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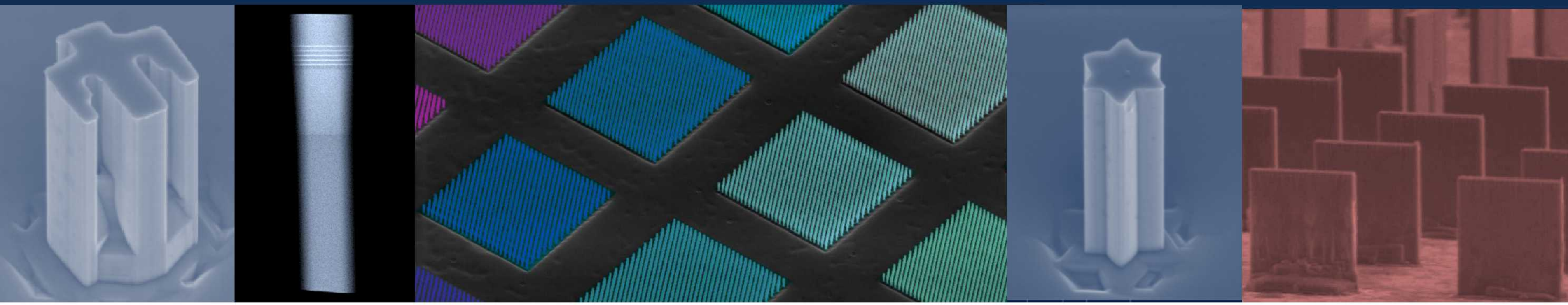

Top-Down Etch Processes for III-Nitride Nanophotonics

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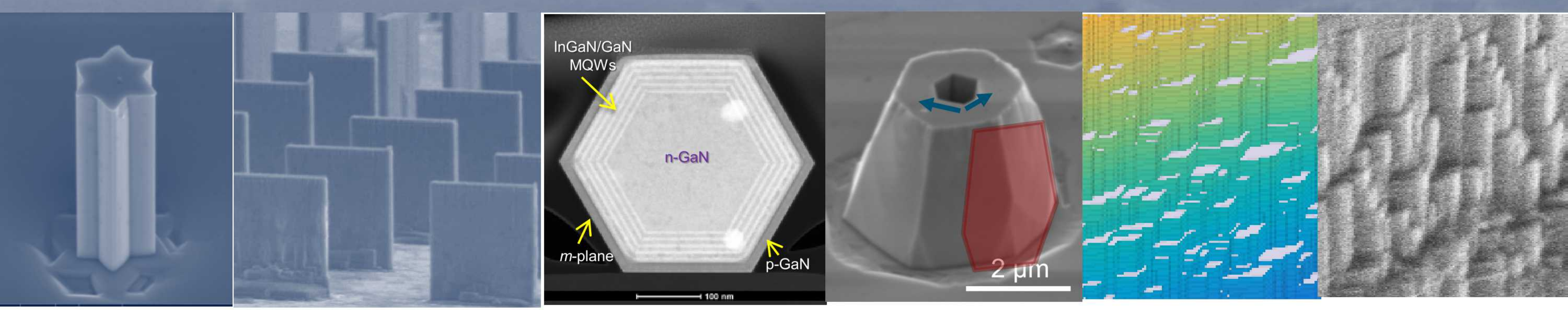
Outline

- Orientation-resolved etch rates
- Prediction of etch geometries
- Mechanism of highly anistropic KOH wet etch
- Tapered phosphoric acid etch
- III-Nitride nanowire photonics

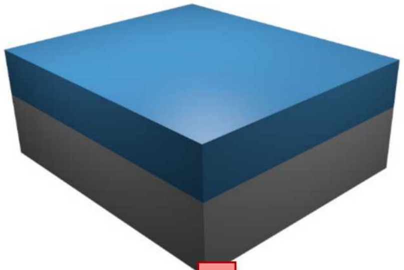


Motivation: Top-down approach for nanostructures

Motivation: Advantages of *top-down approach* for fabrication, for both *material synthesis and integration*

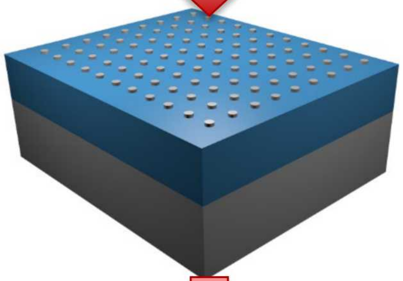
Steps | **Advantages**

Conventional GaN film



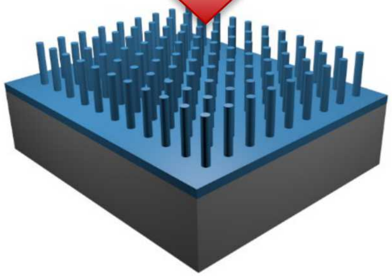
- Standard/optimized growth conditions (not limited by 1D growth window) give control over:
  - Dopant, impurity incorporation
  - Axial heterostructuring
- Can be characterized by standard methods

Lithographic technique



- Ordered and periodic arrays
- Independent control over height, width and pitch
- Cross-sectional shape control

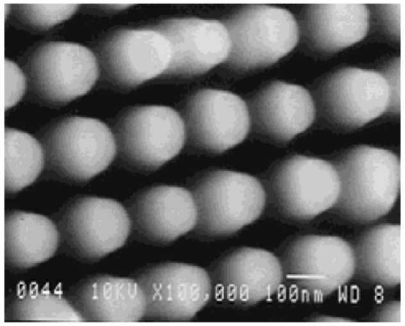
Anisotropic etch



- Potentially less tapered, higher aspect-ratio structures possible for highly anisotropic, crystallographically selective etches

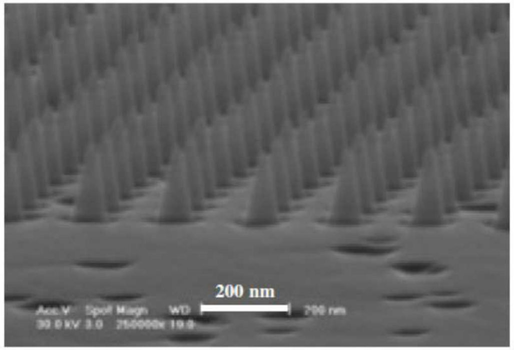
Previous top-down nanopillars by dry etching

InGaN/GaN MQW nanoposts/nanopillars



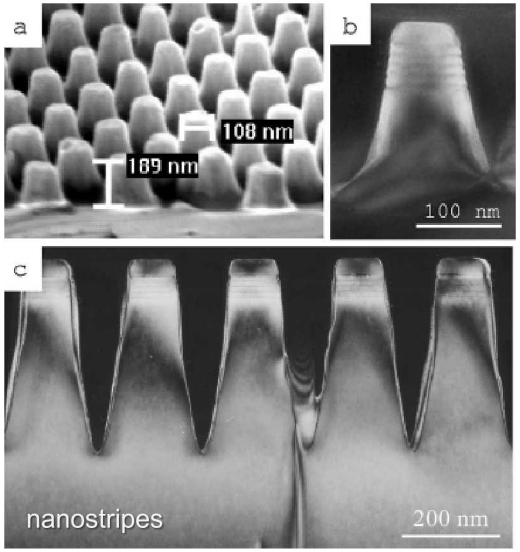
L. Chen et al., PSSa **188** 135 (2001) (Brown, Yale)

- E-beam Ni mask, Cl-based RIE etch



H. S. Chen et al., Nanotechnology **17** 1454 (2006) (NTU)

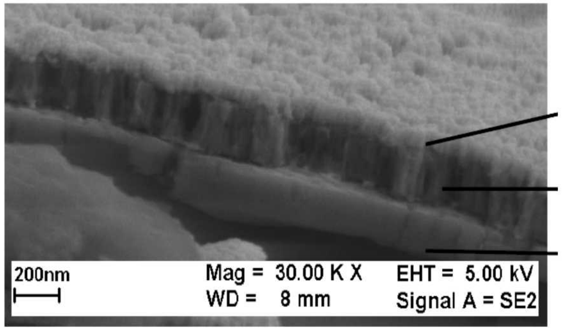
- E-beam Cr mask, Cl-based ICP-RIE etch
- Observed PL blue-shift w/decreasing diameter due to strain relaxation (reduction of QCSE)

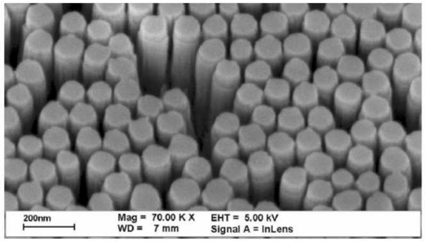


S. Keller et al., J. Appl. Phys. **100** 054314 (2006) (USCB)

Holographic lithography, SiO_2 mask, CHF_3 ICP etch to make strips and pillars

InGaN/GaN MQW nanorod LED





C. Y. Wang et al., Opt. Expr. *16,* 10549, 2008. (NTU)

M. Y. Ke et al., IEEE J. Sel. Top. Quantum Elec. **15** 1242 (2009) (NTU)

SiO_2 nanosphere lithography, Cl-based ICP-RIE etch; electrically injected array

- **Tapered, short aspect ratio nanopillars via plasma etching**
- **Plasma etch causes sidewall damage**

Chemical wet etching of the III-Nitrides: Is it useful ?

Wet etching typically not considered viable due to very low etch rates (< Å/min)

Significant etch rates, but extremely crystallographically anisotropic

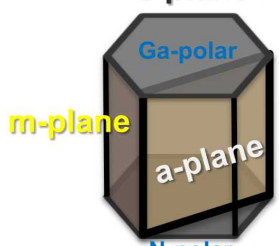
Table 1
GaN and AlN etching results in acid and base solutions

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

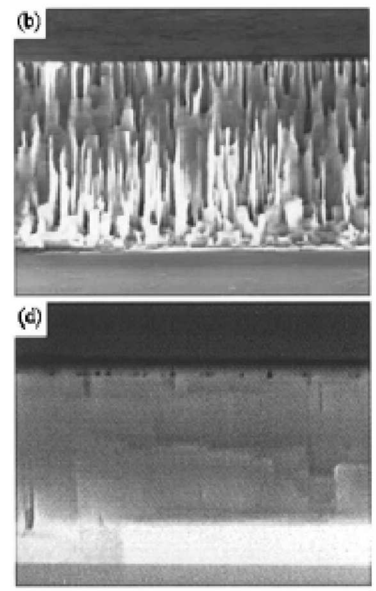
Etching was conducted at room temperature (25 °C) unless otherwise noted (after [31]).

Zhuang and Edgar, MSE R 48 1 (2005)

But actually…

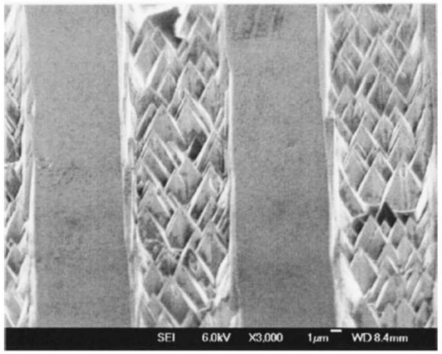


m-plane sidewalls



Stocker et al. *APL* **77**, 4253 (2000)

Ga-polar and N-polar GaN



H. Ng et al., J. Appl. Phys., 94, 650 (2003)

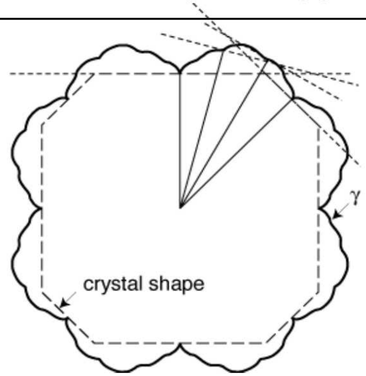
KOH-based wet etches

Anisotropy is **> 2000:1** (GaN/KOH), as compared to maximum anisotropies of ***160:1*** *(Si), and* ***4:1*** *(GaAs)*

This property, however, makes wet etching *ideal for micro/nanostructure fabrication* of the III-nitrides !

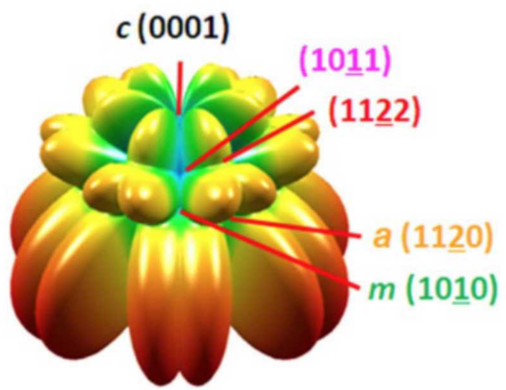
The appearance and evolution of facets

Predicting the equilibrium crystal shape: **The Wulff Plot**



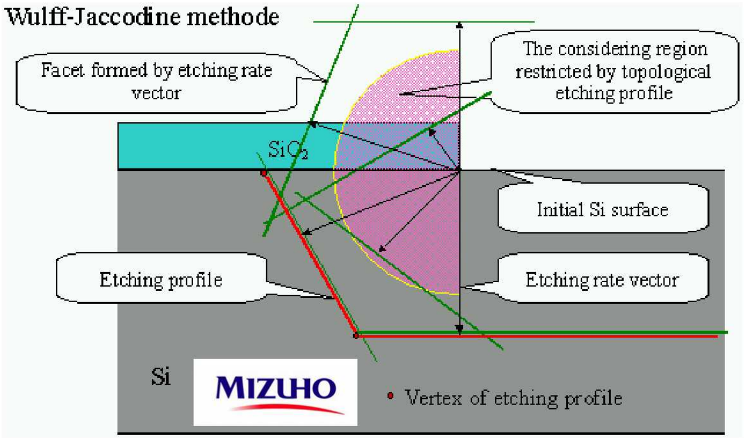
Wulff et al., Semicond. Z. Kristallogr 34, 449 (1901)

For MOVPE growth, use the *kinetic* Wulff plot



B. Leung et al., Semicond. Sci. Tech. 27, 024005 (2012)

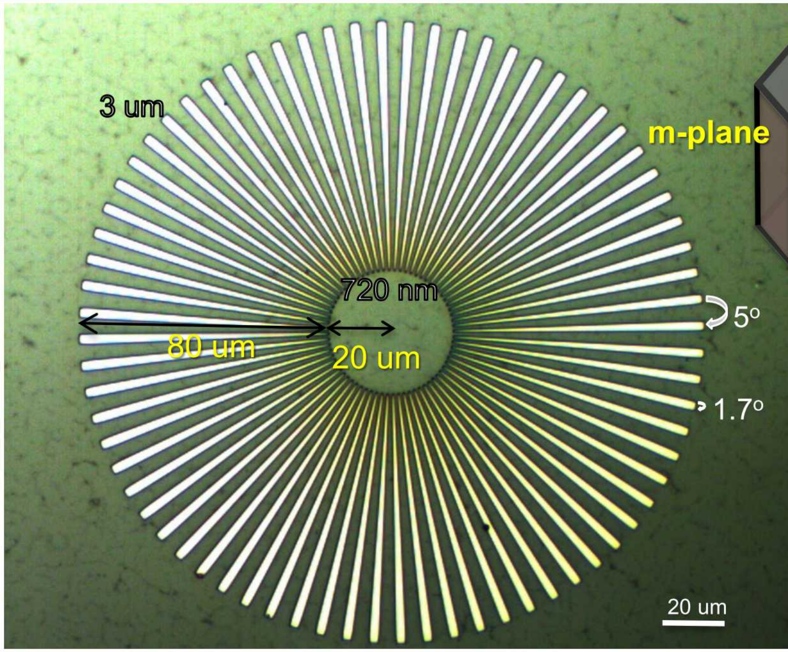
Same method used in commercial silicon wet etch simulators

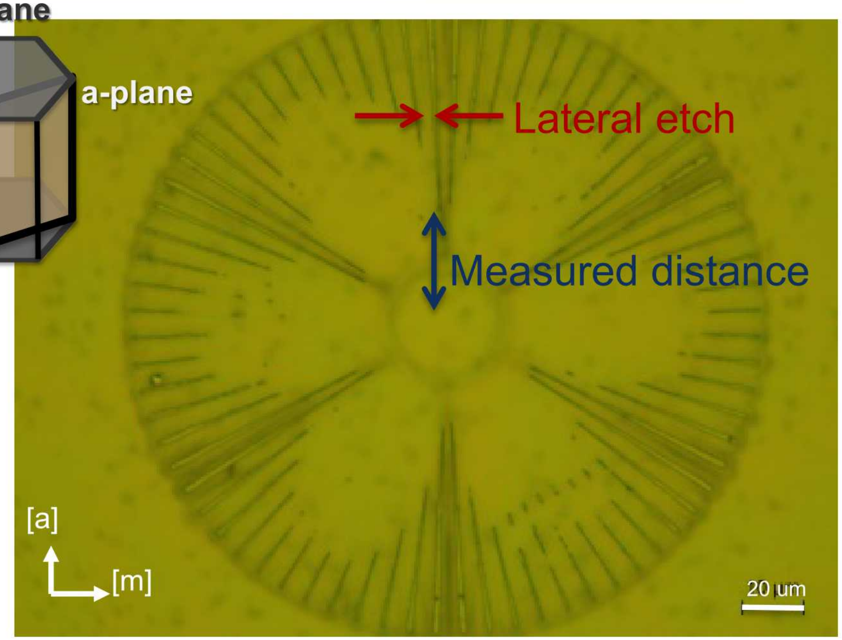


Can we map the “Wulff plot” for etching?

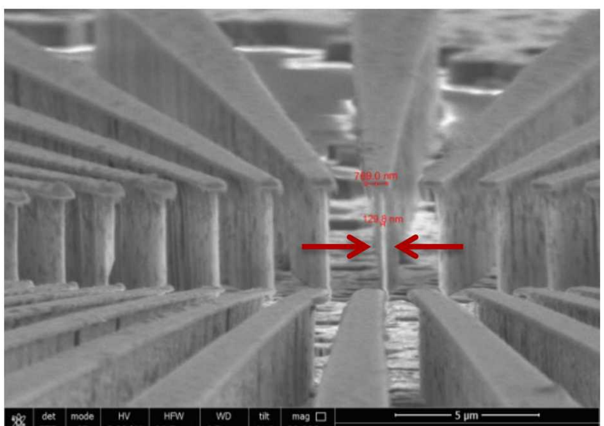
Directly Measuring Orientation Resolved Etch Rates

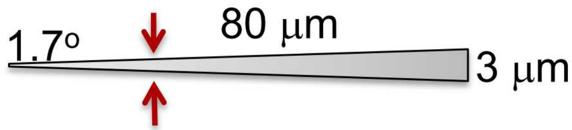
Sandia National Laboratories





5% KOH in ethylene glycol





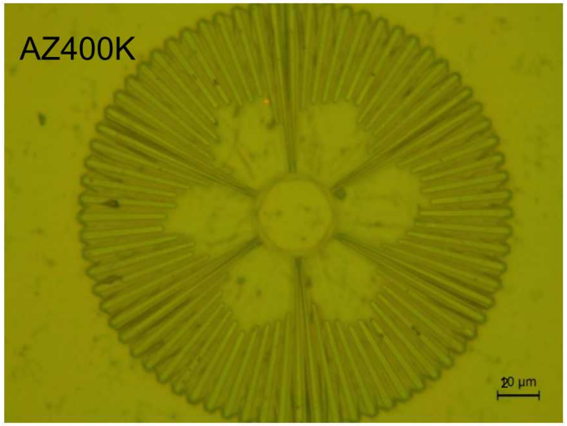
Lateral etch of 100 nm/min →
Wedge retraction of 6.7 μm/min

Etch rate is amplified by a factor of 67

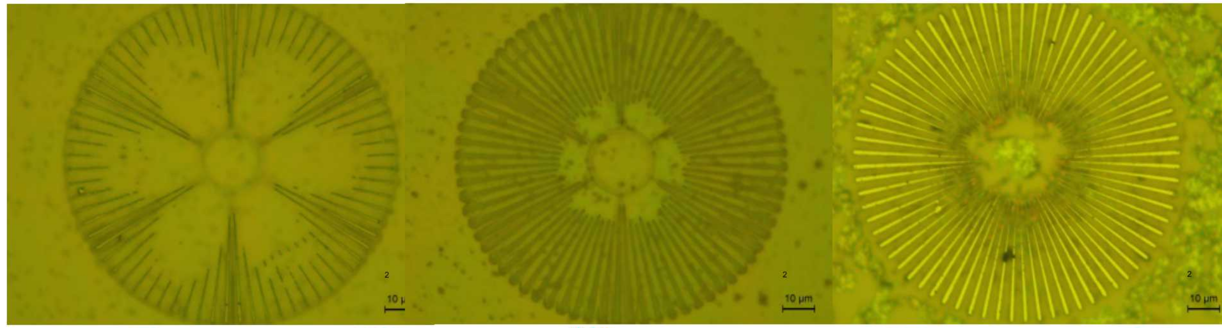
Direct measurement of orientation resolved etch rates for the first time in GaN

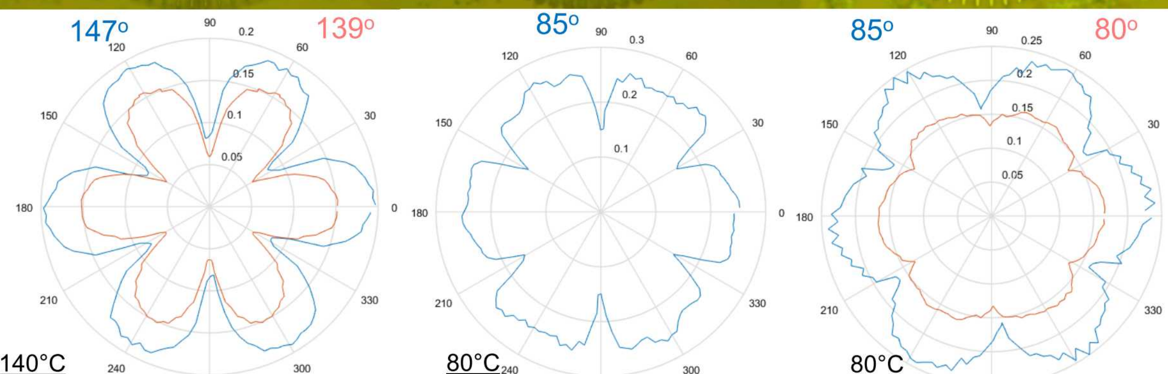
Wagon wheel methodology: see for example: Wind, R. A.; Hines, M. A., *Surf. Sci.* 2000, 460, 21.

Direct Measurements of Orientation Resolved Etch Rates – Chemistries and Temperatures



5% KOH in ethylene glycol | 5% KOH in H_2O | 25% TMAH

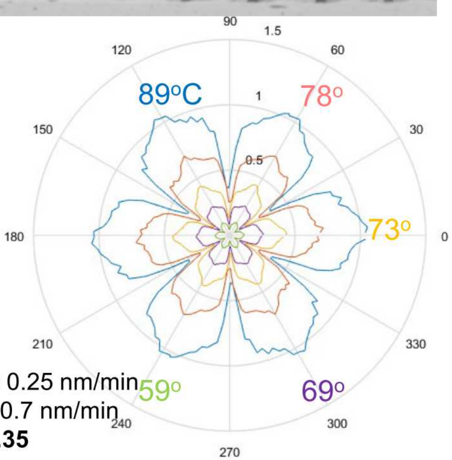




140°C
m-plane 0.06 nm/min
a-plane 0.16 nm/min
m/a ~ 0.37

80°C
m-plane 0.15 nm/min
a-plane 0.27 nm/min
m/a ~ 0.56

80°C
m-plane 0.13 nm/min
a-plane 0.16 nm/min
m/a ~ 0.82



80°C
m-plane 0.25 nm/min
a-plane 0.7 nm/min
m/a ~ 0.35

m-plane: Atomically smooth etch facet
a-plane: Transition from step-flow highly dependent on chemistry
m/a: 0.3 ~ 0.9

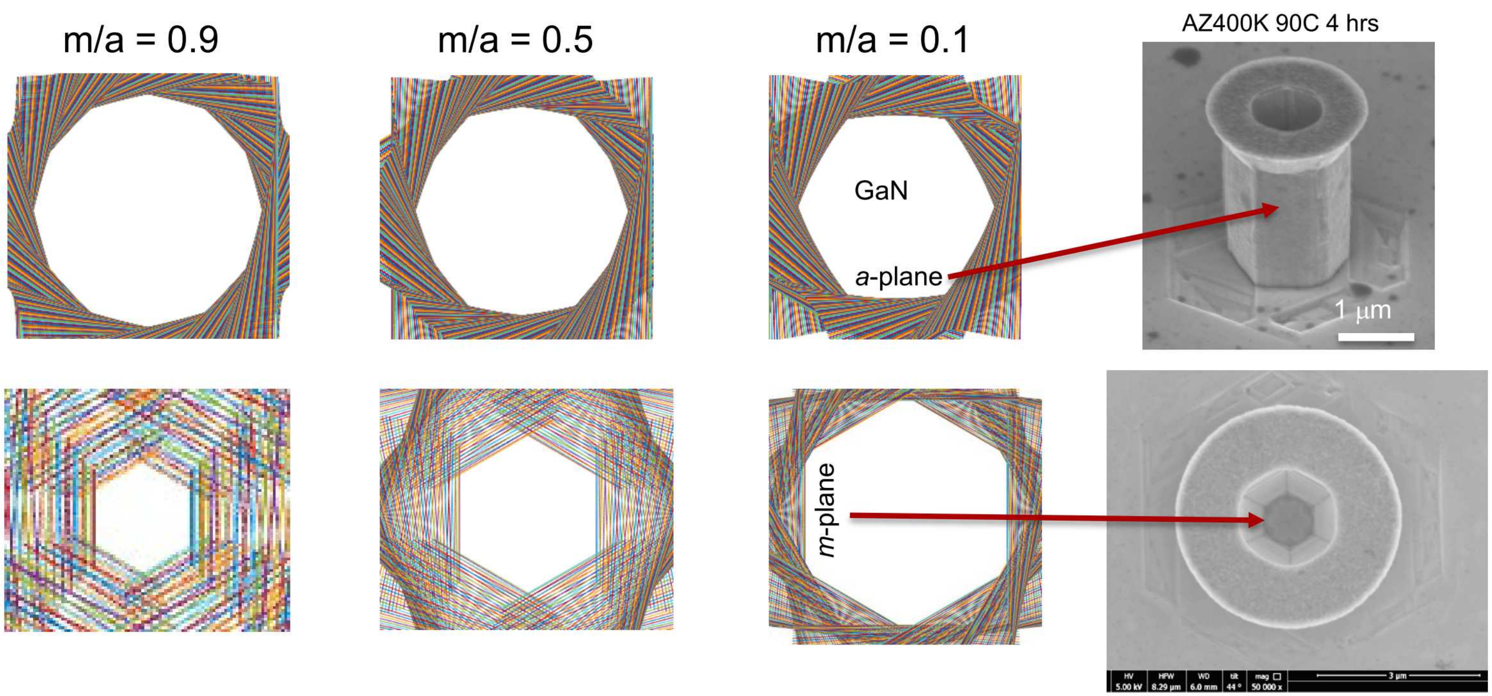
Prediction of Etched Geometry: Implementing the Wulff-Jaccodine Method

Define initial geometry → *Input orientation dependent etch rates for etch condition*

→ *Plot evolution of facets over specified time* → *Final etch geometry predicted by bounding facets*

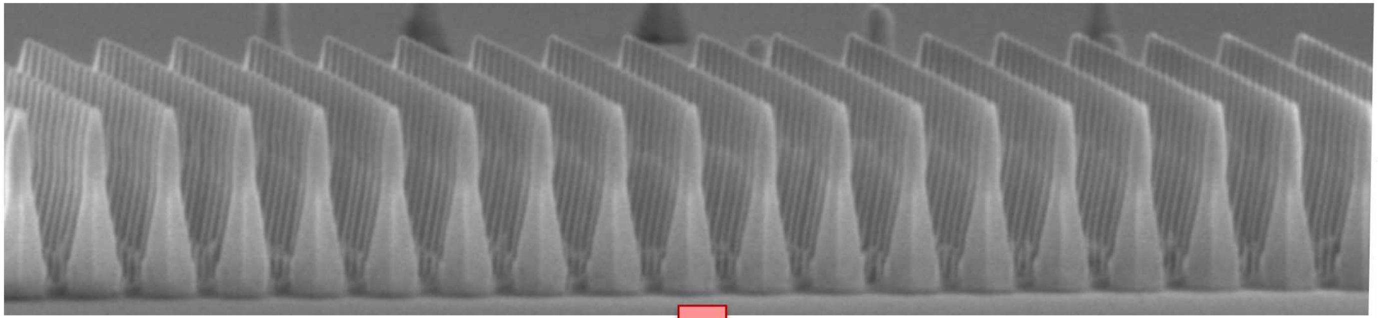
Convex (white region is GaN)

Concave (colored region is GaN)

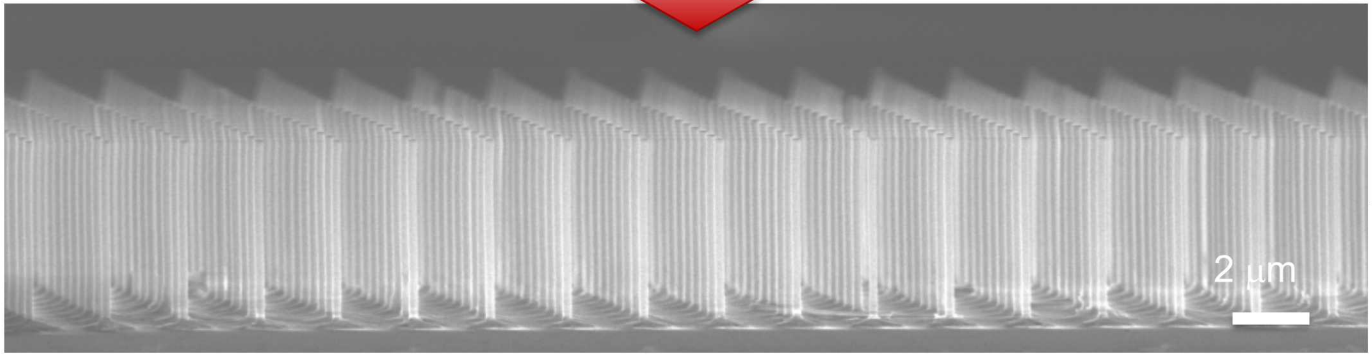


Fabricated top-down GaN nanostructures using two-step dry + wet etch approach

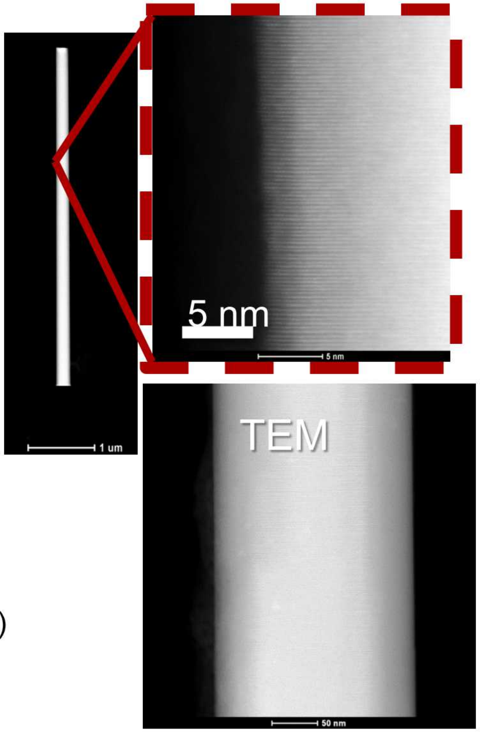
Dry etch (Cl_2 based ICP)



KOH-based wet etch (AZ400K)



TEM shows smooth vertical sidewalls



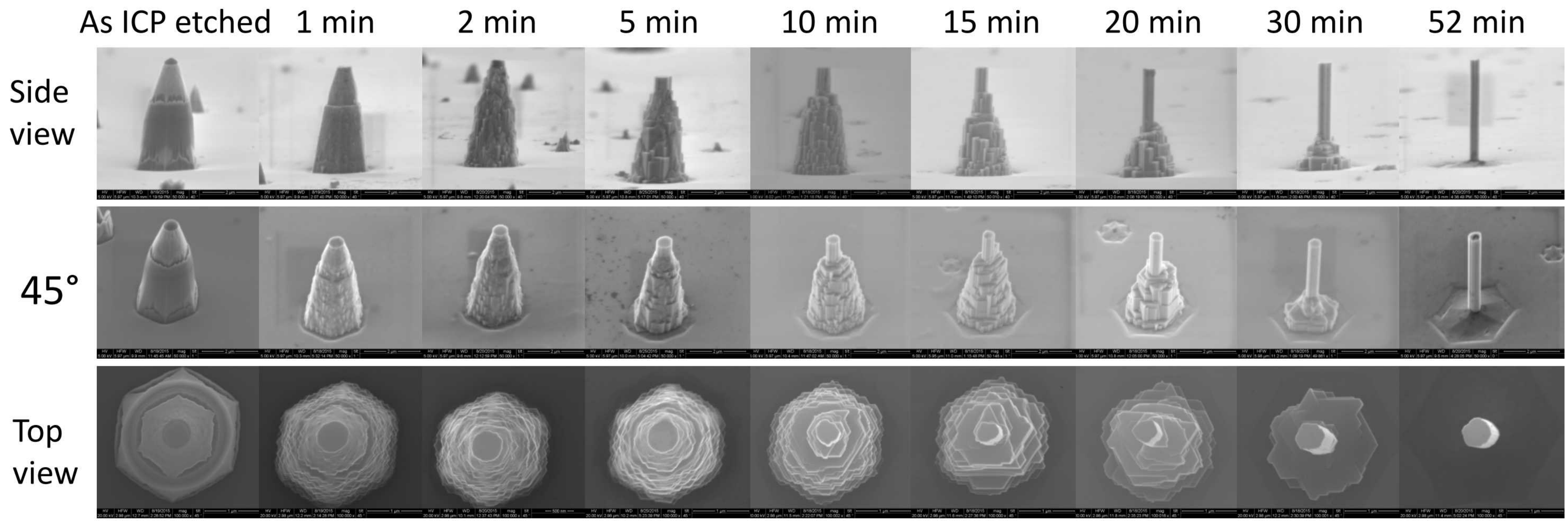
Diameter: 180 nm, Height: 4.5 μm, Pitch: 2 μm (AR: 25)

See: Q. Li et al., Opt. Exp., **20**, 17873 (2012)

Q. Li et al., Opt. Exp., **19**, 25528 (2011) etc....

What is the wet-etch mechanism from *rough tapered to smooth vertical sidewalls*?

Wet etch evolution for nanowires



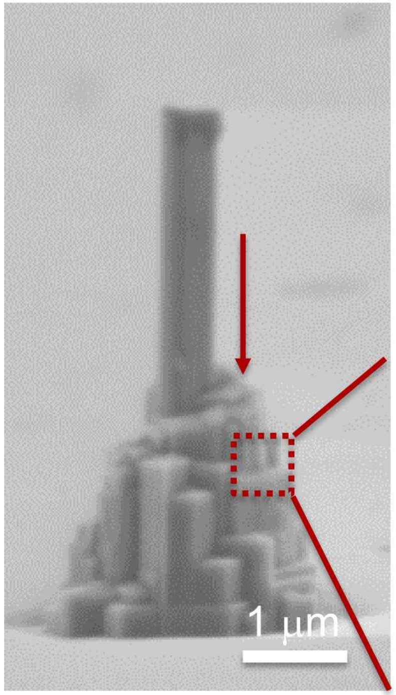
AZ400K, 65^{o}C

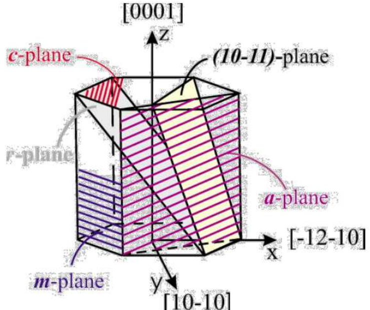
Wet etch proceeds “vertically” rather than horizontally

Mechanism/Basis for evolution of facets during GaN wet etching

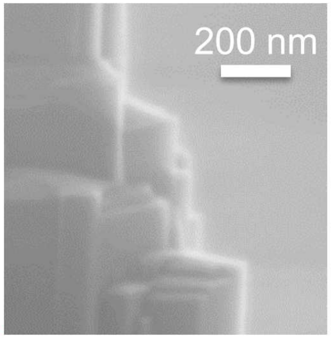
What is the mechanism from *tapered to smooth vertical sidewalls* through faceting?

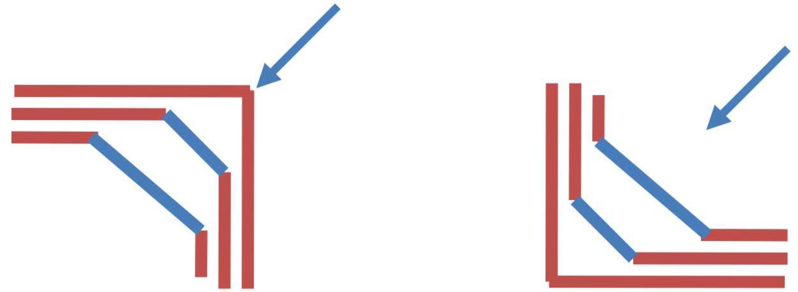
Slow etching: c-plane, *m*-plane
Fast etching: semipolar $(10\bar{1}1)$





V. Darakchieva et al., JAP 108, 073529 (201)

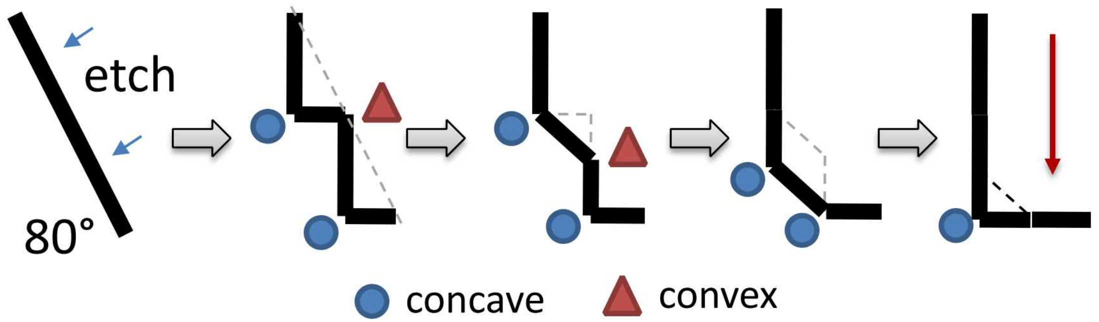




Convex
Fast etch facet persists

Concave
Slow etch facets persists

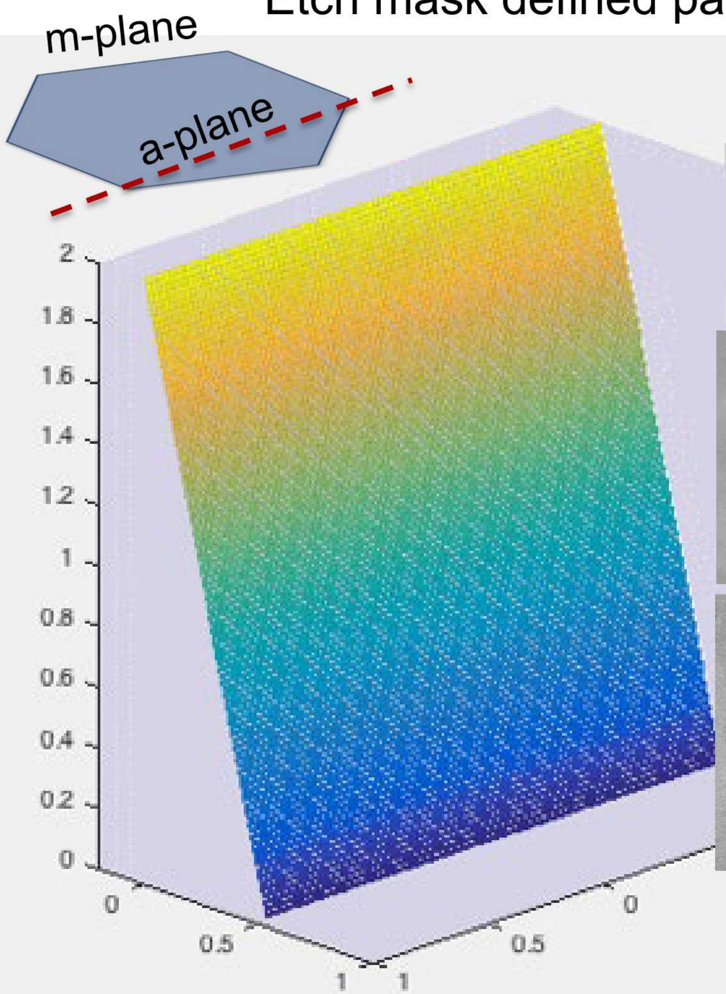
The facet etch sequence:

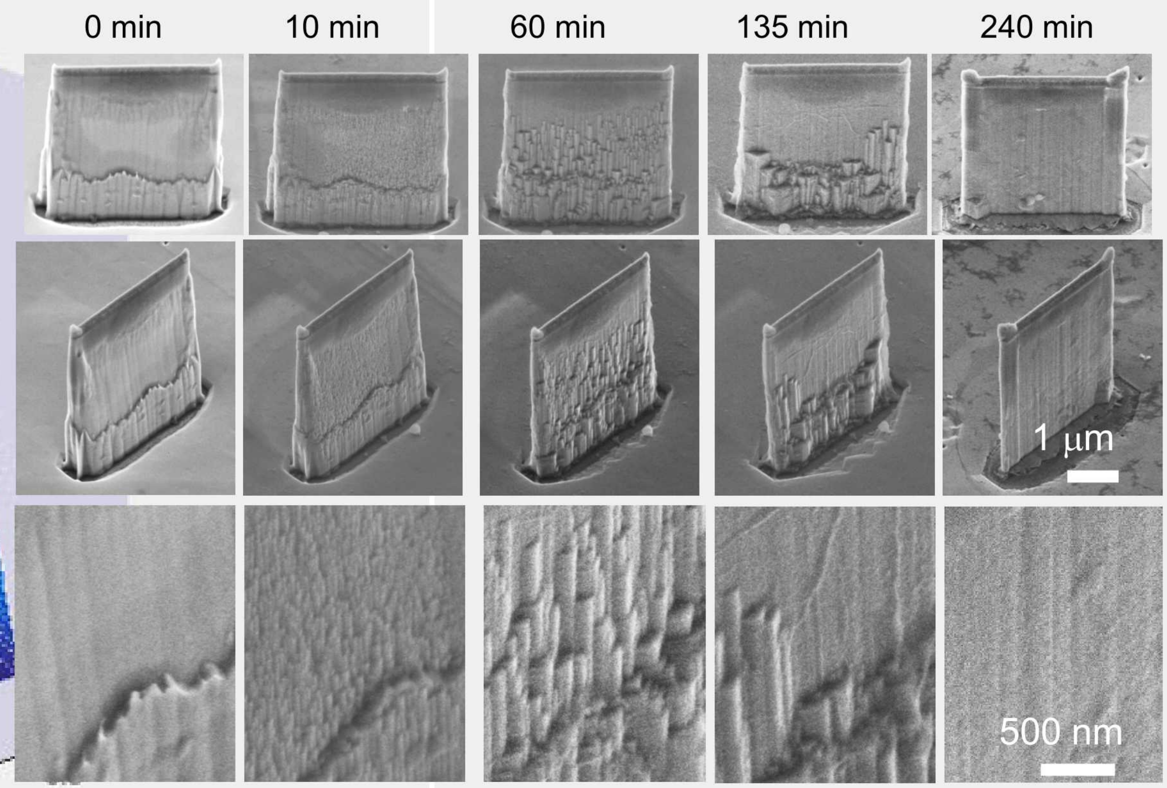


The appearance (disappearance) of fast (slow) etching facets in concave (convex) geometries is the basis of the etch mechanism

Etch evolution of *a*-plane wall

Etch mask defined parallel to *a*-plane

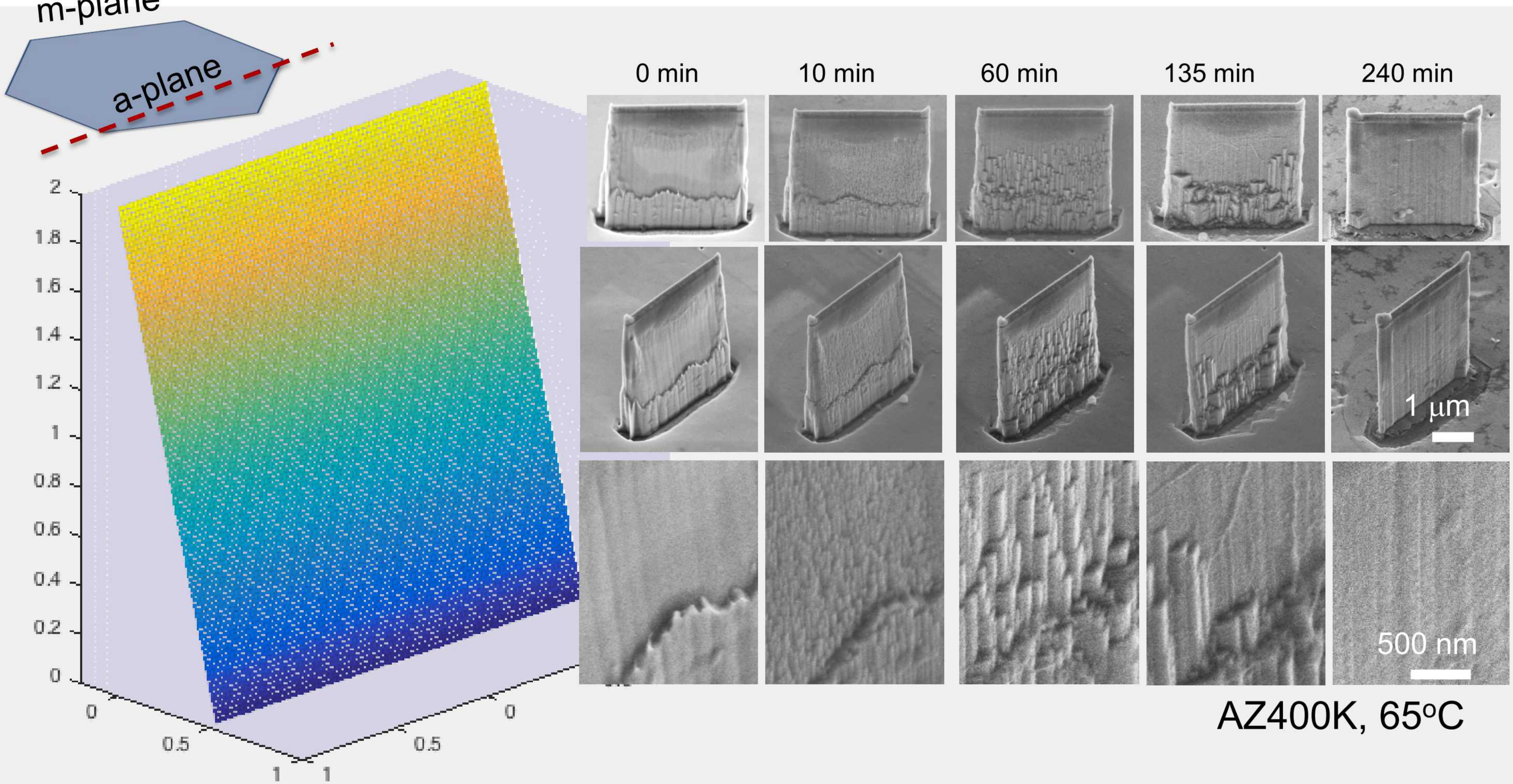




AZ400K, 65°C

Etch evolution of *a*-plane wall

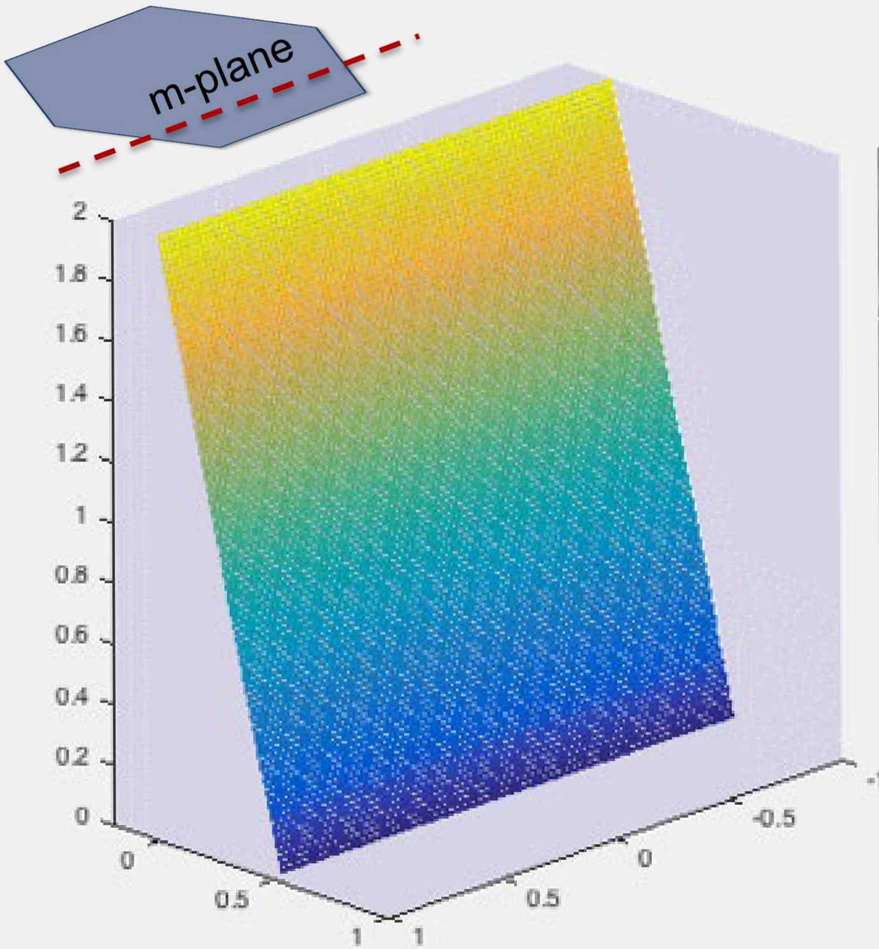
Etch mask defined parallel to *a*-plane

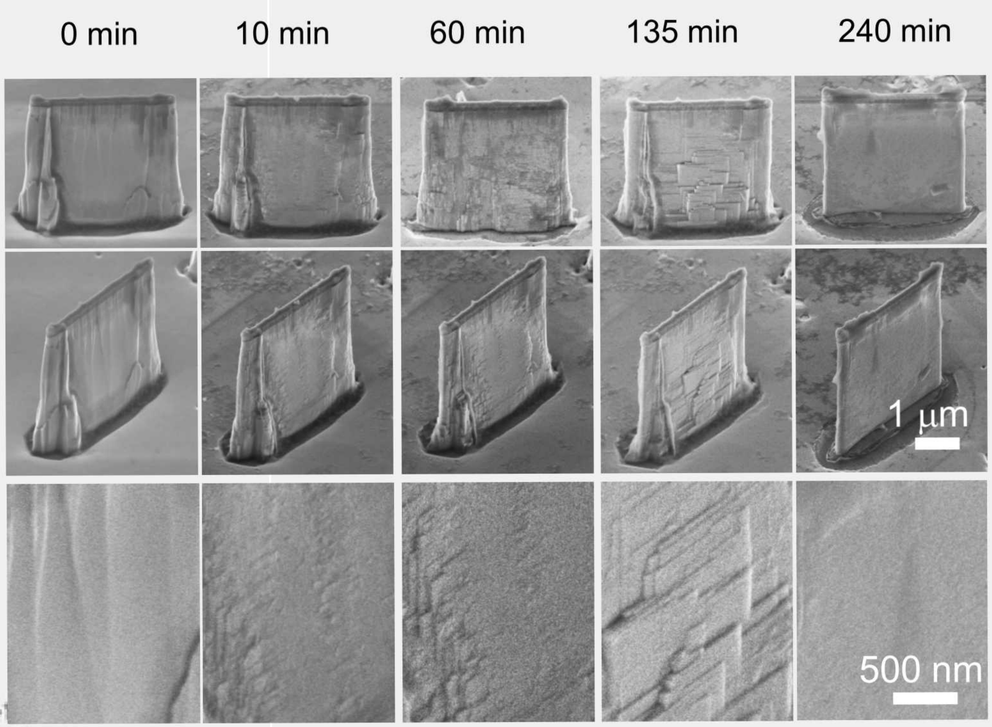


AZ400K, 65°C

Etch evolution of *m*-plane wall

Etch mask defined parallel to *m*-plane

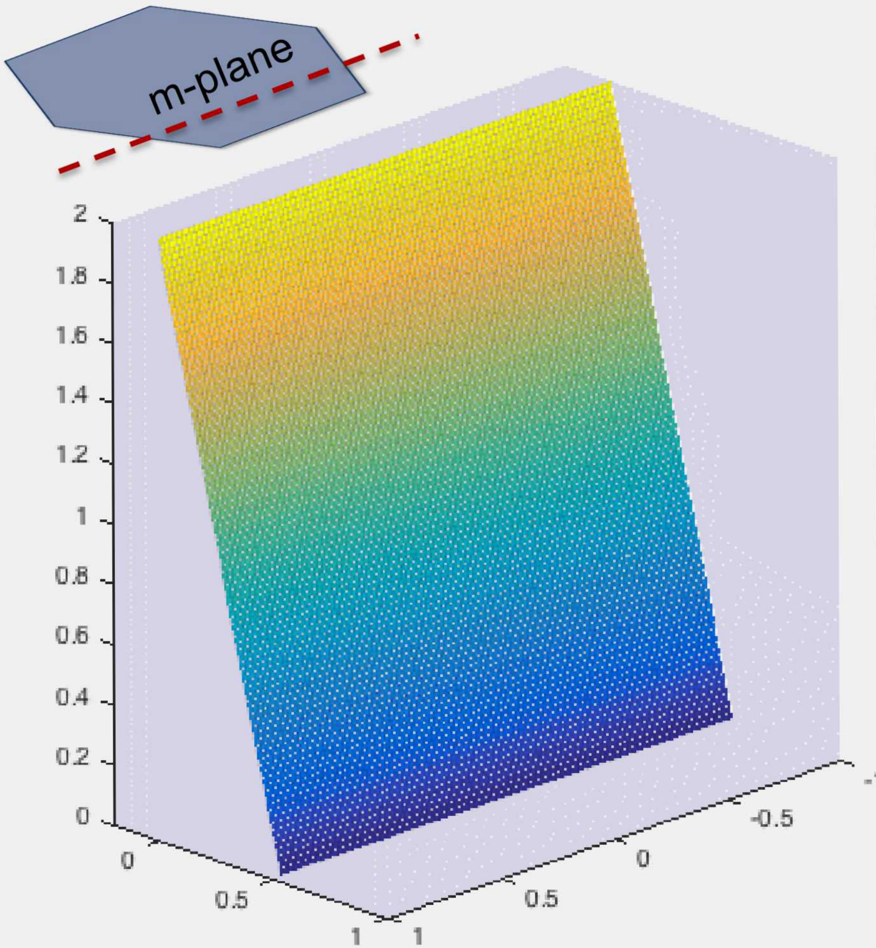


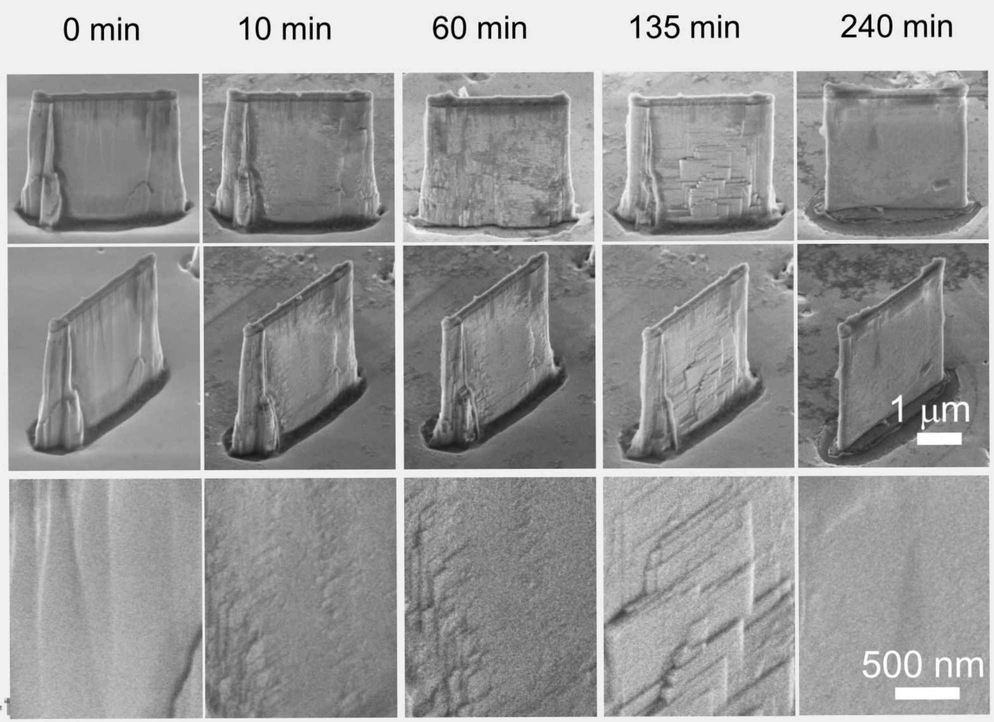


AZ400K, 65°C

Etch evolution of *m*-plane wall

Etch mask defined parallel to *m*-plane

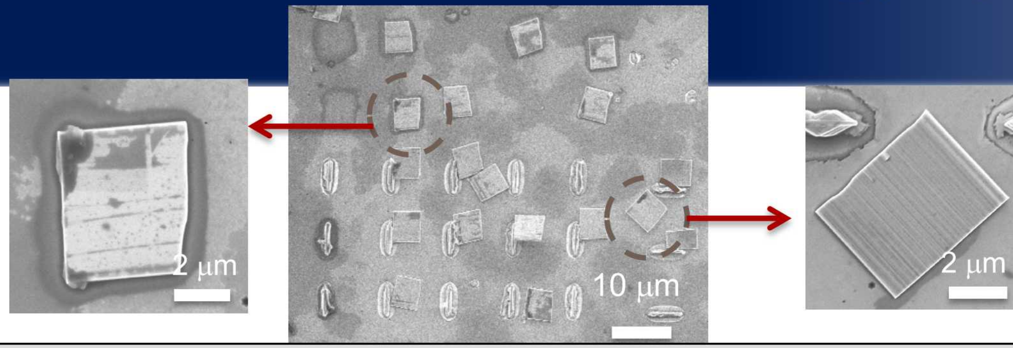




AZ400K, 65°C

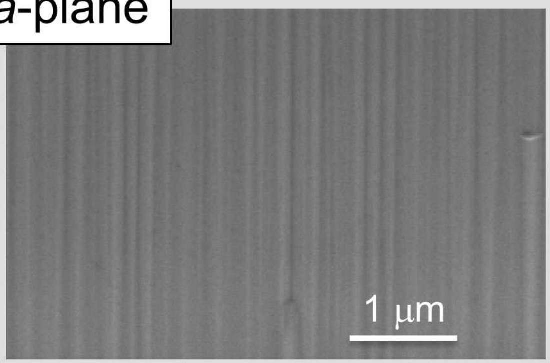
Measured etched nanowall morphology by AFM

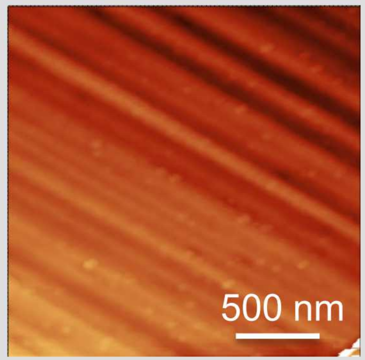
m-plane wall

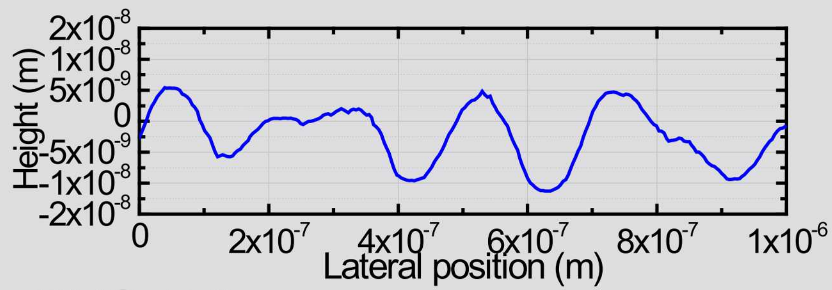


a-plane wall

a-plane

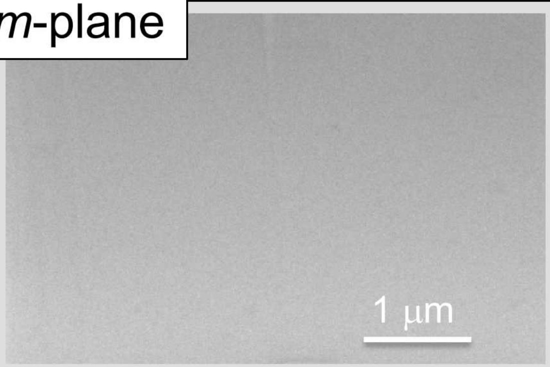


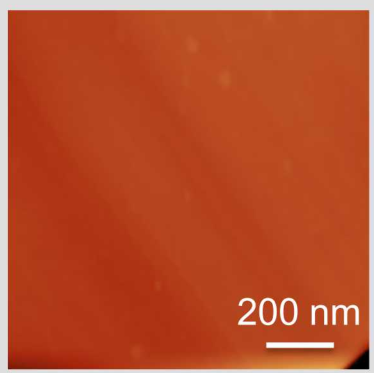


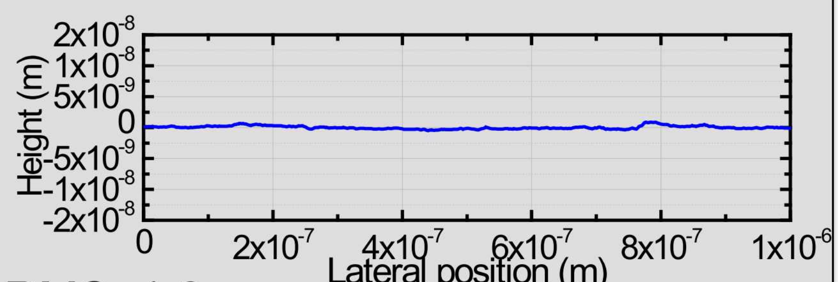


RMS: 7.6 nm

m-plane





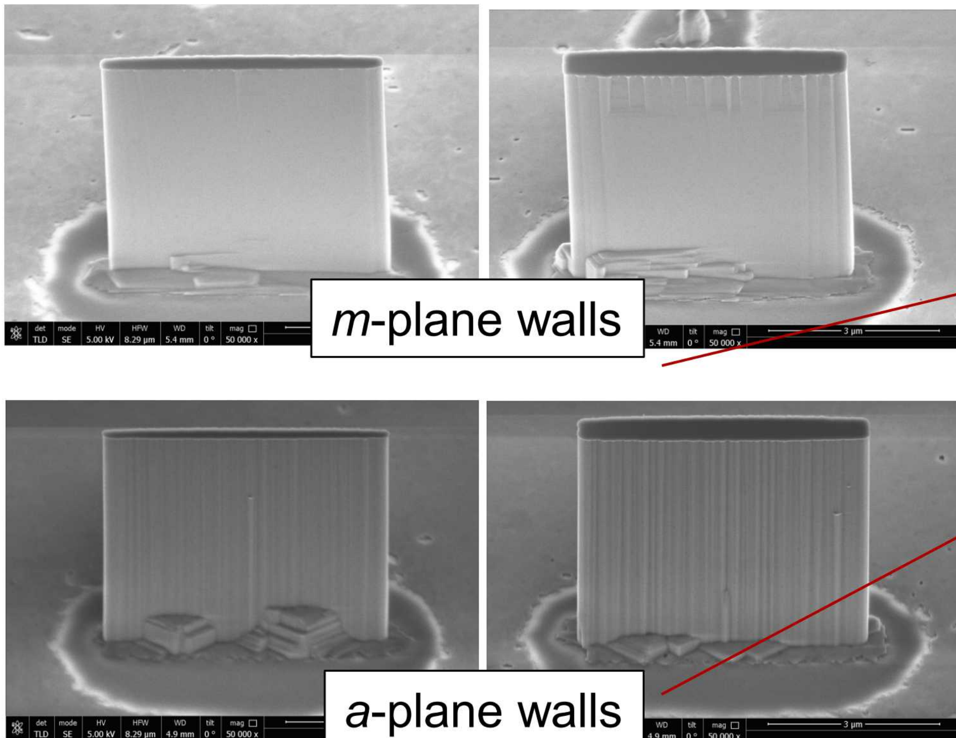


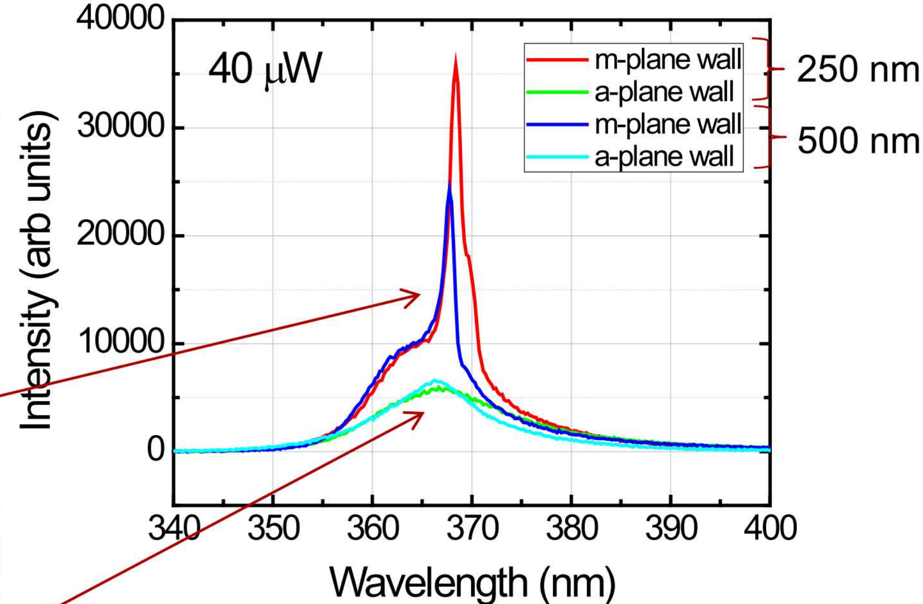
RMS: 1.2 nm

Achieved atomically smooth surfaces through a two-step top-down process!

Cavity modes in nanowalls

Optical pumping of GaN nanowalls
Nd:YAG, 266 nm pulsed laser, μPL

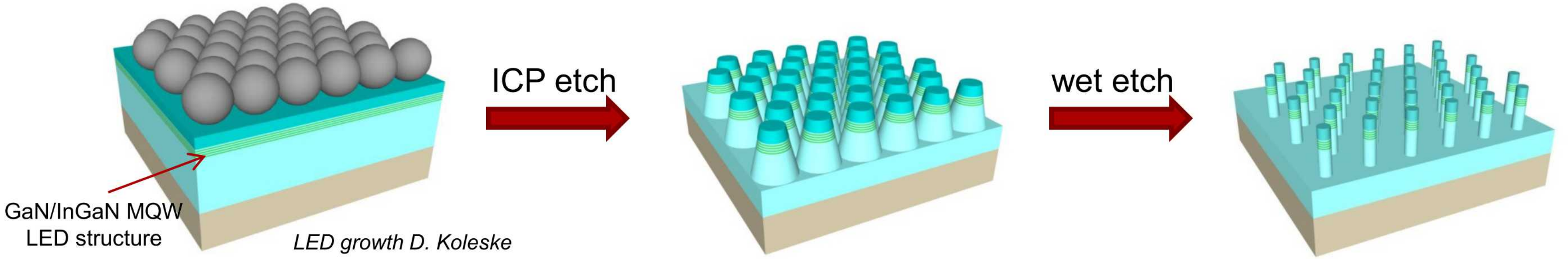


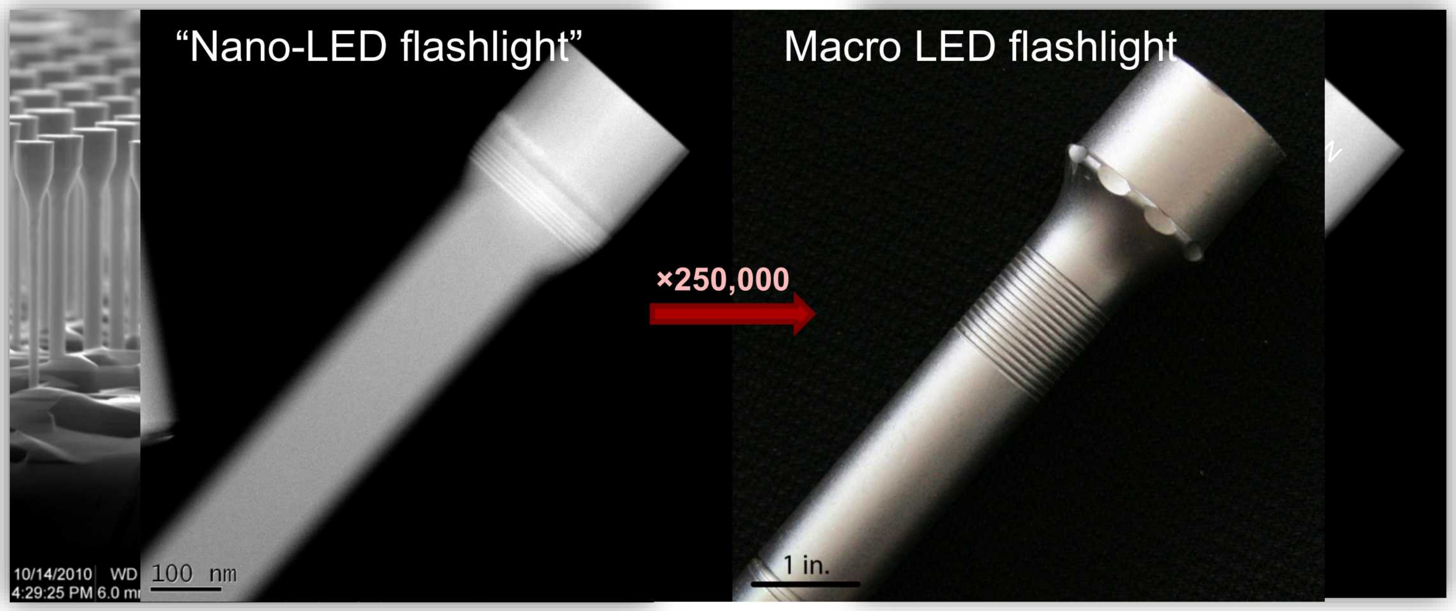


Optically pumped nanowalls shows luminescence coupled to cavity modes only with the smooth m-plane sidewalls

Etched surface morphology has important effects on optical properties of nanostructures

Axial GaN/InGaN nanowire LEDs





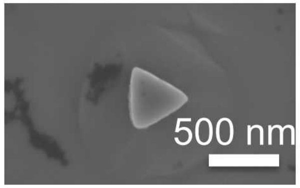
Q. Li et al., *Optics Express* **19**, 25528 (2011)

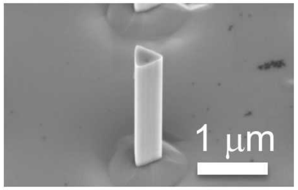
Doping affects etch rate – provides opportunity for 3D shape engineering

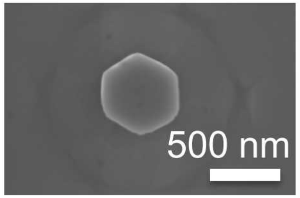
George T. Wang

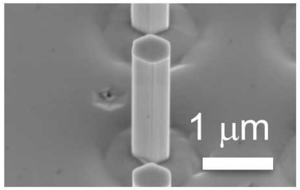
Controlled and complex cross-sections

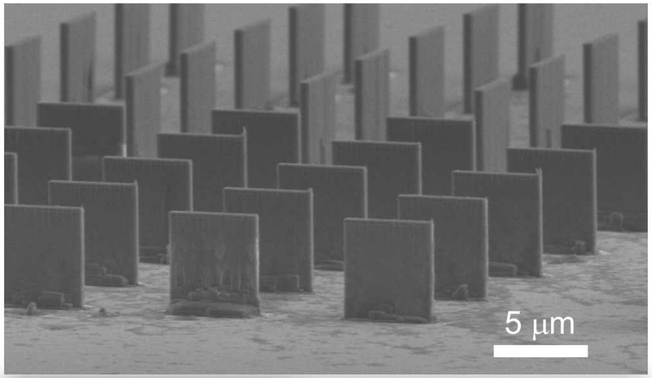
Can we expand to more *complex geometries* ?

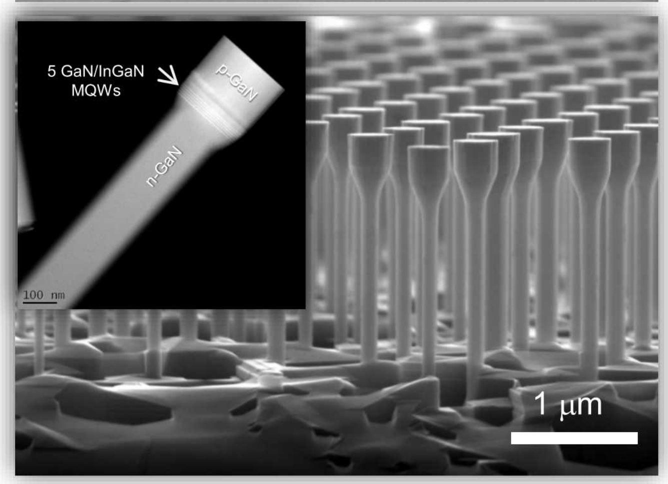


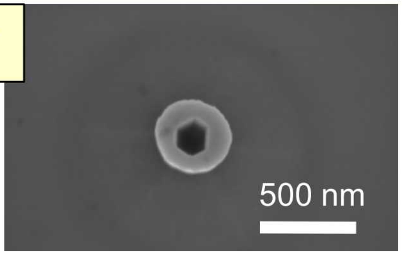


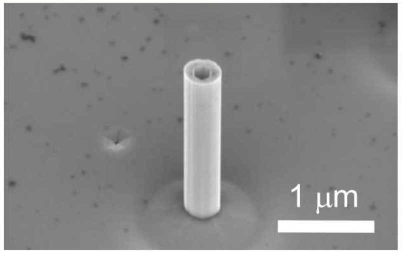


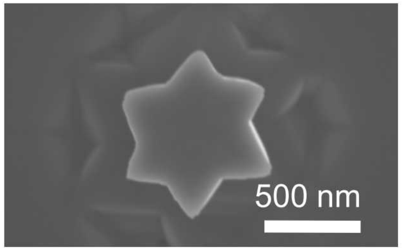


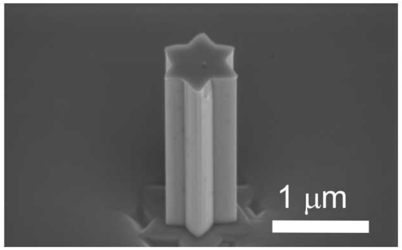


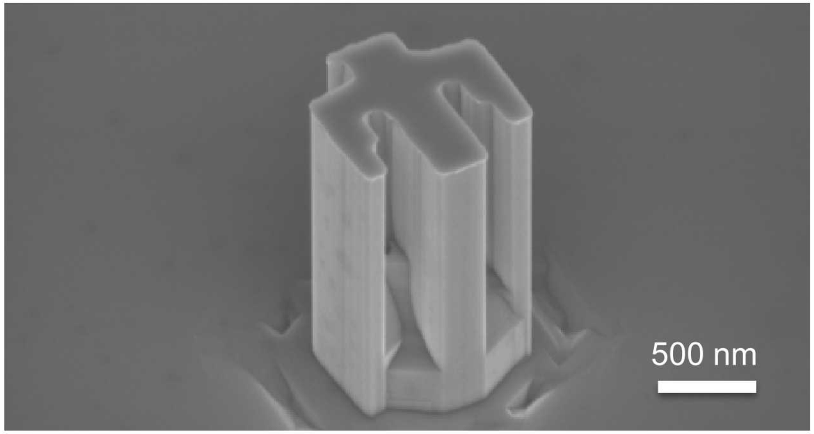










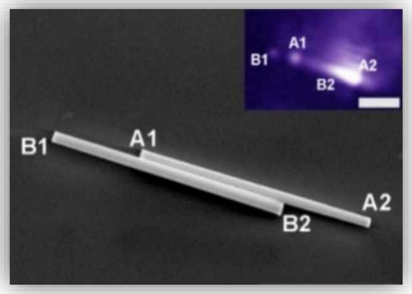


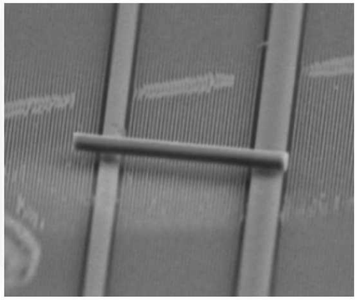
Understanding of the etch evolution enables design of a wide range of smooth faceted vertical nanostructures

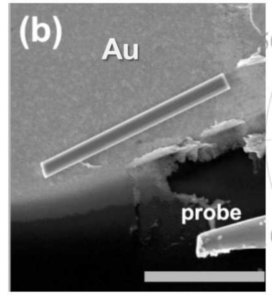
Top down vertical nanostructures for photonics

Sandia National Laboratories

Mode & polarization control in GaN nanowire lasers







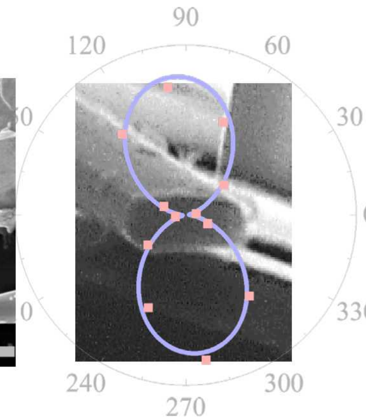
Q. Li et al., *Optics Express* **20** 17874 (2012)

H. Xu et al., *Appl. Phys. Lett.* **101** 221114 (2012)

H. Xu et al., *Appl. Phys. Lett.* **101** 113106 (2012)

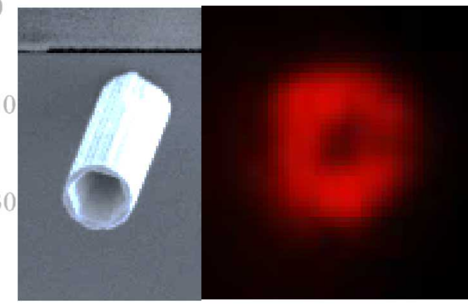
H. Xu et al, *Opt. Exp.* **22**, 19198 (2014)

J.B. Wright et al., *Appl. Phys. Lett.,* 104, 041107 (2014)



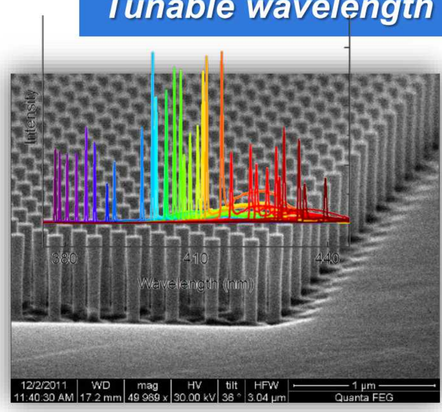
Li, Changyi, et al. *Nanoscale* ***8***, 5682 (2016)

Beam shape control
nanotube lasers

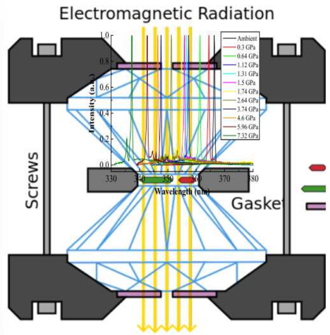


C. Li et al., *ACS Photonics*, **2**, 1025 **(2015)**.

Tunable wavelength nanowire lasers

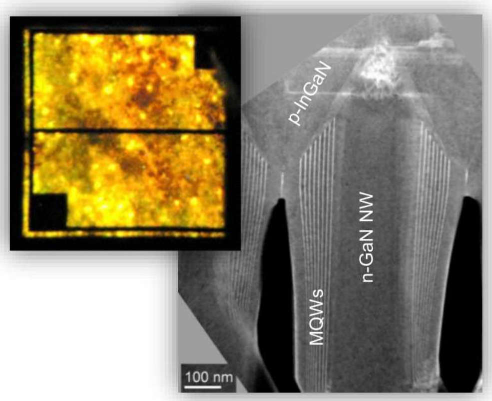


J.B. Wright et al., *Sci. Reports* 3, Art no. 2982 (2013) doi:10.1038/srep02982



S. Liu, C. Li, J. J. Figiel, S. R. Brueck, I. Brener, G. T. Wang, *Nanoscale*, *7*, 9581 **(2015)**.

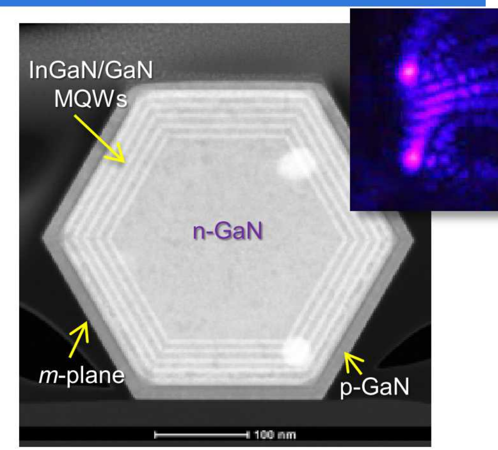
Nonpolar core-shell nanowire LEDs, solar cells, and lasers



J. Wierer et al., *Nanotechnology* **23** 194007 (2012)

Riley, J.; *Nano Lett.* **14**, 4317 (2013).

G. T. Wang et al., *Phys. Stat. Solidi A,* **211**, 748 (2014)



C. Li et al., *Nano Lett*, **17**, 1049 (2017)

Howell, S. L., *Nano Lett.*, **13**, 5123 (2013)

Top-down fabrication of AlGaN nanowires?

After ICP etch only

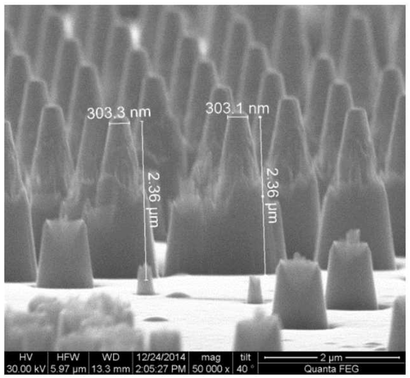
After AZ400K 65°C wet etch

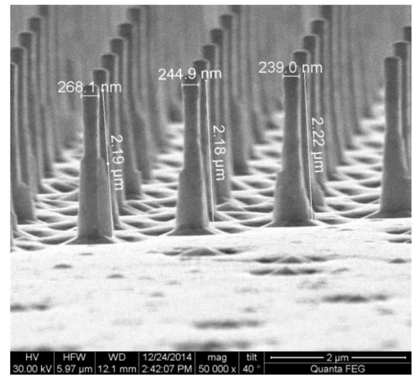
240-500nm diameter

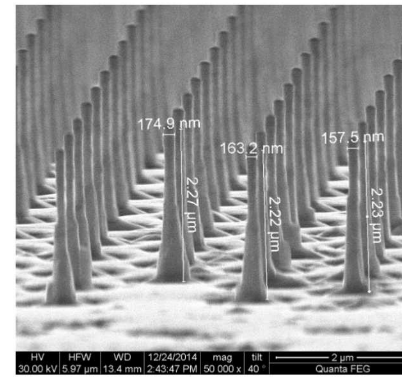
150-250 nm diameter

30% AlGaN

4.0 μm $Al_{0.31}Ga_{0.69}N$ on 1.6 μm AlN on *c*-sapp

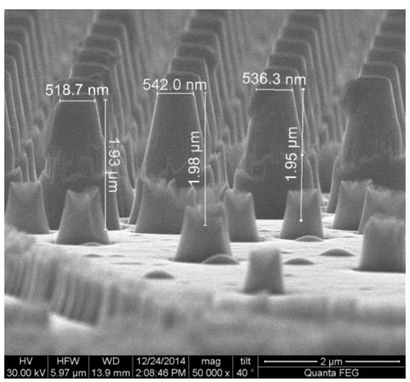


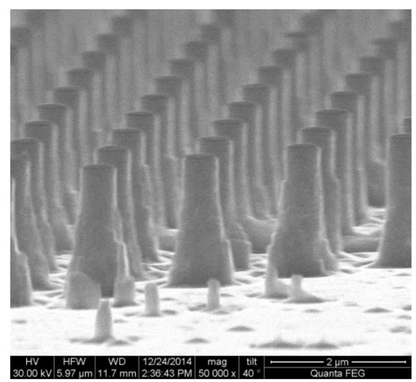


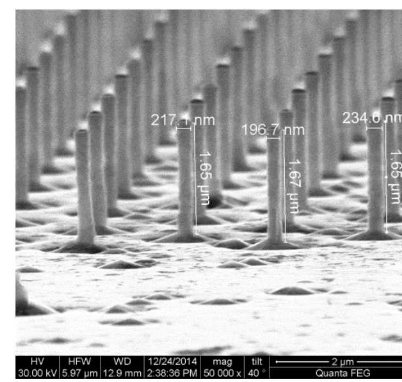


70% AlGaN

3.0 μm $Al_{0.71}Ga_{0.29}N$ on 1.5 μm AlN on *c*-sapp



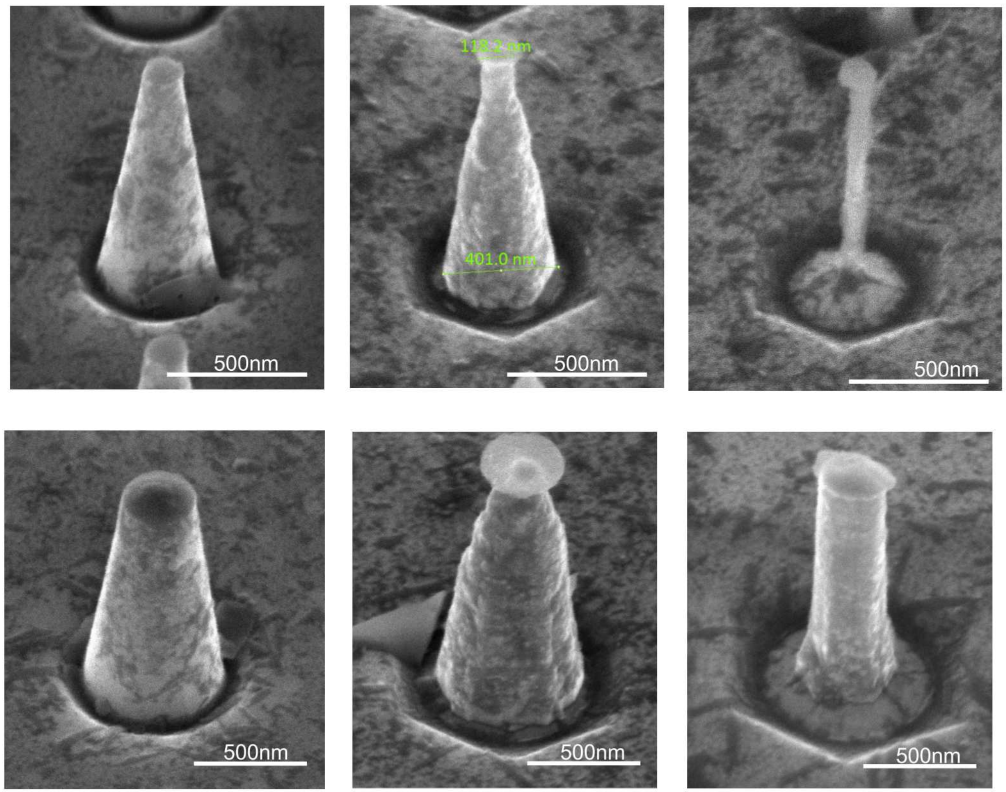




AlGaN samples grown by Andrew Allerman

AlGaN exhibits rougher, less vertical sidewalls than GaN – why??

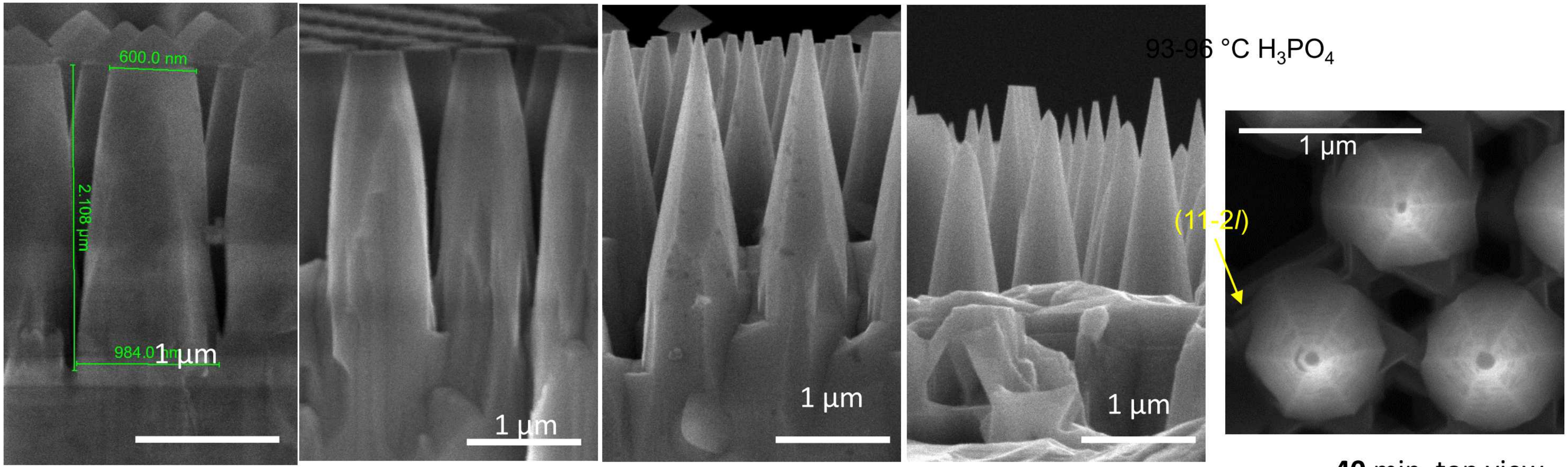
Top-down fabrication of AlGaN nanowires?



65% nAlGaN, 65^{o}C AZ400K

- Preliminary results show initial etch similar to GaN, with the same 'm-' $(1\bar{1}00)$ plane type micro-faceting
- Etch pits aligned with 'm-' $(1\bar{1}00)$ plane
- However, no prominent GaN-like vertical/lateral 'steps' observed during etch duration
- Further work needed to improve or explain etch

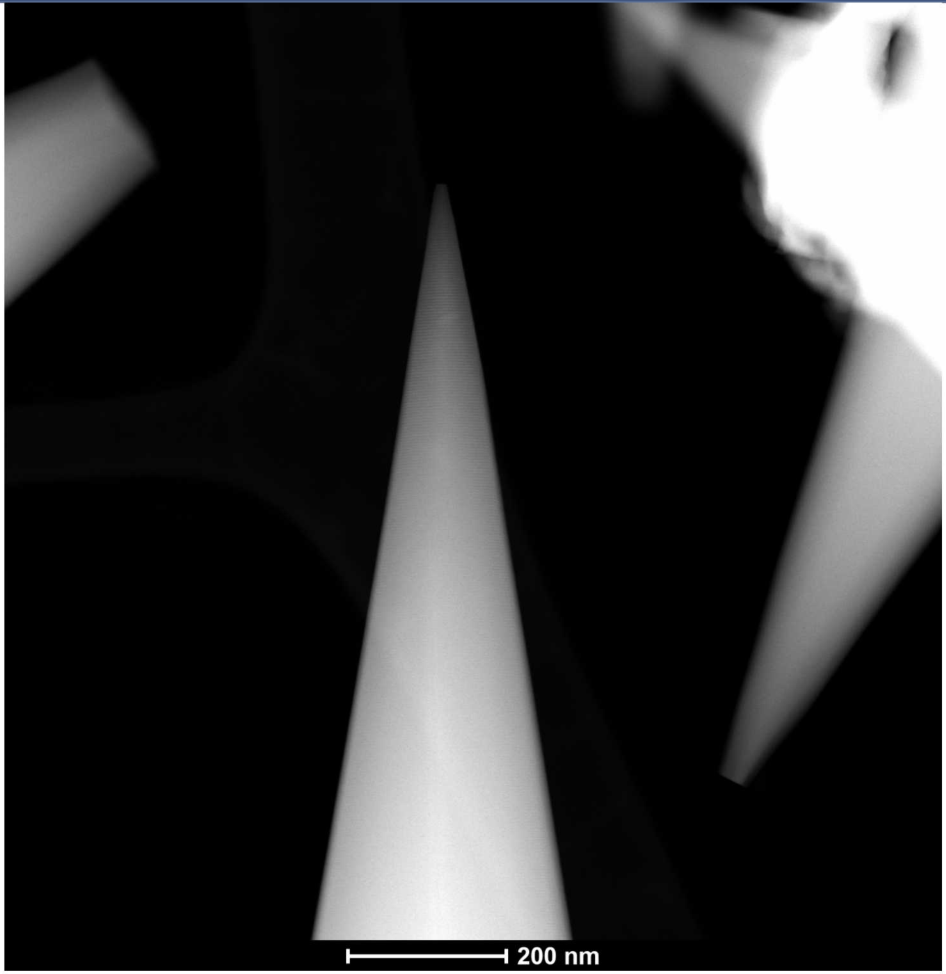
H_3PO_4 wet etching of tapered GaN nanowires

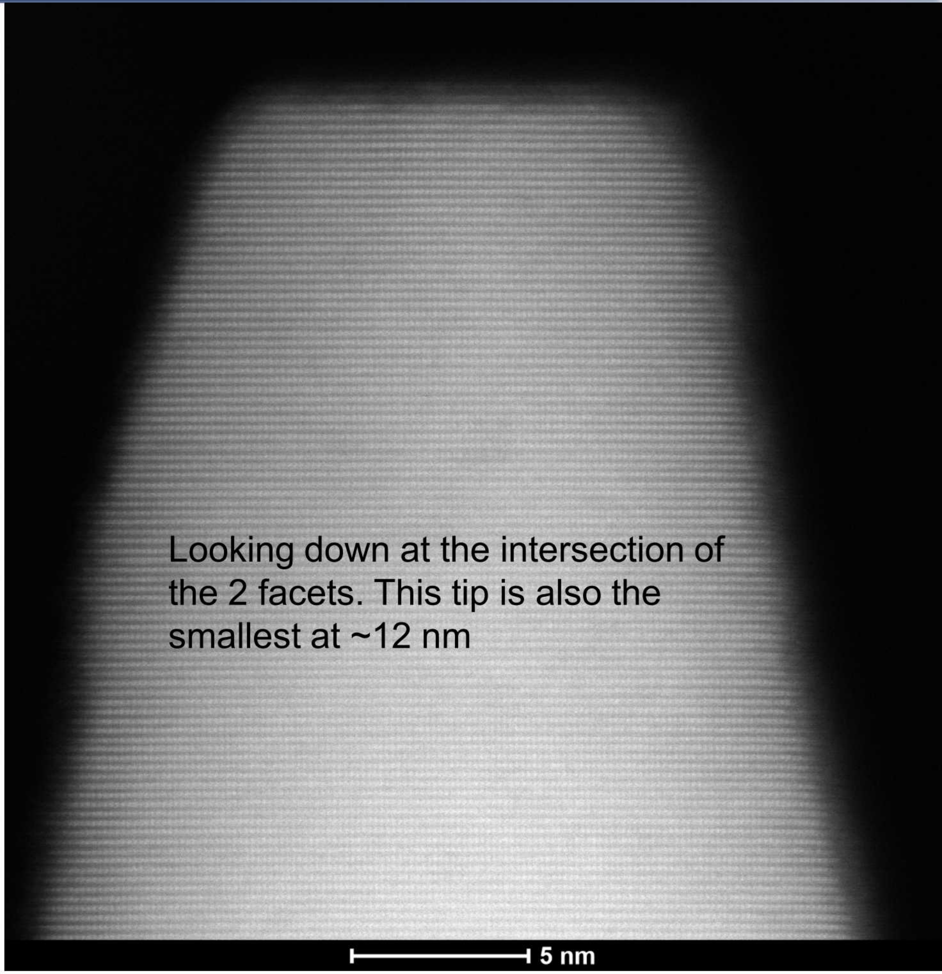


30 min ICP only | **10** min H_3PO_4 (~95°C) | **40** min | **55** min | **40** min, top view

- H_3PO_4 wet etching of ICP dry etched GaN nanowires leads to inclined {11-2*l*} facets not seen in KOH-based etch
- Micro-faceting not observed during etch in contrast to KOH-based etch. Also top corners not “protected” as in KOH-based etch.
- Leads to “pointy” tapered nanowires instead of straight vertical nanowires

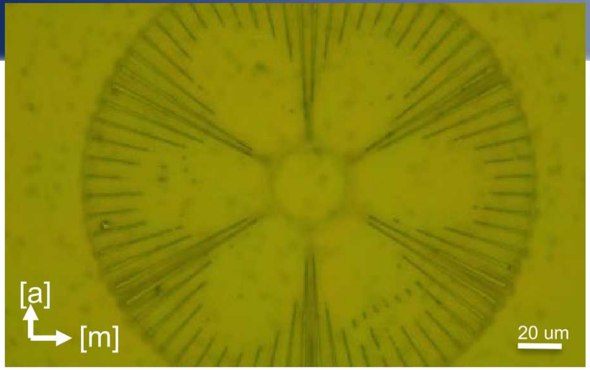
STEM - H_3PO_4 etched nanowires

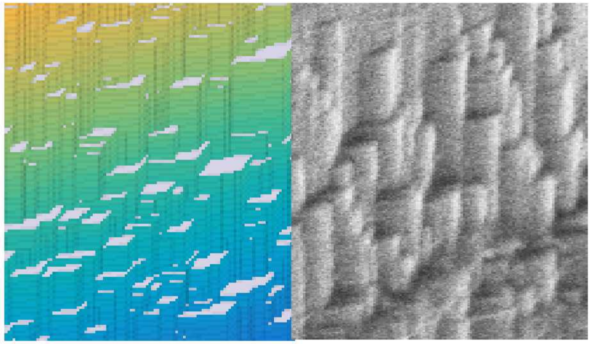


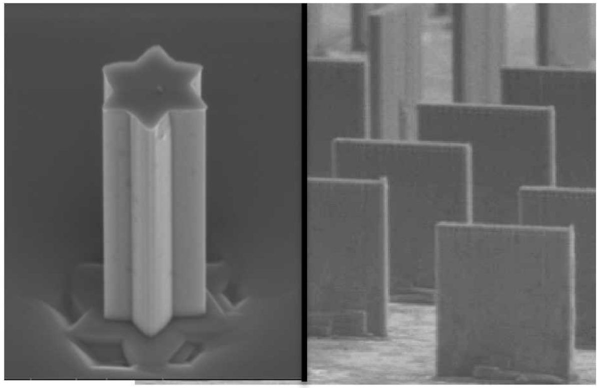


Conclusions

- **Wet etching: ideal technique for III-nitride nanostructure fabrication due to extremely high anisotropy**
  - Wulff-Jaccodine: **prediction of pillar etch geometry and facets**
  - **Mechanism for facet evolution** from tapered to straight
  - Phosphoric acid vs. KOH -> different facets. Possibility for other, different 3D wet etches?
- **Complex cross-sectional geometries** with atomic-scale sidewall smoothness, for **III-nitride based nano-devices**







BACKUP SLIDES

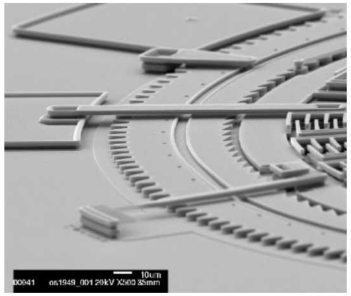
Problem: Lack of 3D nano-microfabrication processes for III-nitrides and III-V compound semiconductors

Sandia National Laboratories

Control over 3D shape and composition at nano-microscale can enable *manipulation of properties, new physics and functionalities, and enhanced performance.*

3D Silicon structures

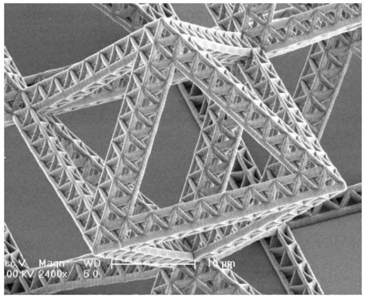
N/MEMS



Torsional Ratcheting Actuator

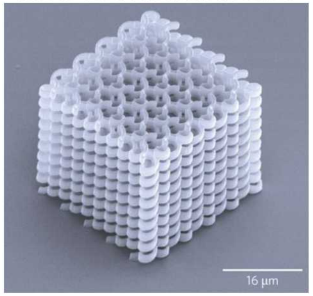
SNL

Nanolattice/truss



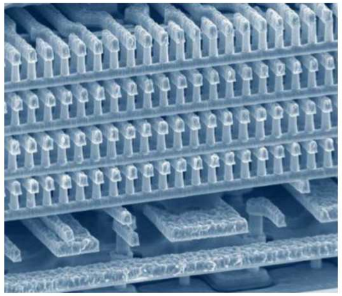
J. Greer, Caltech (2014)

3D Photonic Crystals and Metamaterials



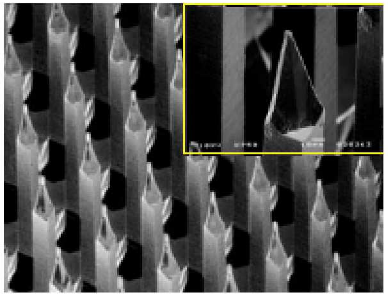
Farsari et al. *Nat. Phot.* (2009)

3D FinFET/NAND



Matrix Semiconductor (2012)

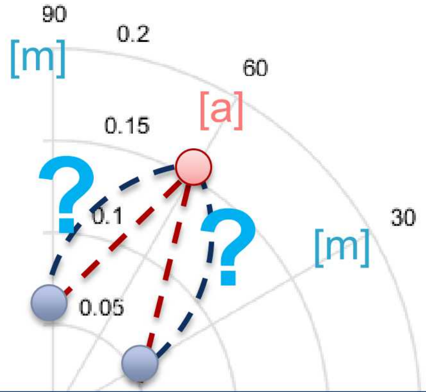
3D Nanoneedles



Shikida et al. (2004)

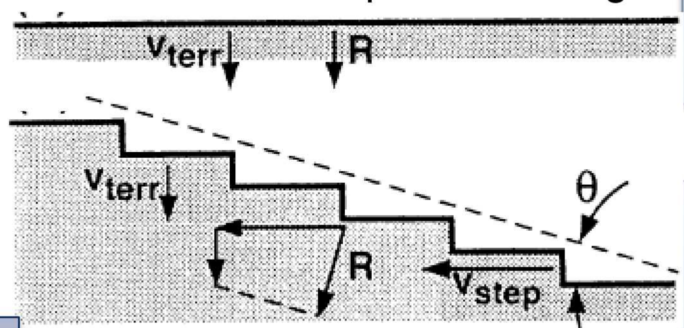
<u>Methods to realize tailored 3D nanostructures are significantly underdeveloped for GaN and even classic III-V semiconductors (e.g. GaAs)</u>, hindering development of novel and next generation nano- and micro- enabled semiconductor structures and devices for solid-state lighting, high-speed and high power computer, quantum emitters, energy harvesting,, etc.

How Does the Etch Rate Depend on Orientation ?



What is the shape of this curve ?

Illustration of step-flow etching



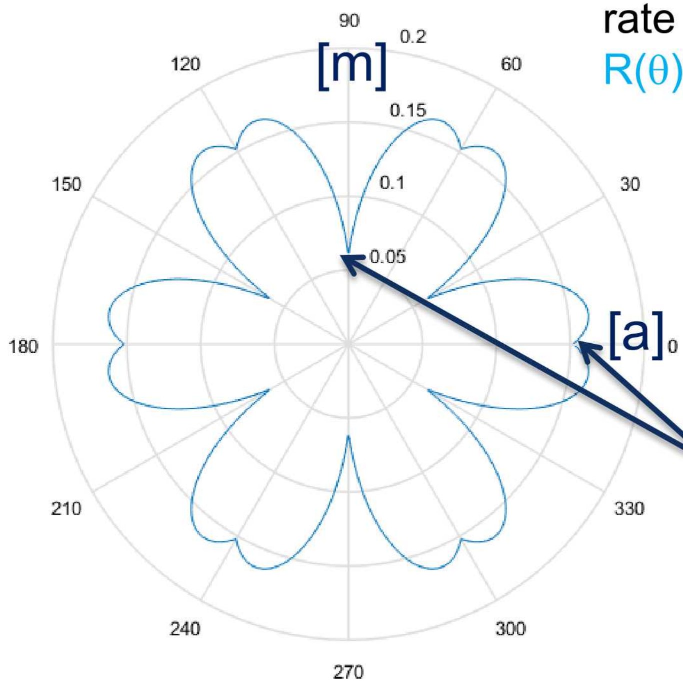
Wind et al., Surf. Sci. 460, 21 (2000)

Atomically flat facet, e.g. m and/or a plane

Misoriented facet with offcut θ, e.g. facets between m and a planes

Between low index facets (i.e. with zero steps), the etch rate as a function of orientation is:

$R(\theta) = V_{terr}\cos(\theta) + V_{step}\sin(|\theta|)$



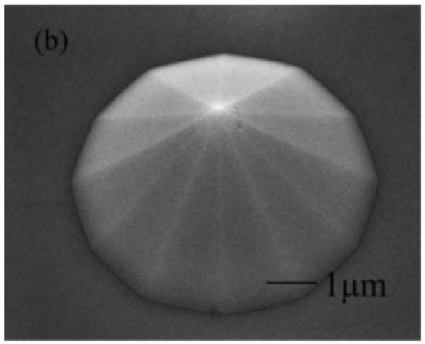
Expected form for orientation dependent etch rates, given m and a etch rates, and that both m and a are atomically flat surfaces

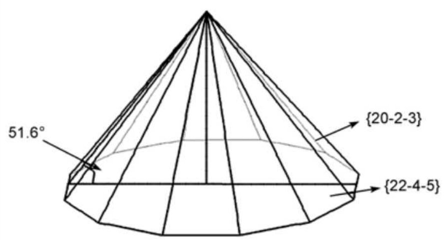
$R(\theta) = m\cos(\theta\pi/(\pi/3)) + a\sin(|\theta\pi/(\pi/3)|)$, for θ: $-\pi/6 < \theta < \pi/6$

Local minima for atomically flat surfaces – as is for the growth Wulff plot

Prior H_3PO_4 Wet etching of planar GaN

N-polar GaN

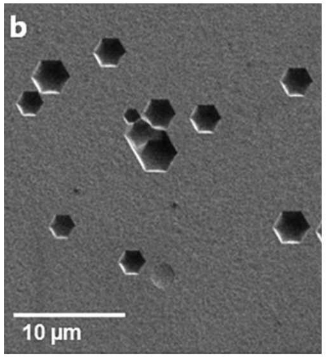


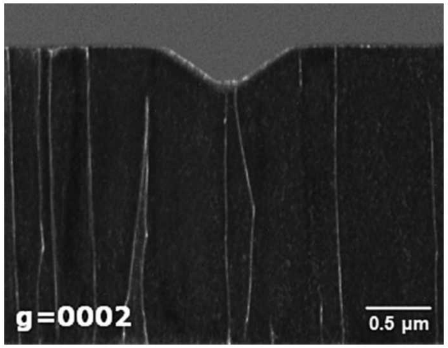


Qi et al., Sci. China, Tech. Sci., 53, 769 (2010)

- N-face GaN etched in H_3PO_4 (120°C) 5 minutes yields dodecagonal pyramids centered around dislocations
- Etching preferentially slows down on$(22\bar{2}\bar{3})/(22\bar{4}\bar{5})$ semipolar planes due to low surface energies

Ga-polar $Al_{0.22}GaN$ (20 nm)/GaN



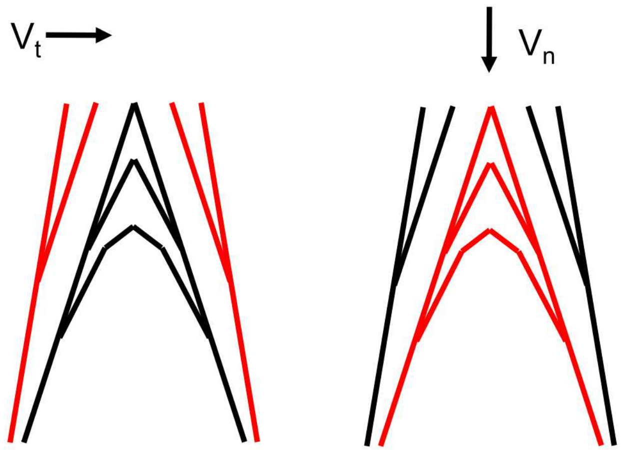


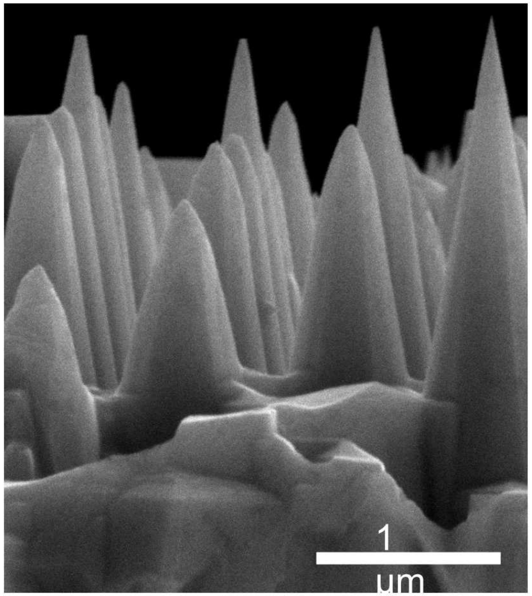
M. Reiner et al., PSSB, 252, 1121 (2015)

- Ga-face GaN etched in H_3PO_4 (150-245°C) yields hexagonal pits centered around dislocations with semipolar {101k} or {112l} facets

Nanowire Etch Progression Hot H_3PO_4

The etch appears to move tangentially and then normally to the Ga surface

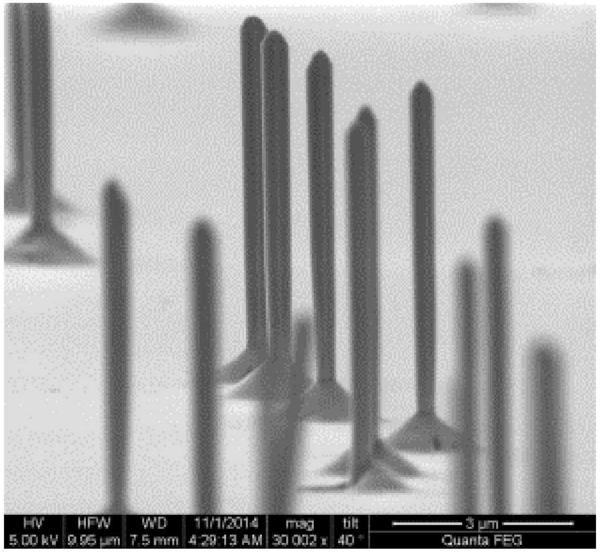


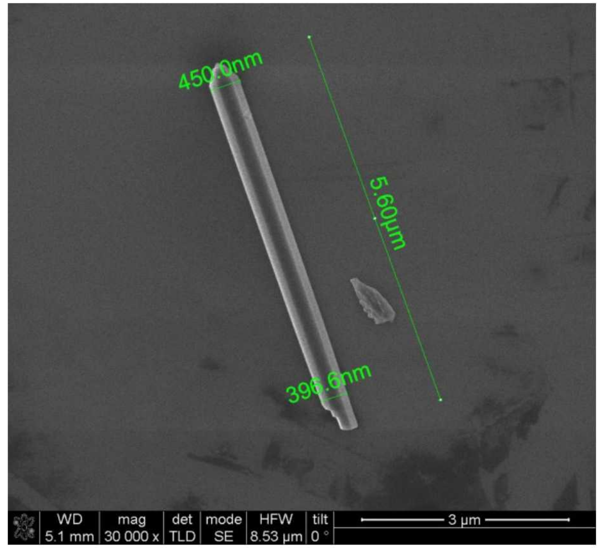


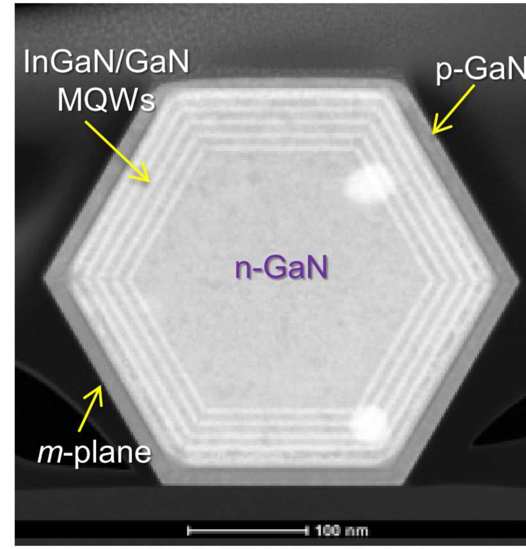
Semipolar facets form due to V_n/V_t ratios. Initially, V_t dominates where it is dominated by concentration (kinetics). When V_n dominates, an increase in semipolar angle occurs, and this is driven more by temperature and surface energy (thermodynamics).

Hybrid top-down bottom-up fabrication of core-shell p-i-n InGaN/GaN core-shell NWs

Sandia National Laboratories

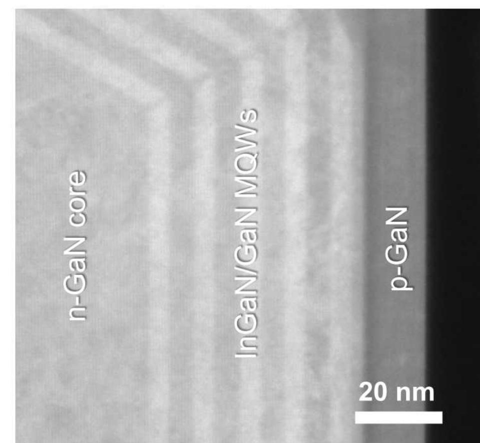






Core-shell radial p-i-n InGaN/GaN MQW nanowires following MOCVD regrowth on top-down fabricated n-type GaN nanowires

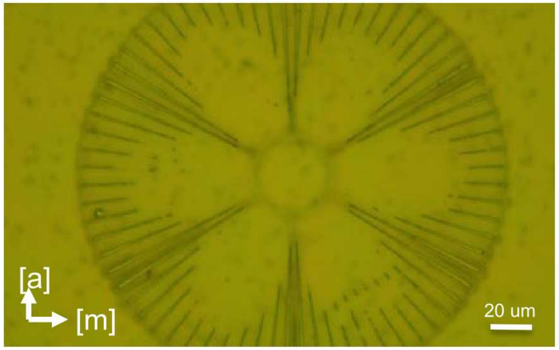
- Regrowth on top-down n-GaN nanowire results in taper. Growth of semipolar planes also results in non-flat tip, which may lower mirror reflectivity
- Growth conditions, layer thicknesses, varied over several runs, then nanowires tested by optical pumping for lasing

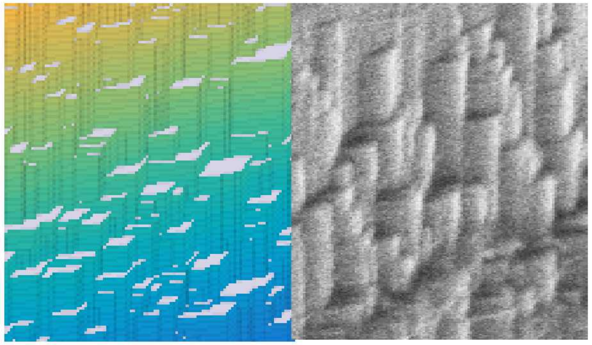


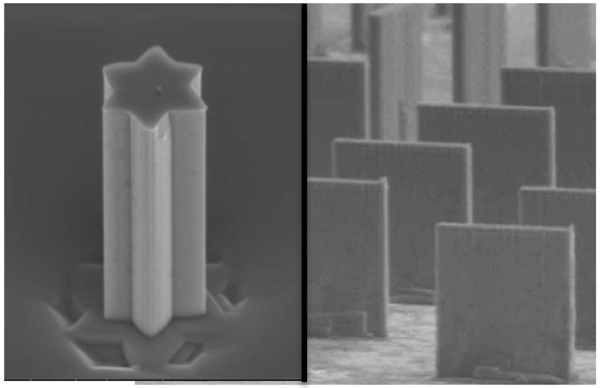
STEM by Ping Lu

Summary – Top-down fabrication of III-nitride nanostructures for photonics

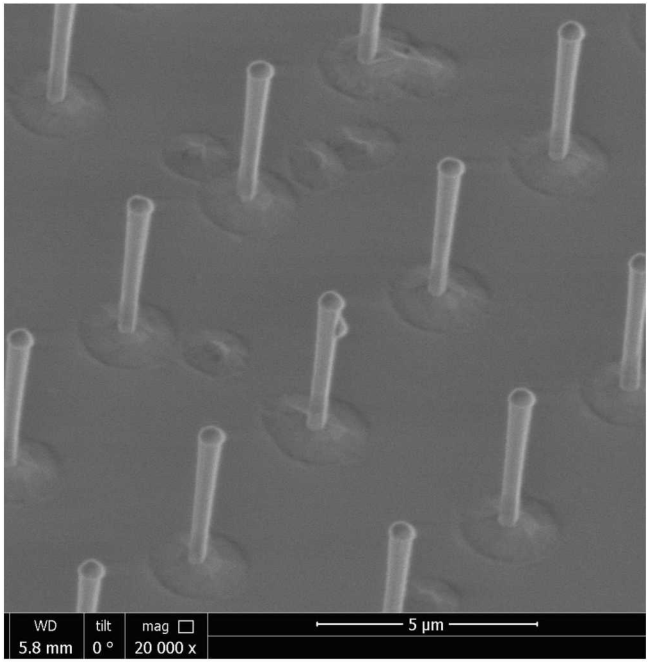
- **First direct orientation resolved wet etch rate measurements** for the nonpolar GaN set of planes
- Implementation of Wulff-Jaccodine method for **prediction of pillar etch geometry and facets**
- **Elucidated mechanism for facet evolution** from tapered to straight nanostructures
- Demonstrated **complex cross-sectional geometries** for vertical nanostructures with possible atomic-scale sidewall smoothness
- Demonstrated **mode, polarization, beam-shape, and wavelength control** in top-down etched nanowire lasers
- **Wet chemical etching is an ideal technique for high-quality III-nitride nanostructure fabrication due to its extremely high anisotropy**



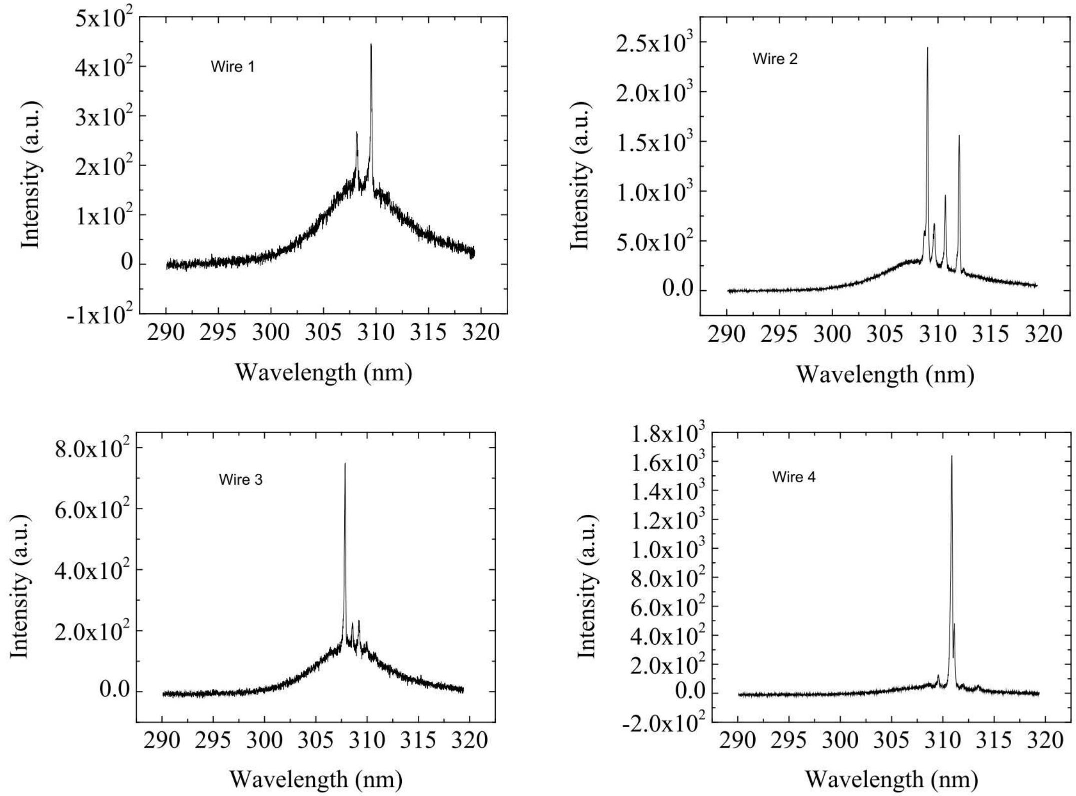




Top-down AlGaN nanowires - lasing achieved

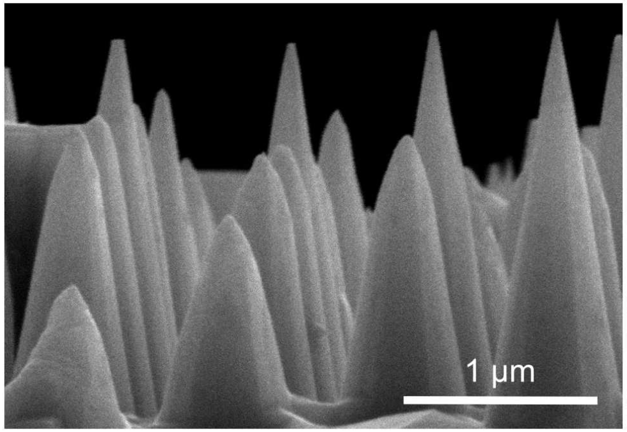


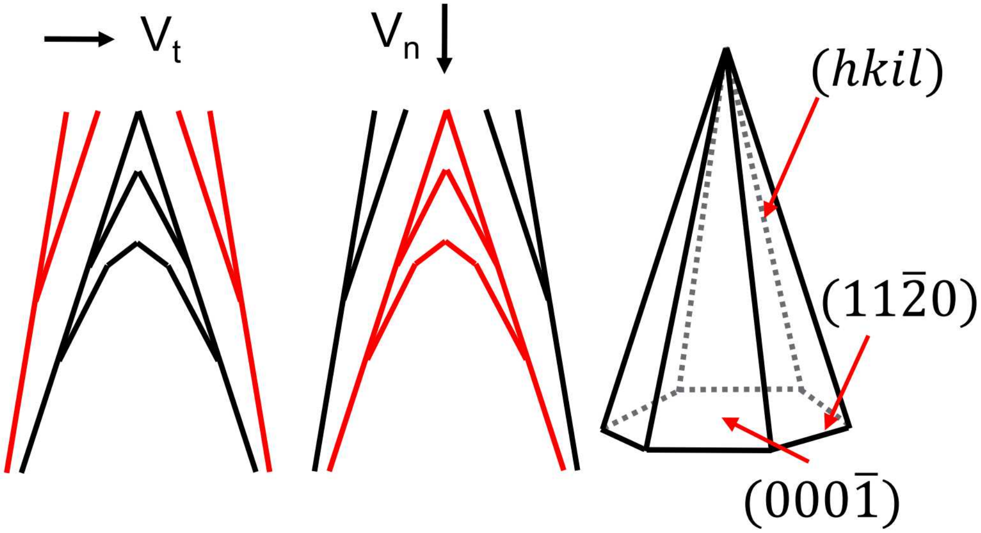
Nanowire Length: 4.0 – 4.1 um
Diameter: Top ~420-440 nm, bottom: 350-380 nm



- Single top-down $Al_{0.31}Ga_{0.69}N$ nanowires show multimode lasing ~308-312 nm
- Estimated threshold ~200 kW/cm^2 (similar to top-down GaN nanowires)
- *Nanowires burn-out after only ~3-6 seconds* (less resilient than GaN nanowires!?)

H_3PO_4 nanowire wet etching evolution

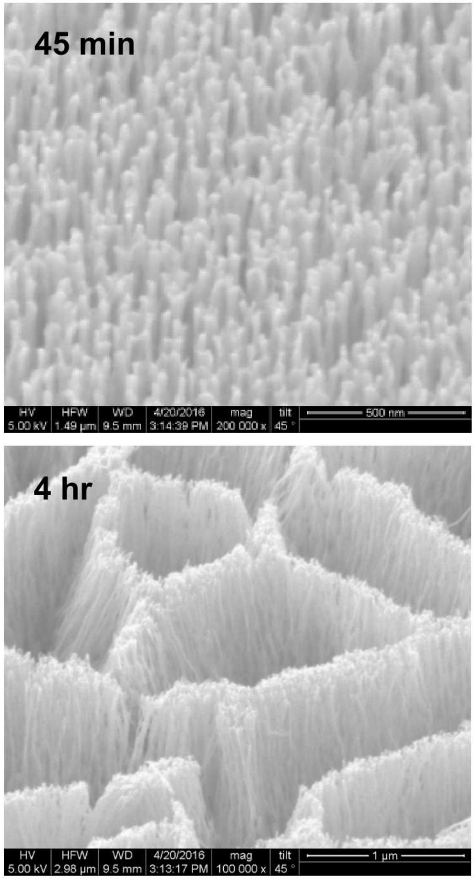




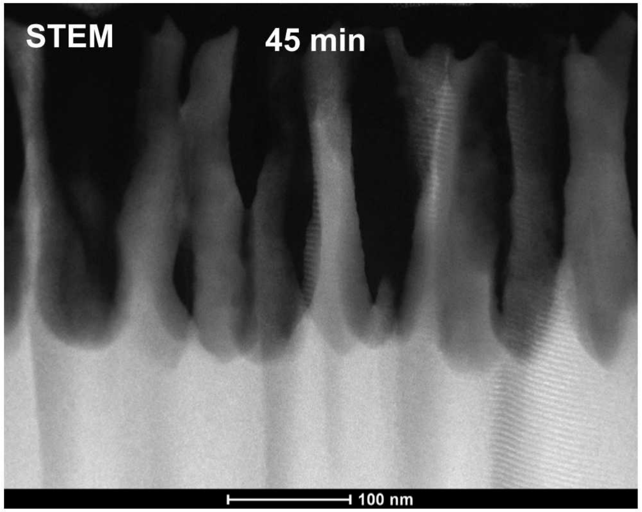
- High-index semi-polar planes are etched
- Semi-polar facets form due to V_n/V_t ratios
- V_t initially dominates → driven by concentration (kinetics)
- V_n driven by surface energy (thermodynamics)
- Semi-polar (*hkil*) plane progression: $73-82°\sim(11\bar{2}1) \rightarrow 60°\sim(11\bar{2}2) \rightarrow 50-45°\sim(11\bar{2}3)$
- Preliminary results support sequential increase of '*l*' index

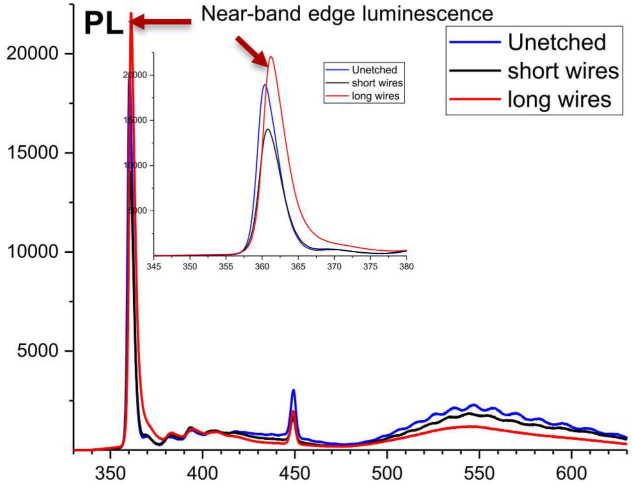
PEC etched GaN nanowires with very high aspect-ratios

PEC etch: 370 nm, 4 mW, 1V, 2M H_2SO_4



- GaN epilayer PEC etched at 370 nm results in dense array of thin GaN nanowires
- Cross-sectional STEM shows single-crystalline GaN nanowires; not related to dislocation cores, as previous reports showed
- Vertical etch through entire GaN film with little diameter change – self limiting lateral etch – near-surface carrier depletion effects?
- Despite high surface/volume, PEC etched NWs show comparable or better optical properties compared to unetched GaN film



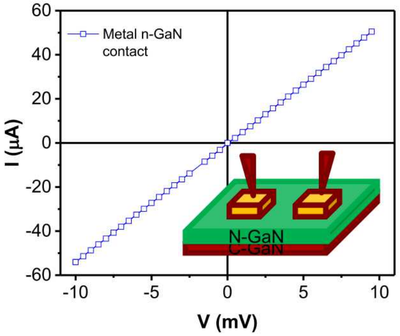


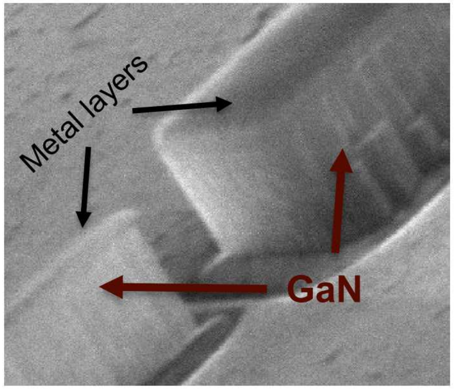
Working GaN field emission devices (nanodiodes)!

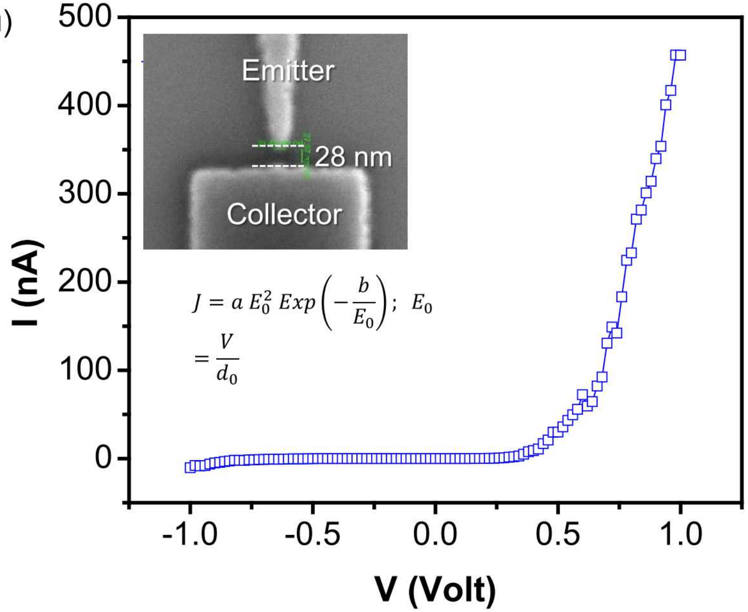
Proof-on-concept: Successful field emission (FE) in air with low turn on voltage and high emission current!

Field emission is diode-like for sharp emitter and flat collector (expected)

Ohmic contacts to n-GaN (Ti/Ni/Au)

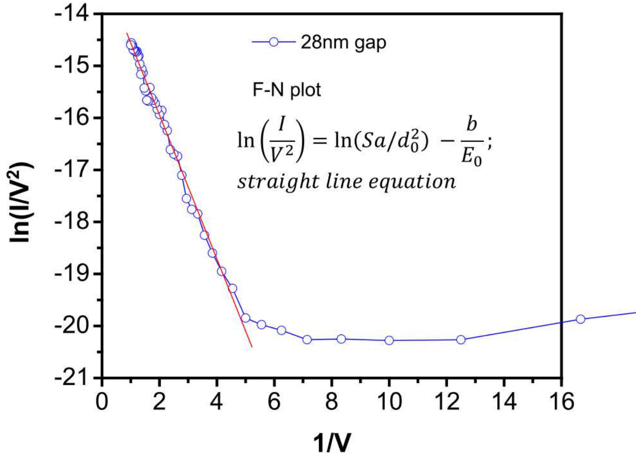






IV measurement: **Diode** characteristics

"Hero" device shows very low turn on and very high FE current!



Fowler-Nordheim (FN) test for field emission

Straight line fitting of data

Slope = -1.40; Y-intercept = -13.16

$\boldsymbol{Field\ enhancement\ factor\ \beta = 920\ using\ \phi = 4\ eV}$