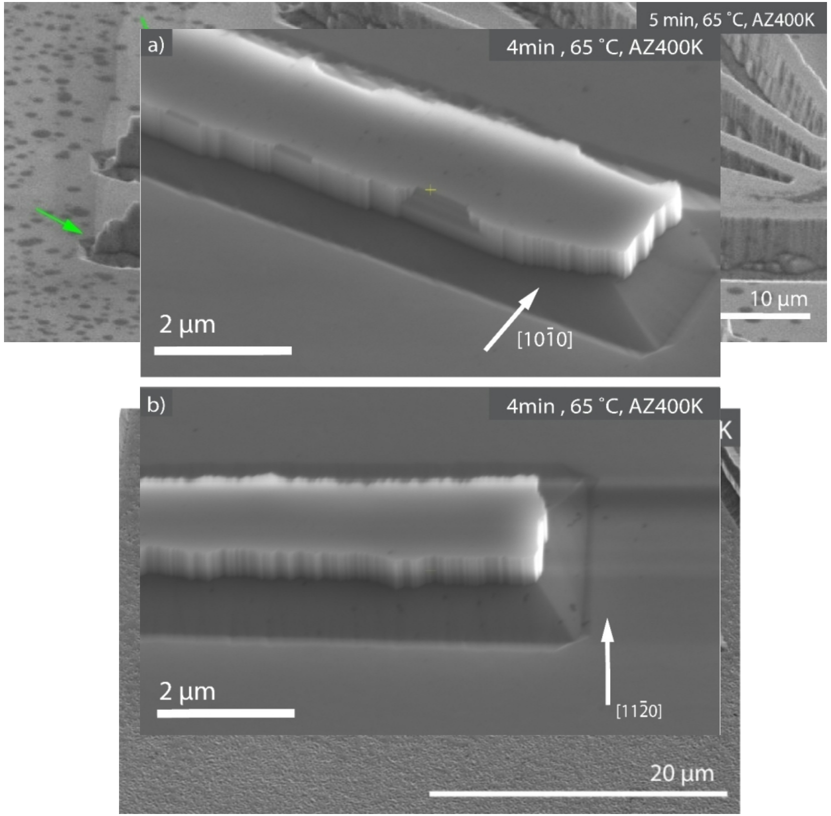
- EBI does not take into account surface reconstructions and preferred configurations

EBI is a good first estimate for etching potential of a plane.

Etch evolution for high Al-content AlGaN

- 65% AlGaN etches via triangular and rectangular microfaceting
- AlN etches via triangular and rectangular microfaceting
- Larger microfacets than in GaN/14% AlGaN
- Less uniformity
- ‘cuboid’ foot structure seen in both

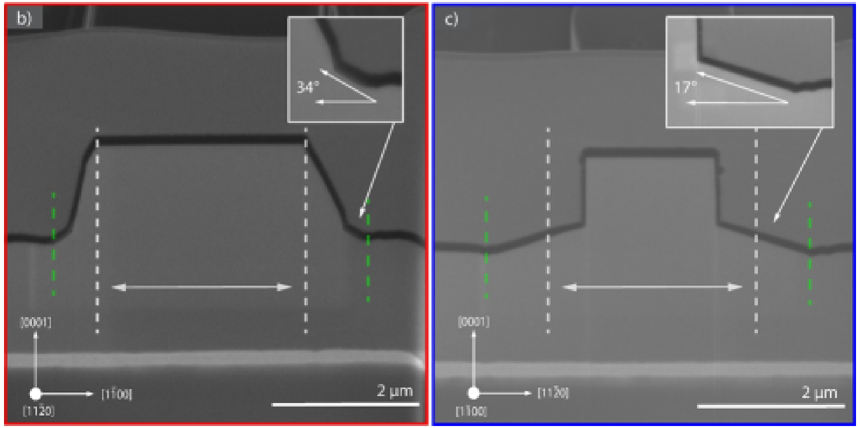
Are there similarities in the semi-polar facets visible?



‘cuboid’ assignment for high Al-content AlGaN

- Same angles measured bounding the semi-polar facets!

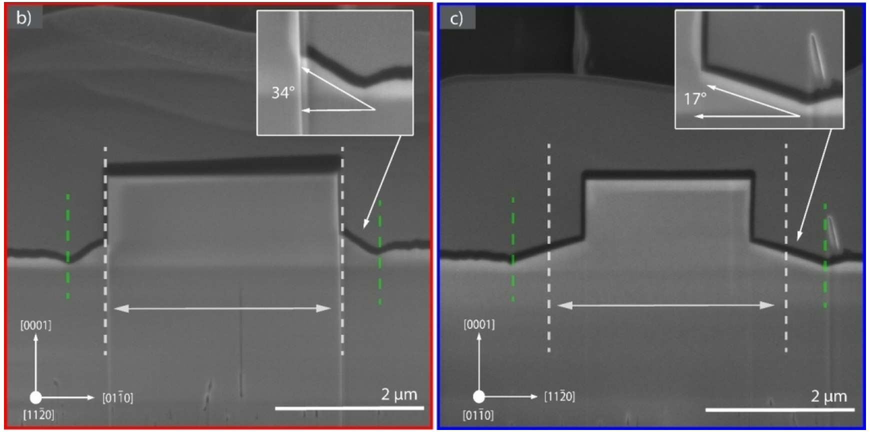
65% AlGaN



$\{2\ 0\ \bar{2}\ 5\}$ at 36.7

$\{1\ 1\ \bar{2}\ 10\}$ at 17.8

AlN



$\{2\ 0\ \bar{2}\ 5\}$ at 36.4

$\{1\ 1\ \bar{2}\ 10\}$ at 17.7

There exists a continuity in the alkaline etching of $Al_{(X)}Ga_{(1-X)}N$

Motivation and thesis structure

Motivation: build off two-step top-down approach, explore $Al_{(X)}Ga_{(1-X)}N$ substrates and extend method to other etch chemistries

How does changing the etch environment affect etching of pre-defined GaN structures?

Alkaline Etching of AlGaN

- Directionally resolved non-polar etch rates and energetics in KOH
- Macroscopic etch progression
- Non-polar and semi-polar geometries?
- Etching Barrier Index (EBI)

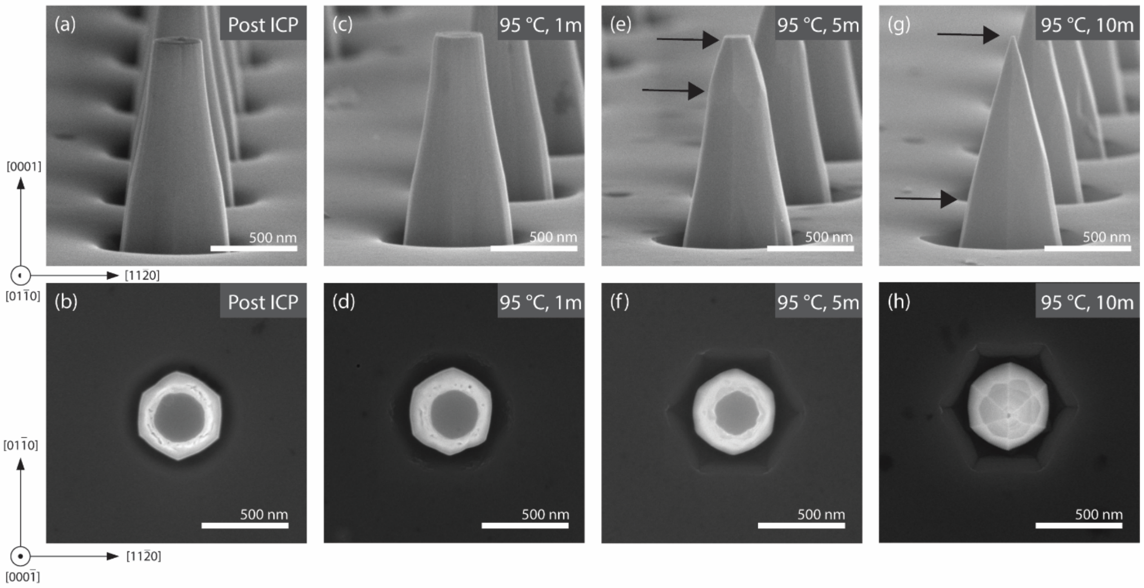
Motivated by

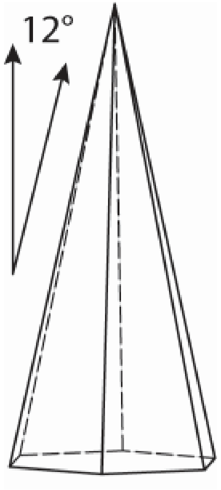
- Step away from KOH-based etch chemistries
- Semi-polar planes revealed during non-polar etch -> nanowires

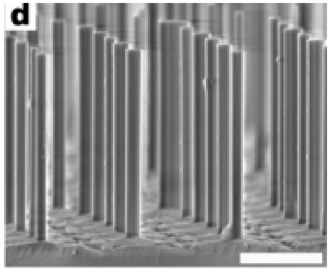
Acidic Etching of GaN NWs

- Directionally resolved etch rates and energetics
- Macroscopic etch progression
- Previously unseen geometries
- Field emission study of GaN NWs

GaN nanowires etched in 95˚C H_3PO_4







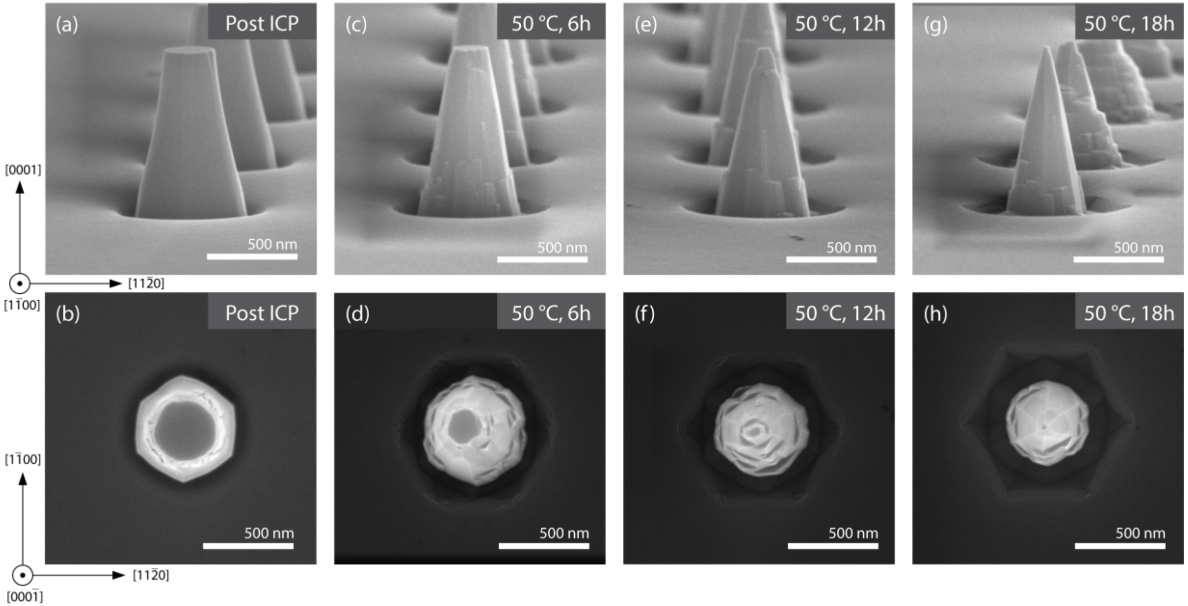
Previous GaN in KOH?!

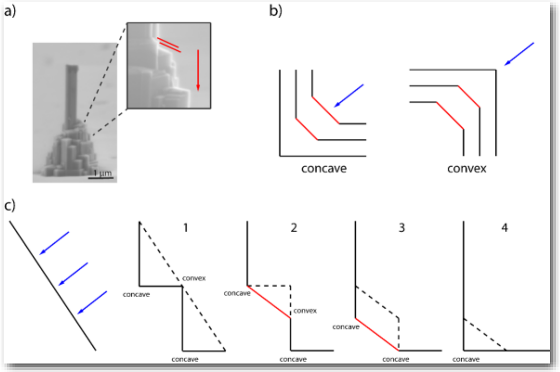
- Faceting observed at nanowire base and tip after etching in hot phosphoric acid
- The top angle was 12 degrees offset from the vertical axis, and the semipolar facets are of the $(11\bar{2}l)$ family

Does temperature affect this etch?

Kazanowska et al., ***Nanotechnology***, 2021

GaN in H_3PO_4: microfaceted etch evolution at 50˚C





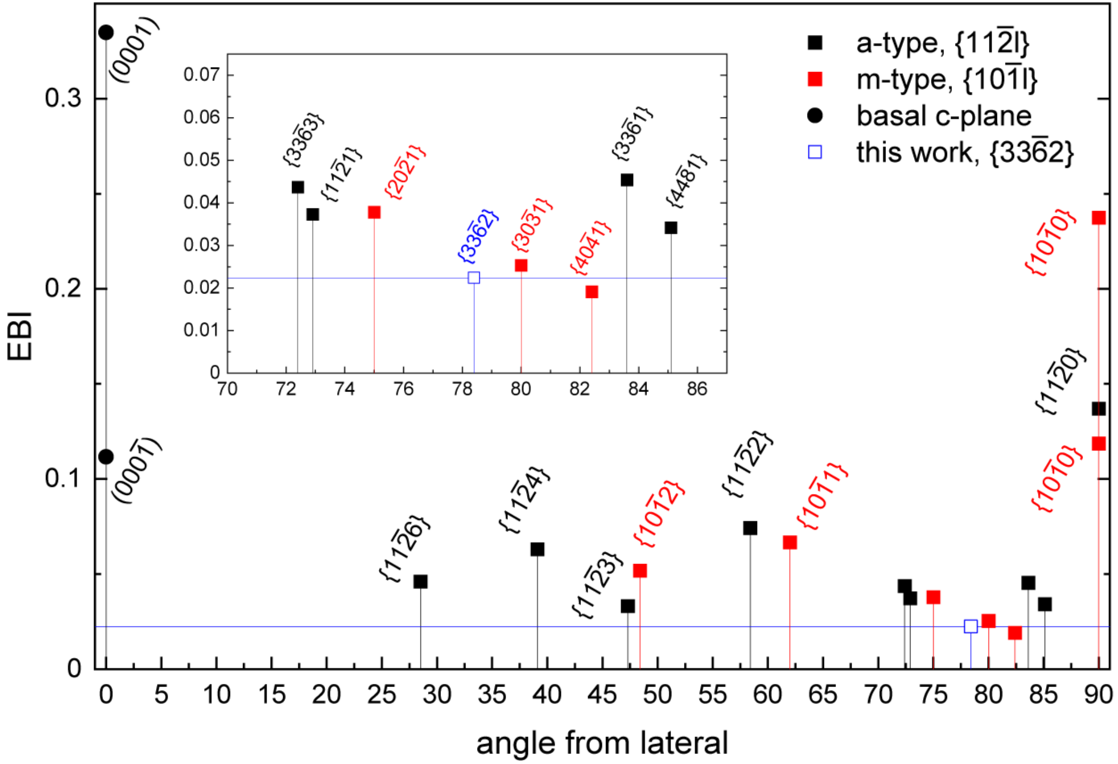
Previous GaN microfacets in KOH?!

- Micro-faceting etch progression very similar to KOH, except final structure is tapered vs vertical
- Concave vs convex etch progression similar to proposed mechanism for GaN in KOH!
- Same end geometry for all temperatures

What planes make up this nanowire geometry?

Kazanowska et al., ***Nanotechnology***, 2021

GaN in H_3PO_4: EBI of semi-polar planes in vicinity



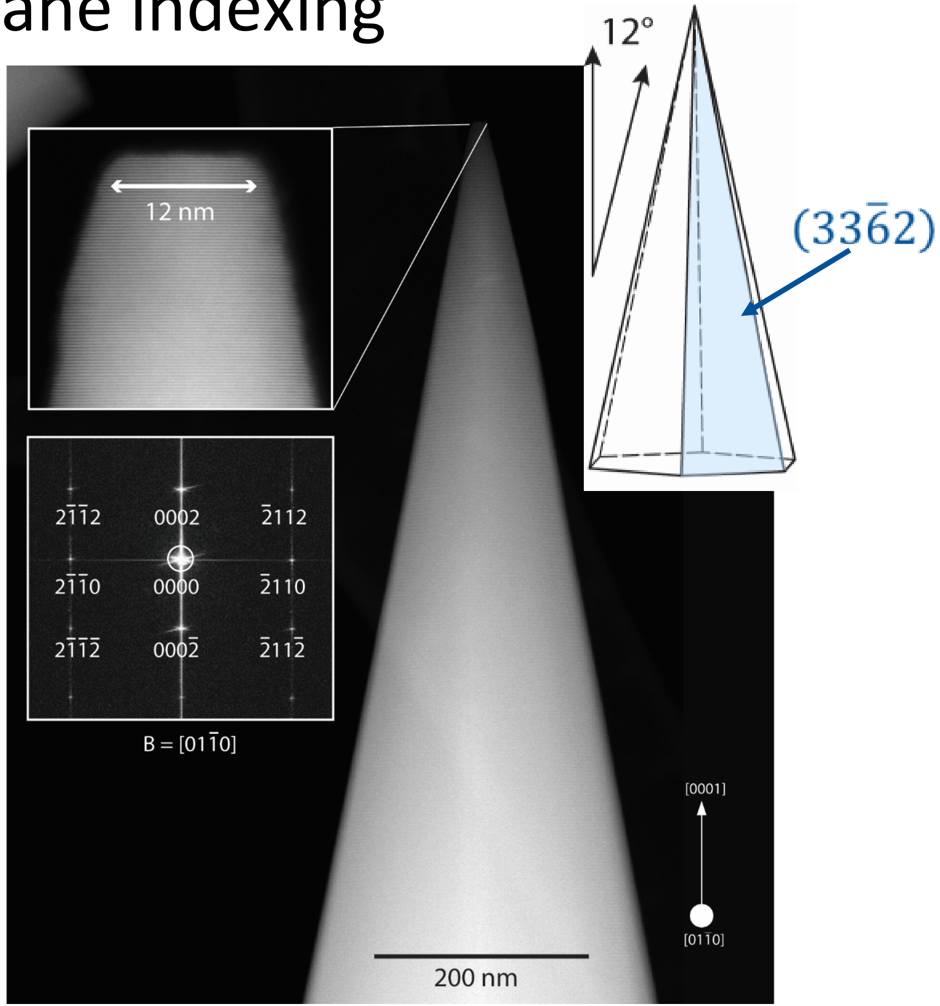
- Manual calculations point to certain high-index planes
- EBI calculations for semi-polar planes in vicinity indicate $\{33\bar{6}2\}$ plane

Can we confirm this?

Kazanowska et al., ***Nanotechnology***, 2021

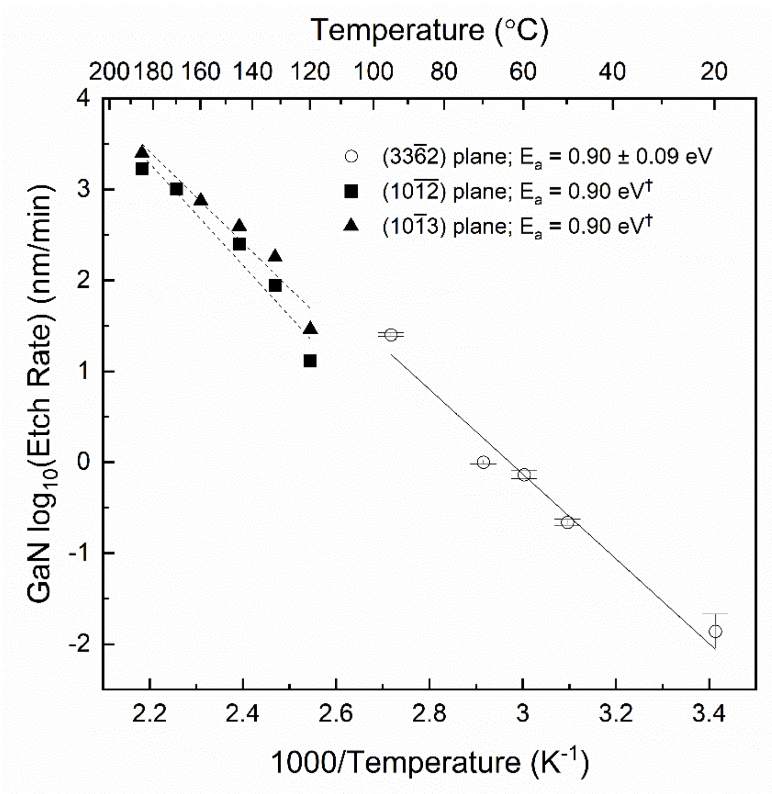
GaN in H_3PO_4: semi-polar plane indexing

- HAADF-STEM was used to characterize the surface of the nanowires
  - Atomically smooth semi-polar facets
  - Tips on the order of 8-12 nm
- FFT of HAADF-STEM image was used to assign the semi-polar planes bounding the nanowire
  - $\{33\bar{6}2\}$
- In line with EBI calculations!



Kazanowska et al., ***Nanotechnology***, 2021

GaN in H_3PO_4: activation energy of etching



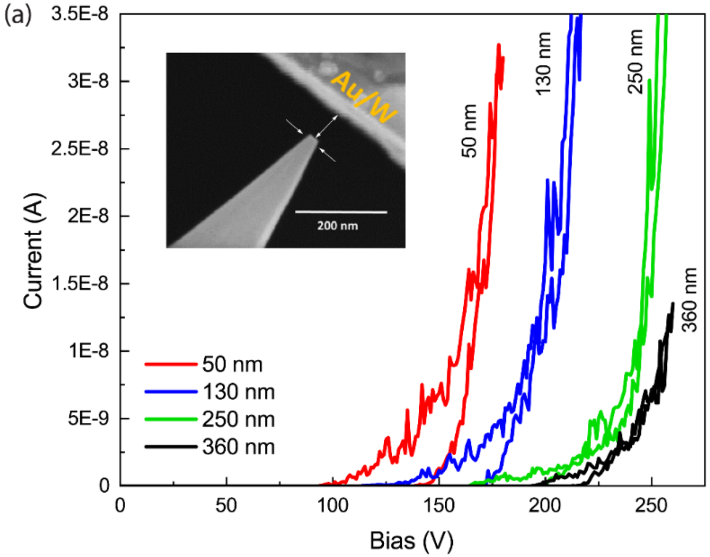
D.A. Stocker et al.

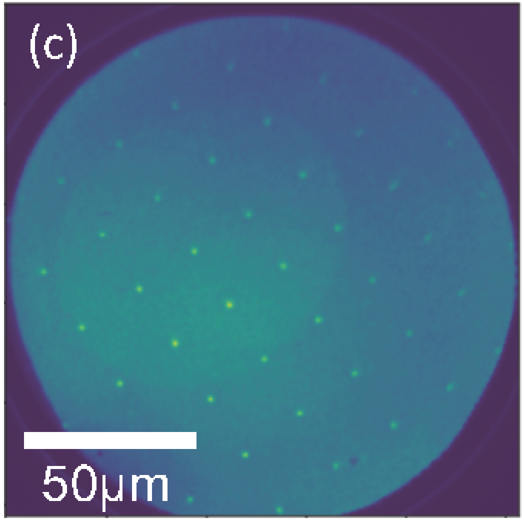
- GaN in H_3PO_4 E_a = 0.90 +/- 0.09eV
- Indicates **reaction-limited** regime
- In line with literature data for E_a of GaN in H_3PO_4
- Key difference:
  - Planar GaN coupons etched in H_3PO_4

What can we do with these nanowires now?

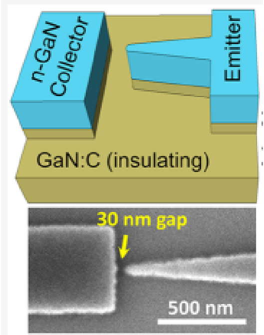
Kazanowska et al., ***Nanotechnology***, 2021

GaN in H_3PO_4: field emission from nanowires and arrays





Lateral vacuum nanoelectronic diode



Sapkota et al., ACS Nano, (2021)

- Field emission possible from individual nanowires
- Uniform field emission from nanowire arrays
- Next step: integrate in vertical devices

Tapered GaN nanowires show promise as field emitters!

Kazanowska et al., ***Nanotechnology***, 2021

Conclusions

How is the alkaline etching of nanostructures affected by the substrate Al content?

- First directionally resolved non-polar etch rates for AlGaN
  - Increase in Al content increases etch rate; decreases E_a
  - AlN reaction energetics explain E_a inconsistency
- *a*-plane etch rates and E_a always higher than that of *m*-plane
  - Consistent across all Al compositions
- AlGaN and AlN etch to reveal basal ‘cuboid’ structure

How does changing the etch environment affect etching of pre-defined $Al_{(X)}Ga_{(1-X)}N$ structures?

- Novel, tapered, never-before seen GaN nanowire geometry revealed in H_3PO_4 etch
  - Field emission possible, uniform across array
- Results consistent with EBI calculations

Built off two-step top-down approach, explored $Al_{(X)}Ga_{(1-X)}N$ substrates, extended method to other etch chemistries

Acknowledgments

- Thank you to my advisor, Dr. Kevin Jones, and to my co-advisor, Dr. George Wang
- Thank you to my committee for their involvement and time
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- Thank you to family and friends for their continued support

SWAMP
Research Group

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