SAND2019-5954C

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Top-Down Etching of III-Nitride Nanostructures

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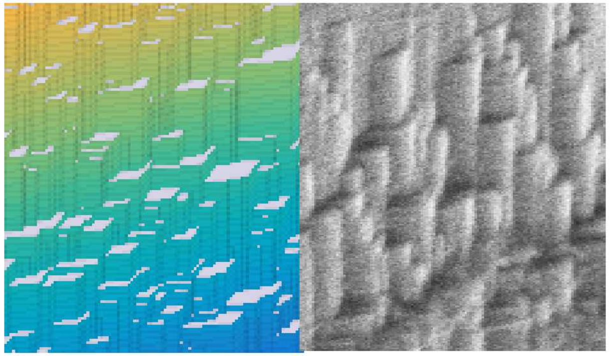
This work was funded by DOE BES Materials Science and Engineering Division, DOE Energy Frontier Research Center for Solid-State Lighting Science, and Sandia's LDRD program. This work was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. Department of Energy, Office of Basic Energy

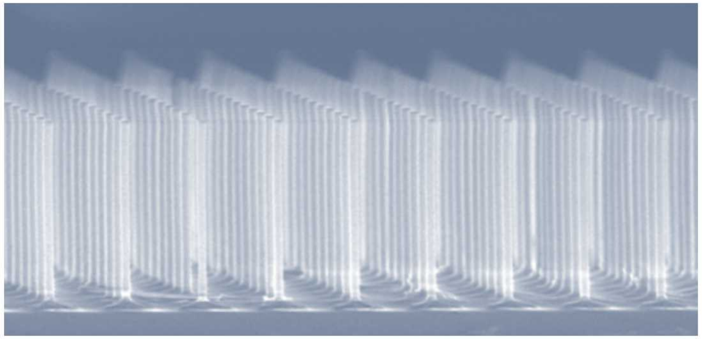
U.S. DEPARTMENT OF ENERGY

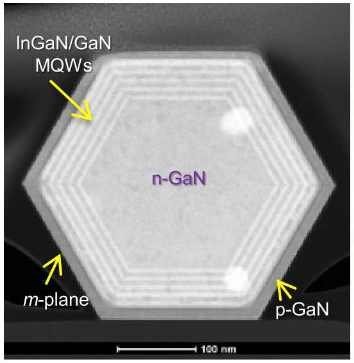
NNSA National Nuclear Security Administration

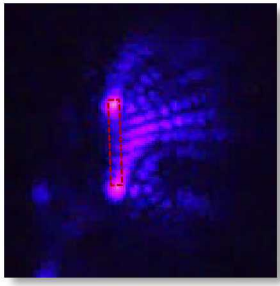
Outline

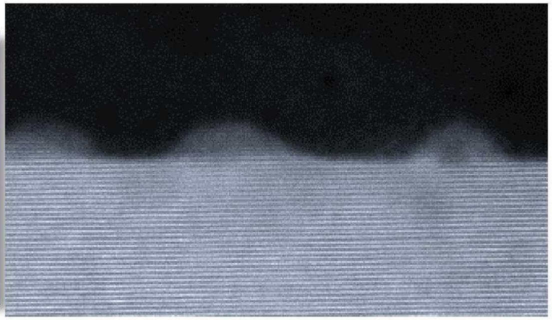
- Top-down fabrication – wet etching of GaN
  - III-Nitride nanowire photonics
- Quantum-size controlled etching of InGaN quantum dots







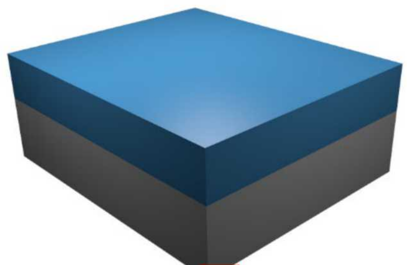


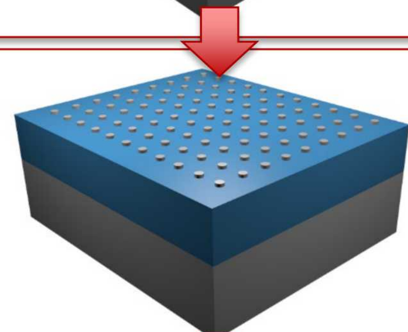
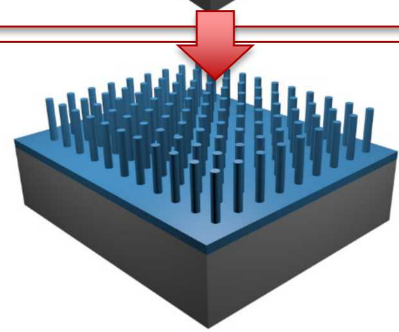


Motivation: Top-down approach for nanostructures

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 (e.g. e-beam, nanoimprint, interferometric)		• 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

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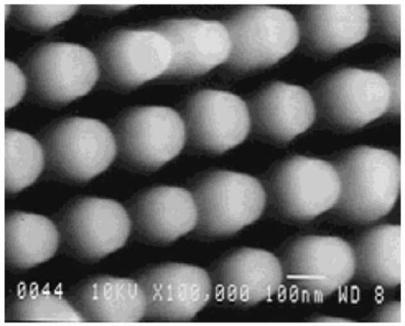
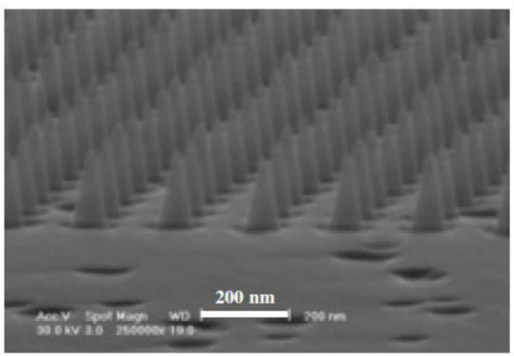
InGaN/GaN MQW nanoposts/nanopillars



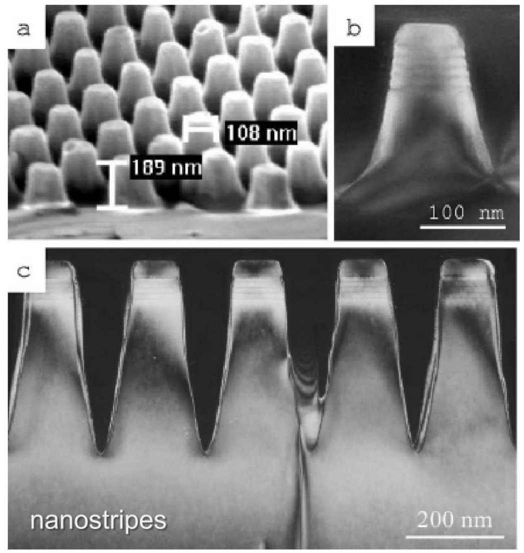
L. Chen et al., PSSa **188** 135 (2001) (Brown, Yale)

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



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

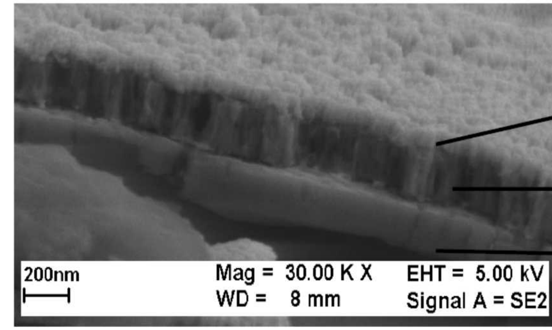
- E-beam Cr mask, Cl-based ICP-RIE etch
- Observed PL blue-shift w/decreasing diameter due to strain relaxation (reduction of QCSE)

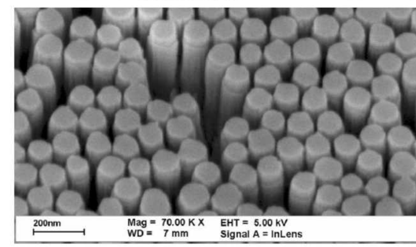


S. Keller et al., J. Appl. Phys. **100** 054314 (2006) (USCB)

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)

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

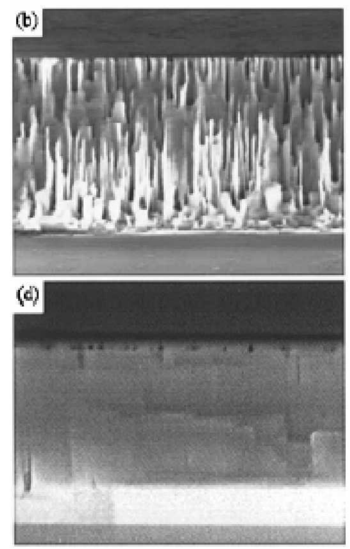
Etching was conducted at room temperature (25 °C) unless otherwise noted (after [31]).

Zhuang and Edgar, MSE R 48 1 (2005)

But actually…

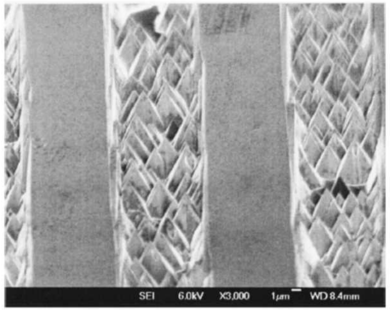
Significant etch rates, but extremely crystallographically anisotropic

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)

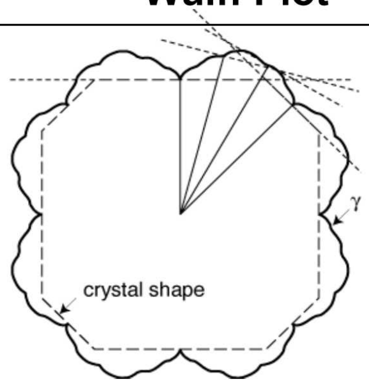
KOH-based wet etches

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 !

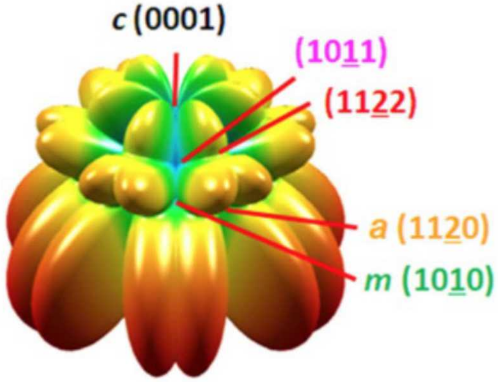
The appearance and evolution of facets

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



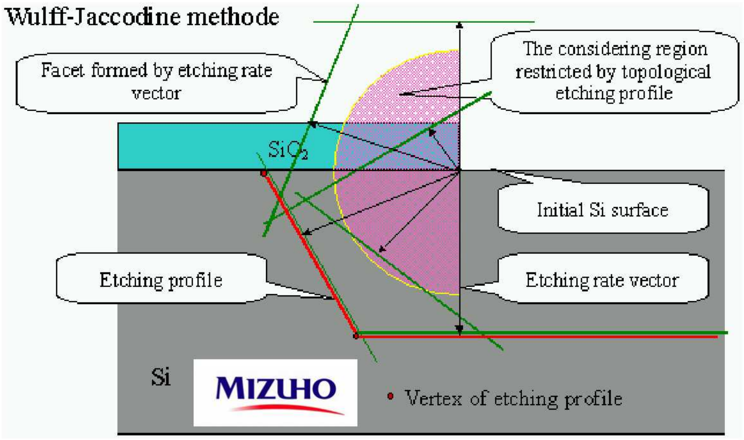
Wulff et al., Semicond. Z. Kristallogr 34, 449 (1901)

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

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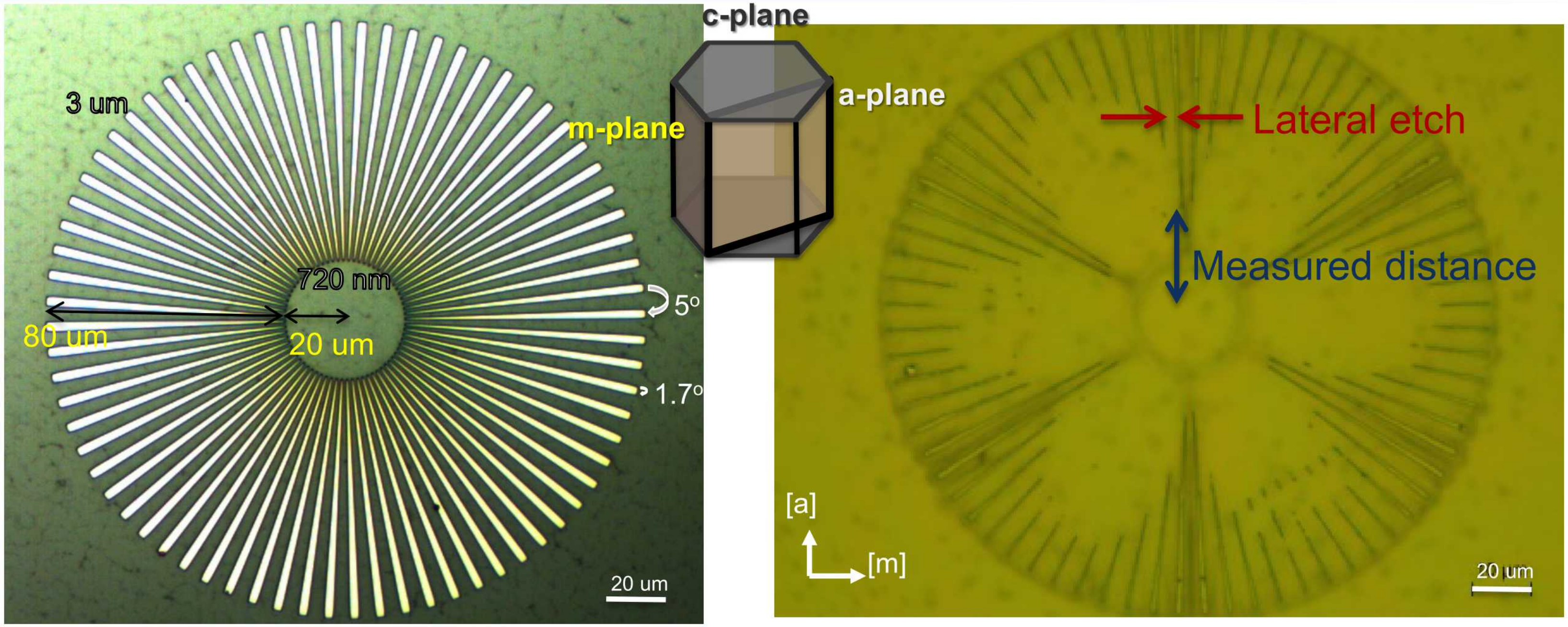
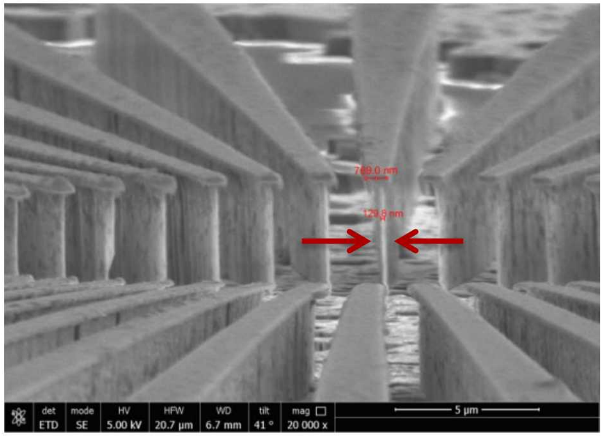
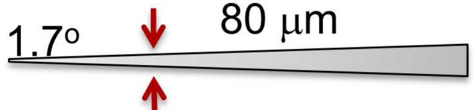


5% KOH in ethylene glycol



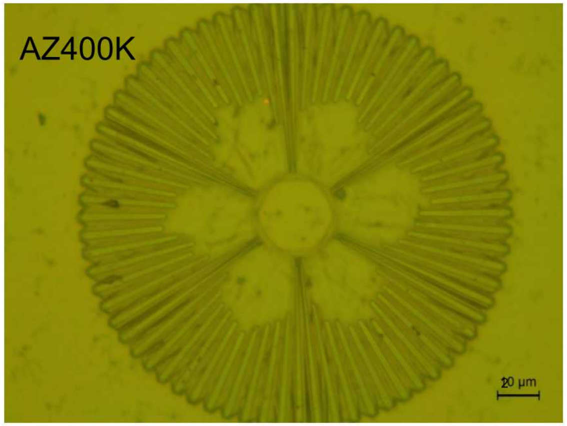


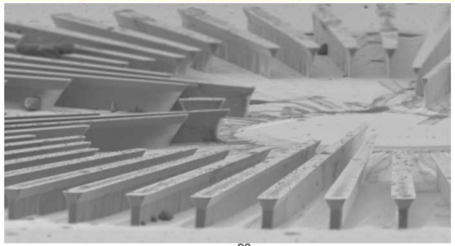
Lateral etch of 100 nm/min →
Wedge retraction of 6.7 µm/min

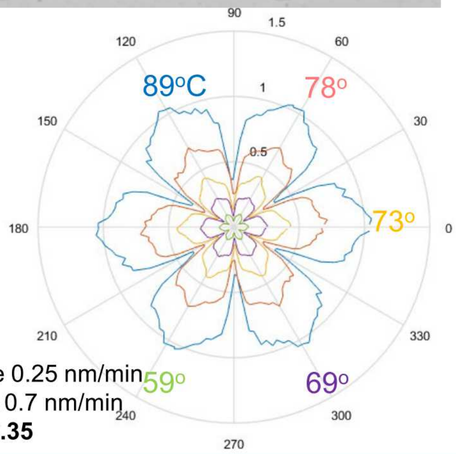
Etch rate is amplified by a factor of 67

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

Direct Measurements of Orientation Resolved Etch Rates – Chemistries and Temperatures

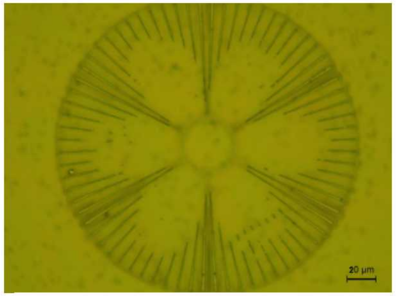


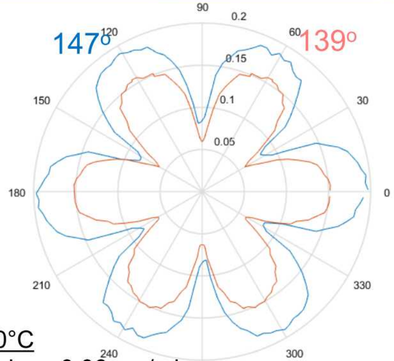




80°C
m-plane 0.25 nm/min
a-plane 0.7 nm/min
m/a ~ 0.35

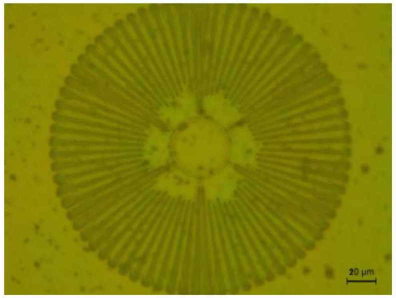
5% KOH in ethylene glycol

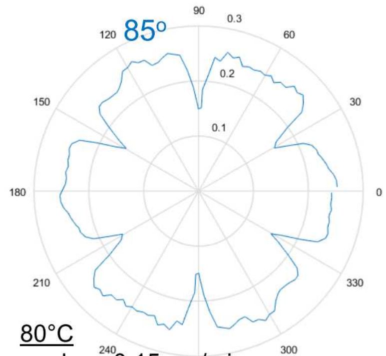




140°C
m-plane 0.06 nm/min
a-plane 0.16 nm/min
m/a ~ 0.37

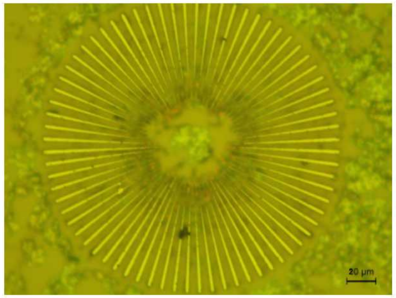
5% KOH in H_2O

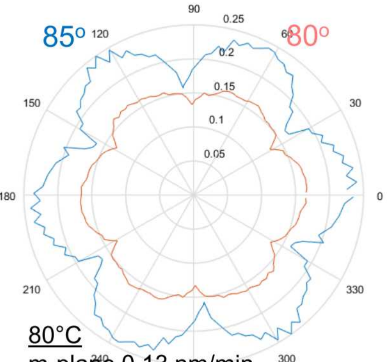




80°C
m-plane 0.15 nm/min
a-plane 0.27 nm/min
m/a ~ 0.56

25% TMAH





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

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

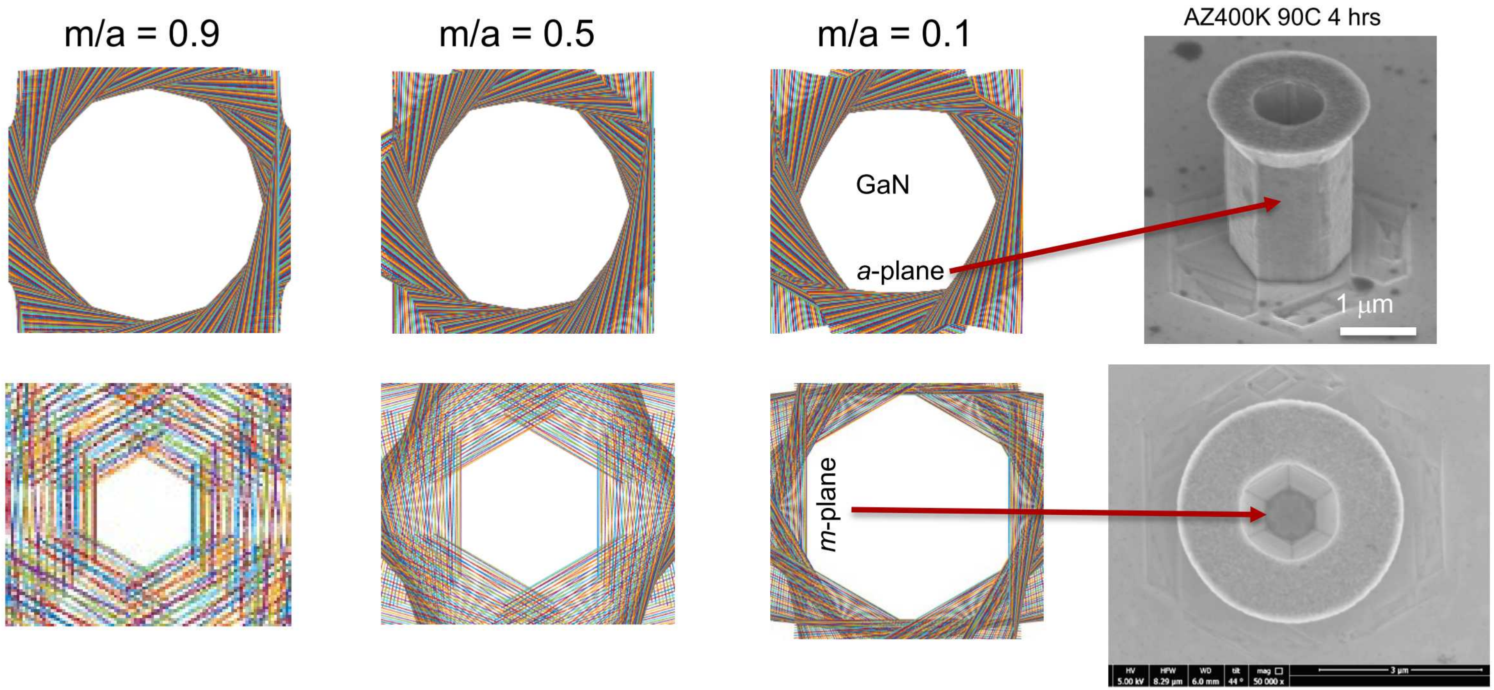
Prediction of Etched Geometry: Implementing the Wulff-Jaccodine Method

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*

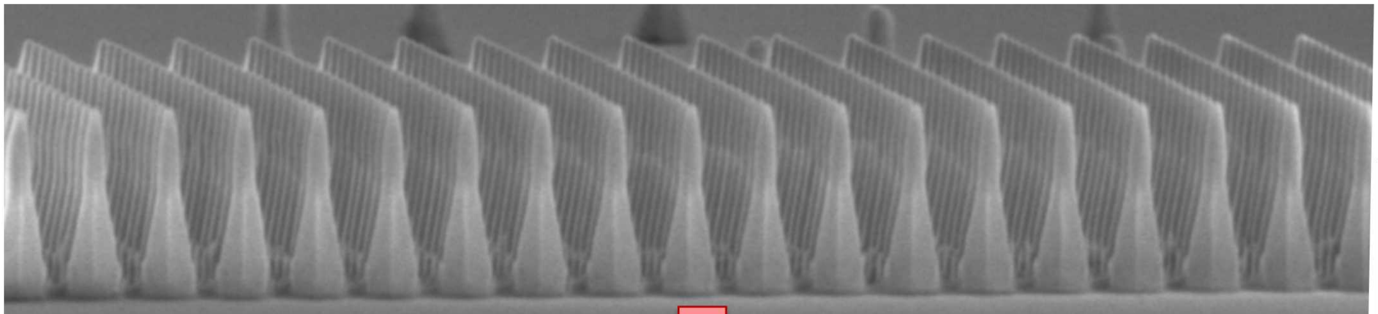
Convex (white region is GaN)

Concave (colored region is GaN)

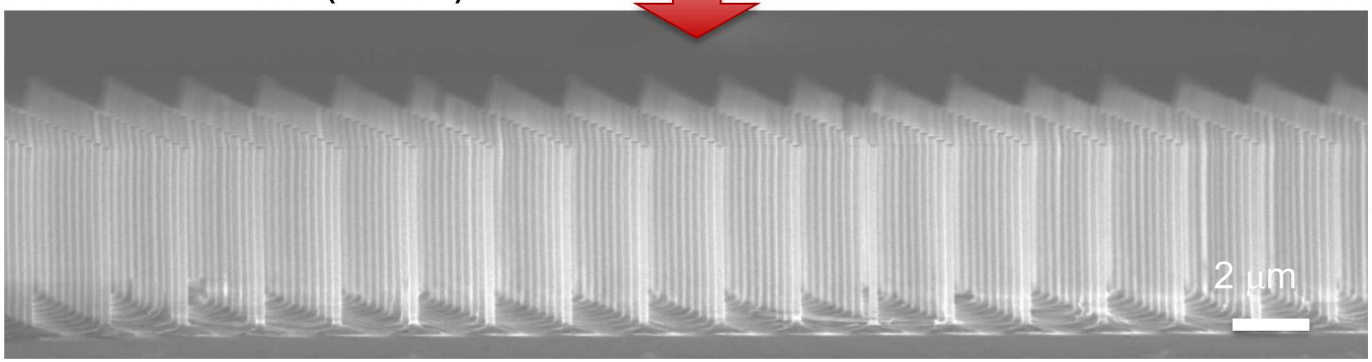


Fabricated top-down GaN nanostructures using two-step dry + wet etch approach

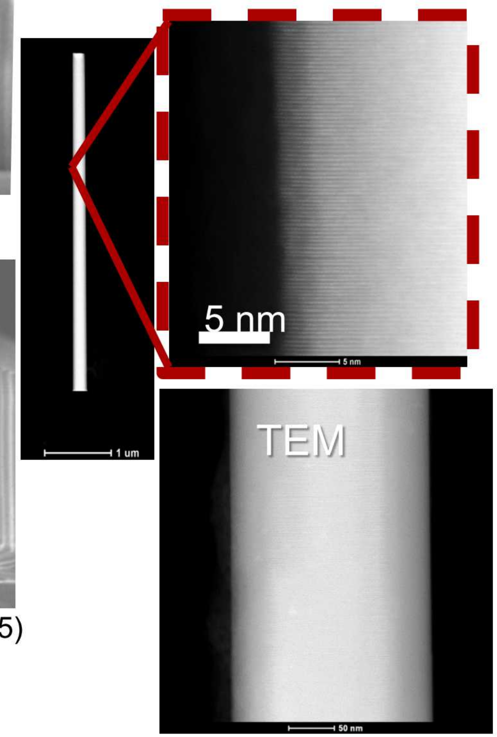
Dry etch (Cl_2 based ICP)



KOH-based wet etch (AZ400K)



TEM shows smooth vertical sidewalls



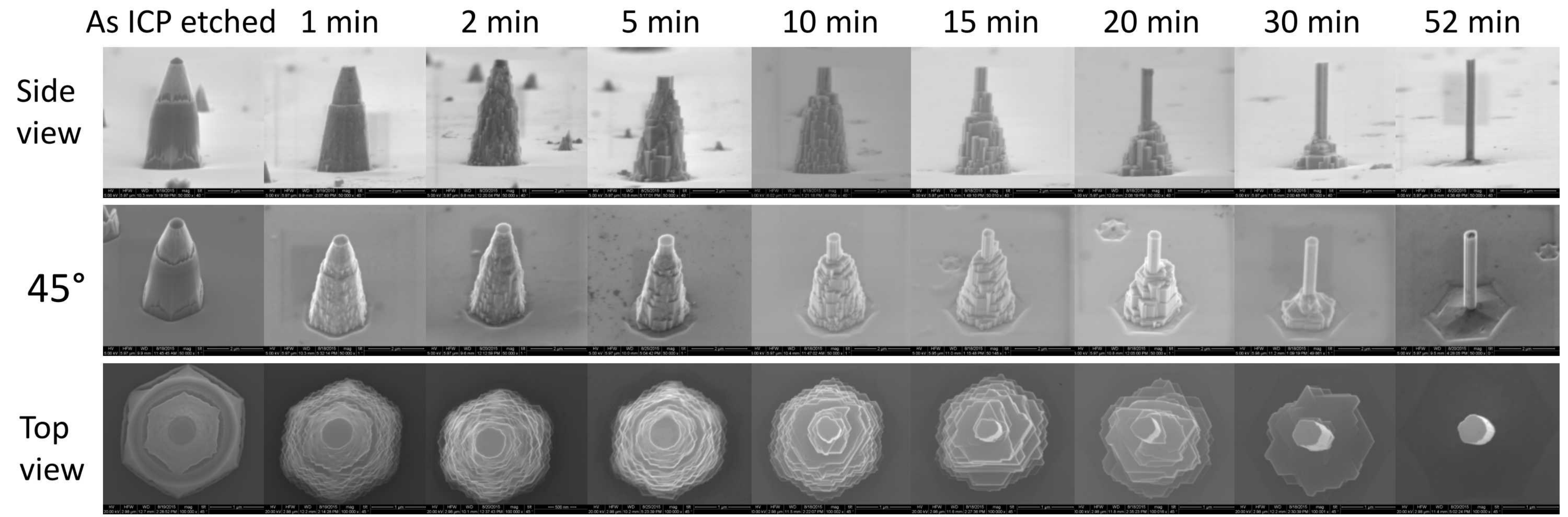
Diameter: 180 nm, Height: 4.5 µm, Pitch: 2 µm (AR: 25)

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

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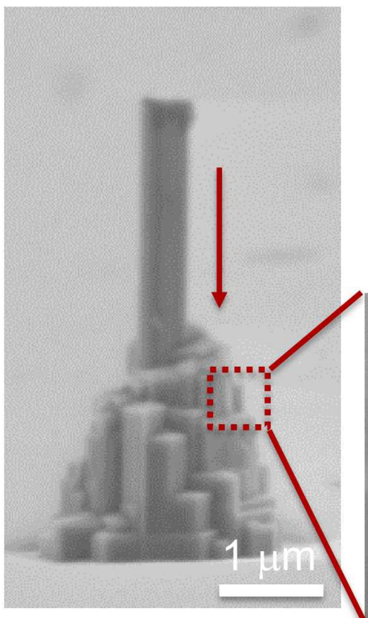
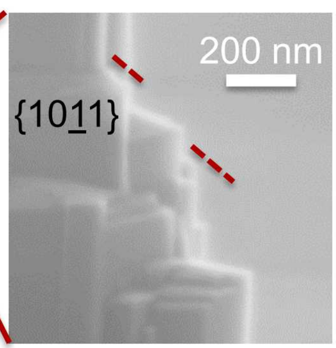
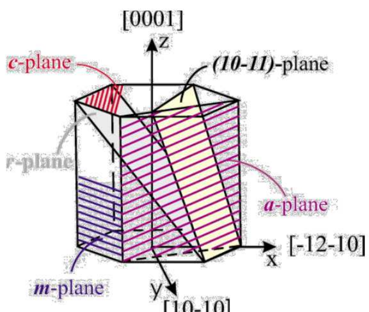
What is the mechanism from *tapered to smooth vertical sidewalls* through faceting?

Slow etching: c-plane, *m*-plane

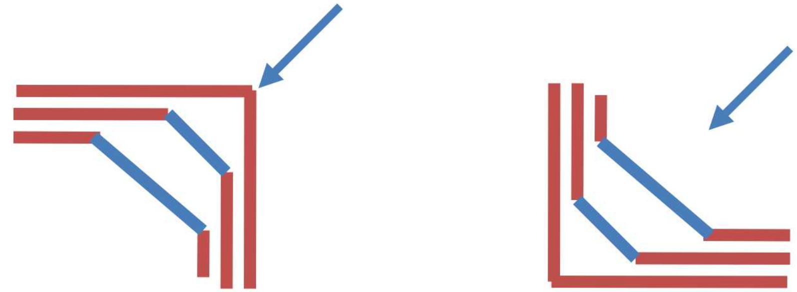
Fast etching: semipolar (10$\bar{1}$1)







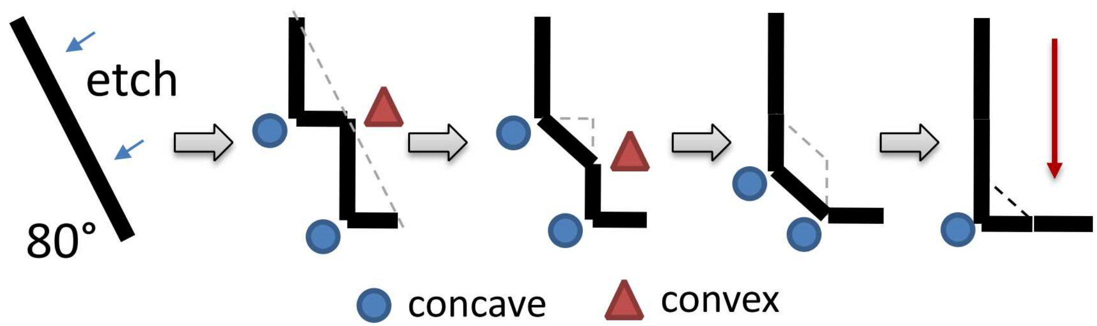
V. Darakchieva et al., JAP 108, 073529 (201)



Convex
Fast etch facet persists

Concave
Slow etch facets persists

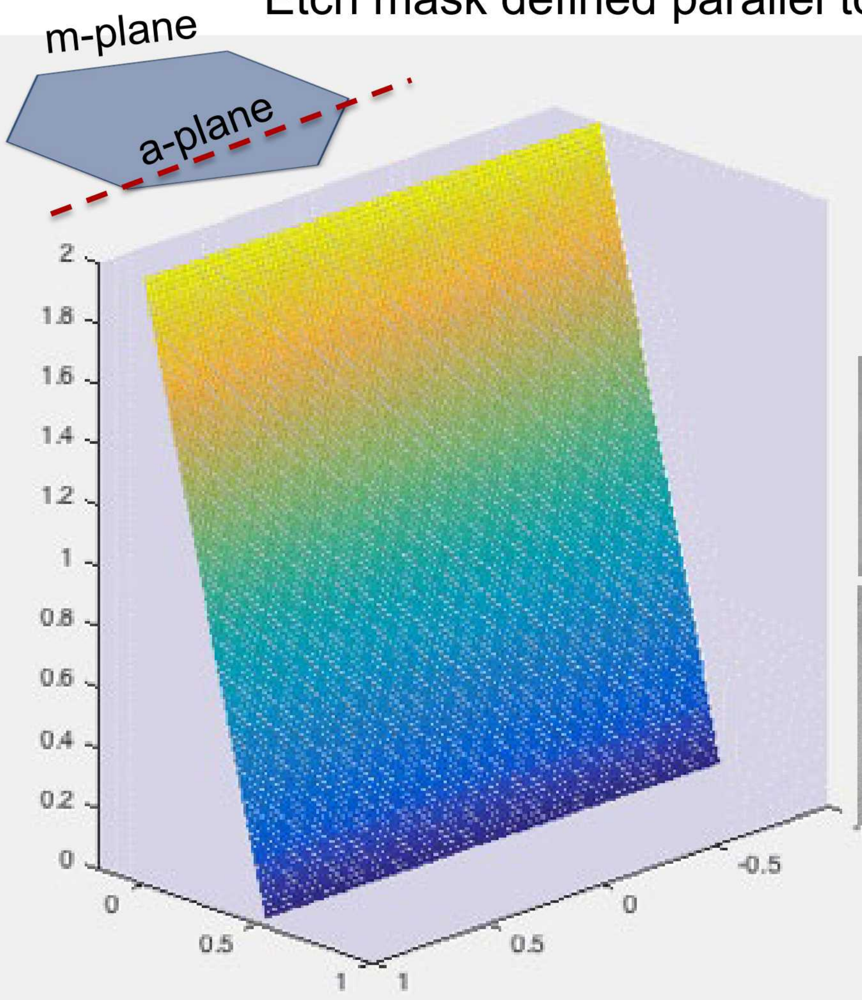
The facet etch sequence:

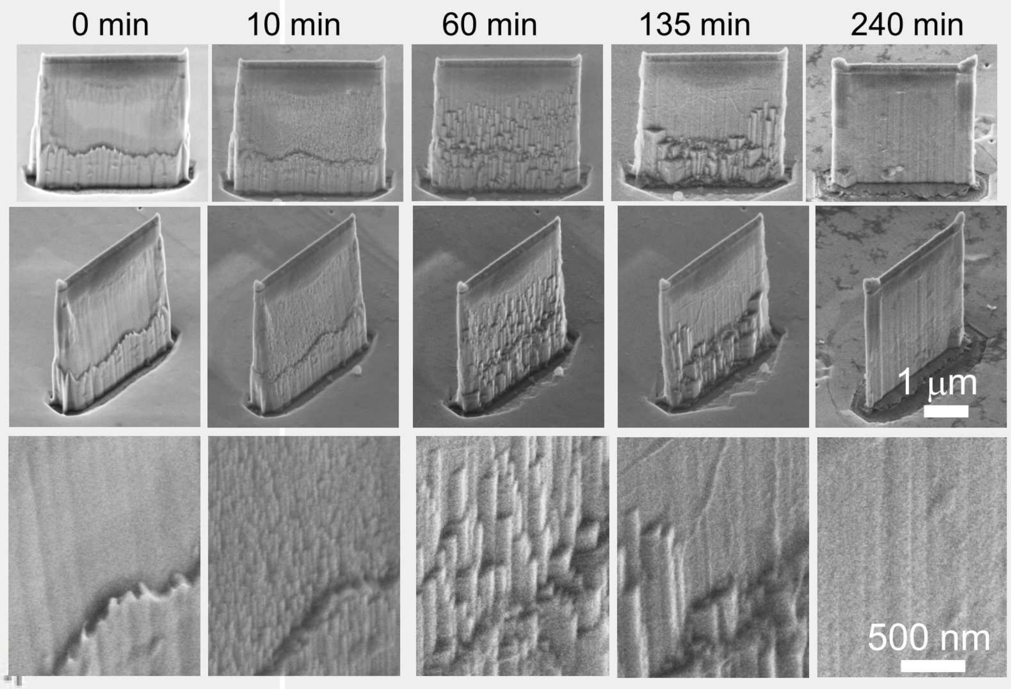


The appearance (disappearance) of fast (slow) etching facets in concave (convex) geometries is the basis of the etch mechanism

Etch evolution of *a*-plane wall

Etch mask defined parallel to *a*-plane

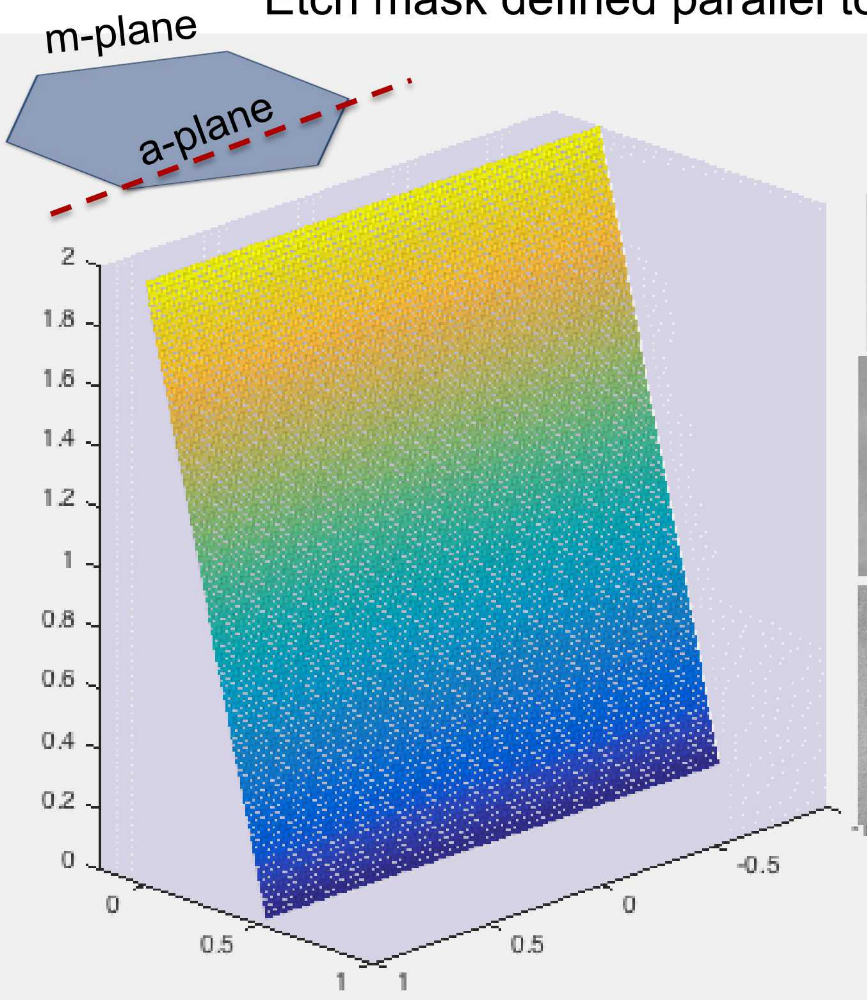


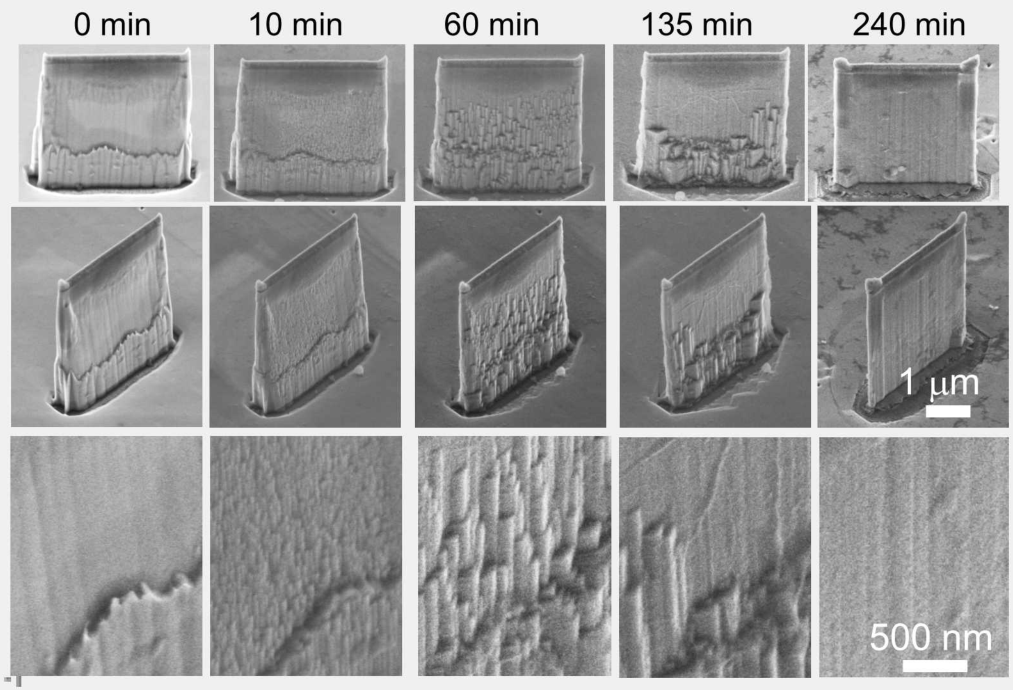


AZ400K, 65°C

Etch evolution of *a*-plane wall

Etch mask defined parallel to *a*-plane

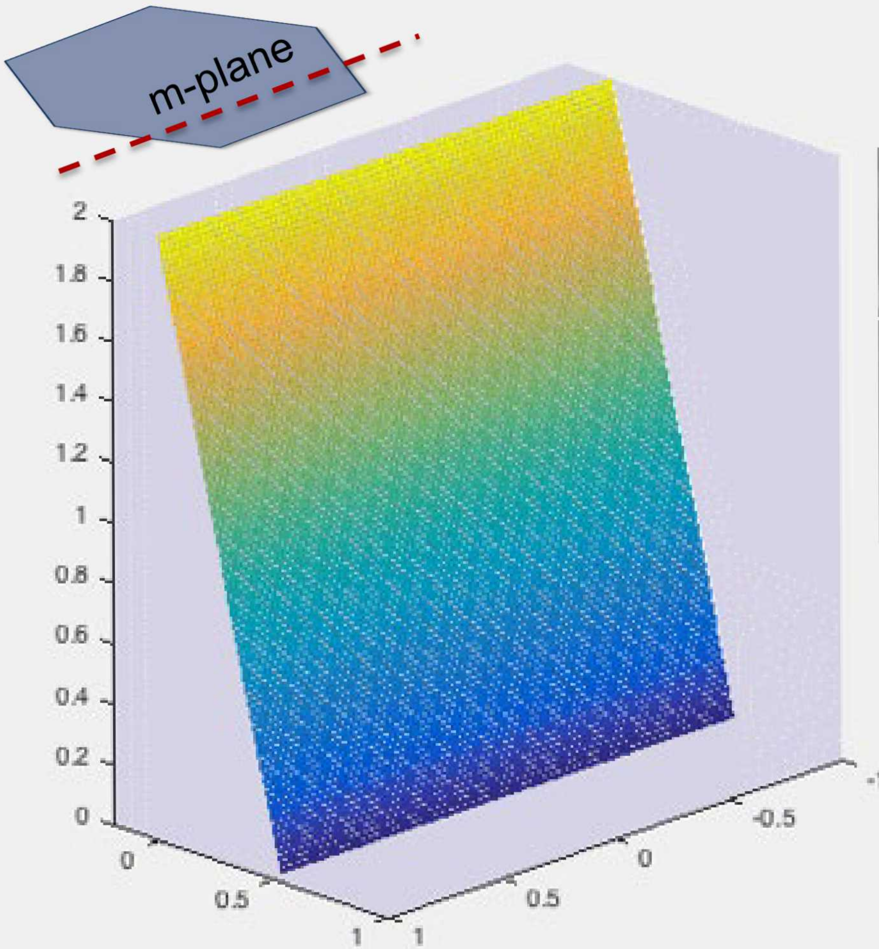


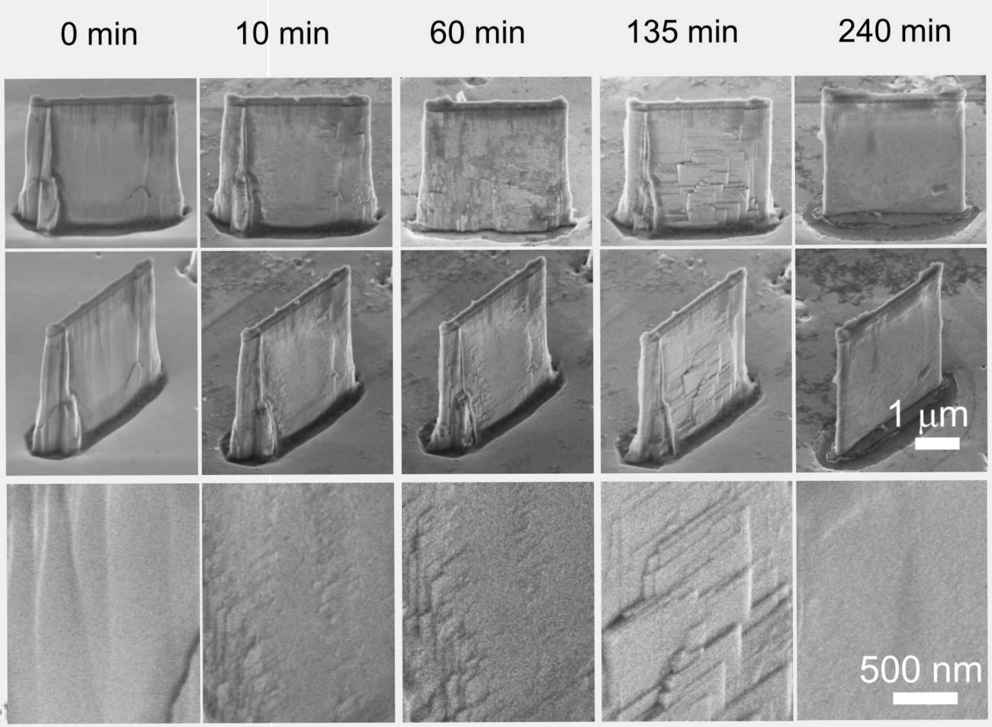


AZ400K, 65°C

Etch evolution of *m*-plane wall

Etch mask defined parallel to *m*-plane

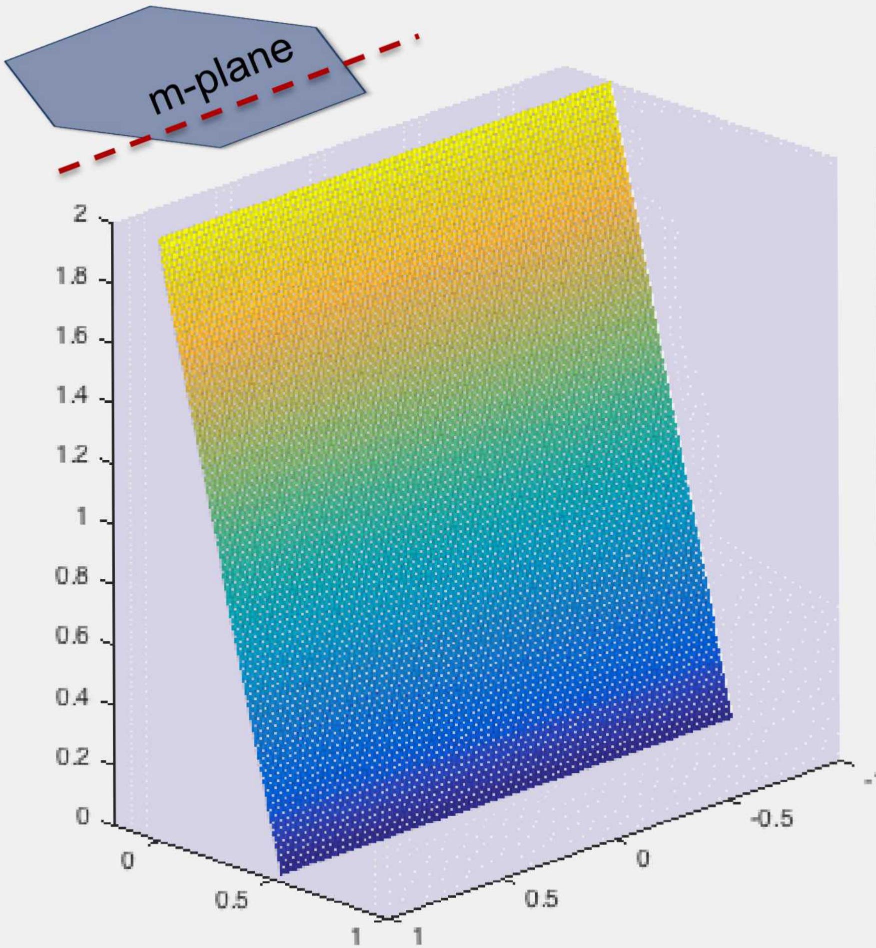


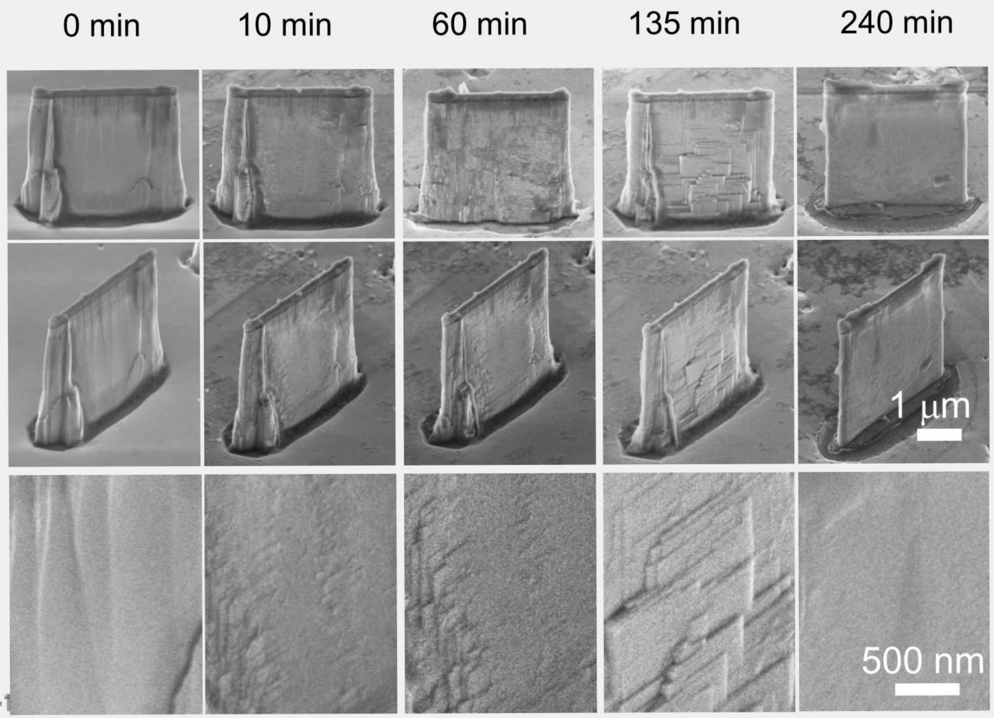


AZ400K, 65°C

Etch evolution of *m*-plane wall

Etch mask defined parallel to *m*-plane

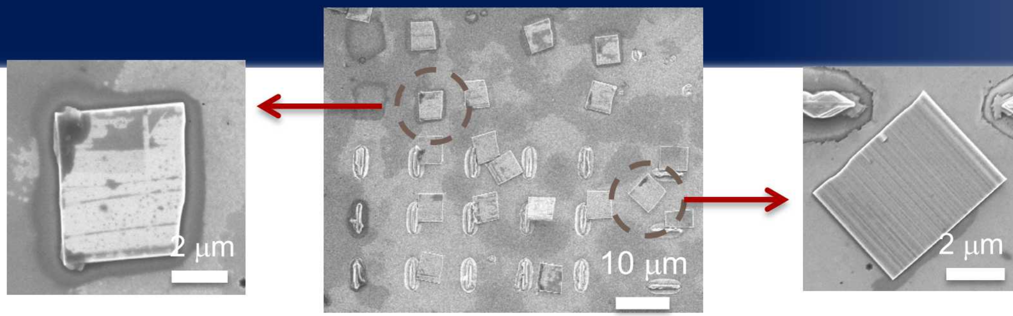




AZ400K, 65°C

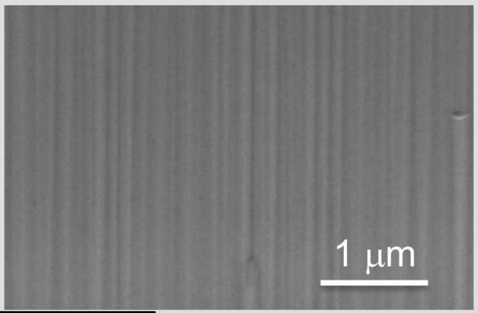
Measured etched nanowall morphology by AFM

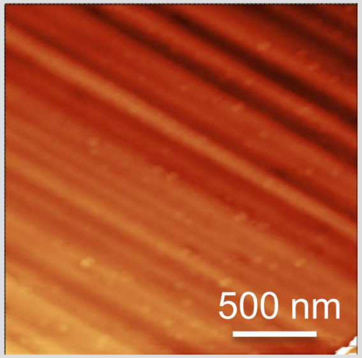
m-plane wall

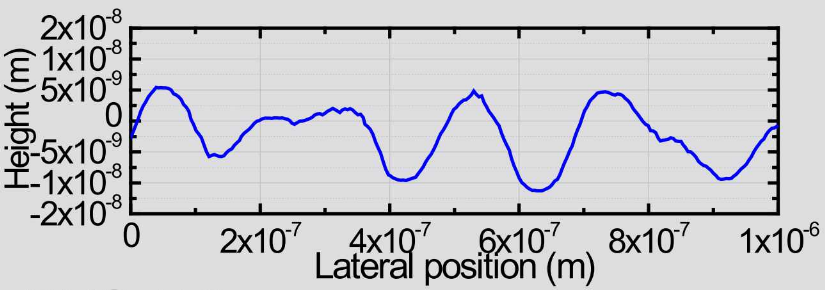


a-plane wall

a-plane

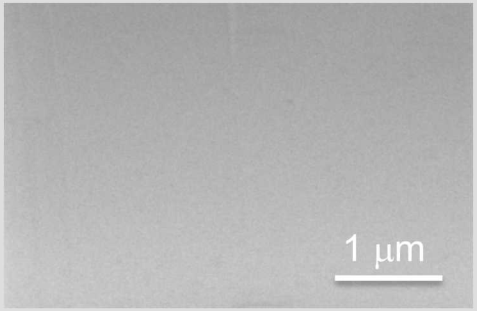


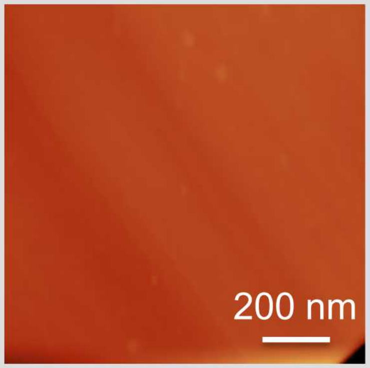


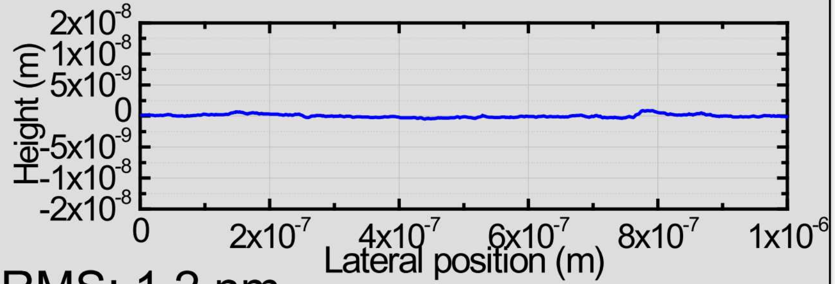


RMS: 7.6 nm

m-plane





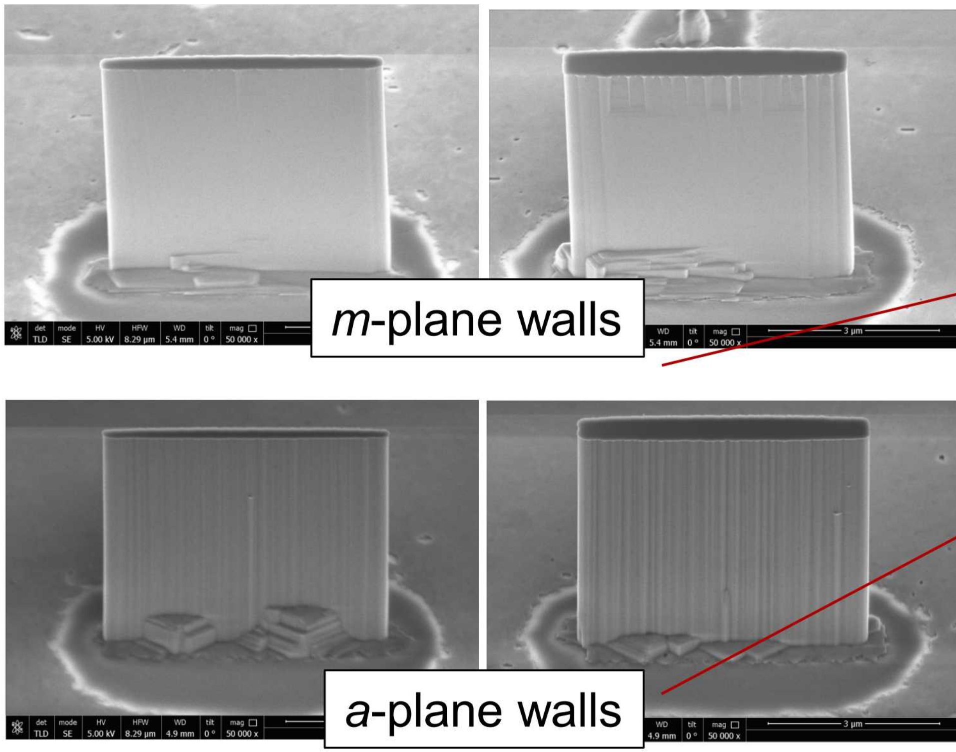


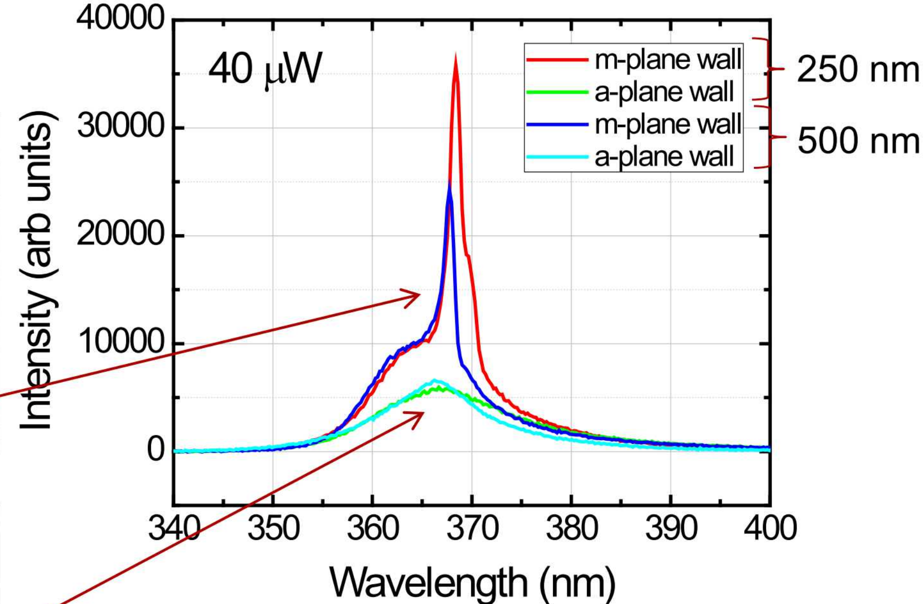
RMS: 1.2 nm

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



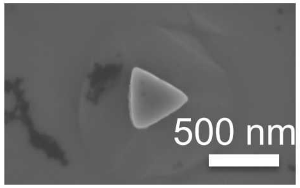


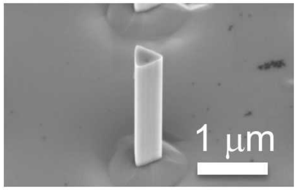
Optically pumped nanowalls shows luminescence coupled to cavity modes only with the smooth m-plane sidewalls

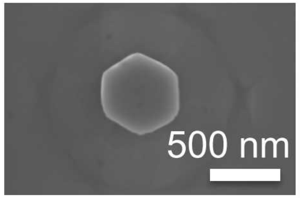
Etched surface morphology has important effects on optical properties of nanostructures

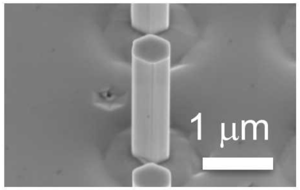
Controlled and complex cross-sections

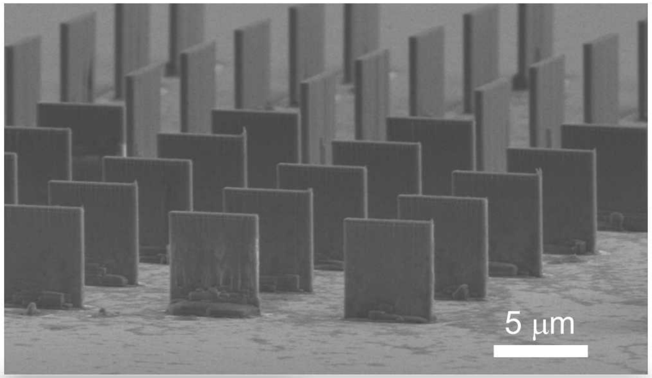
Can we expand to more *complex geometries* ?

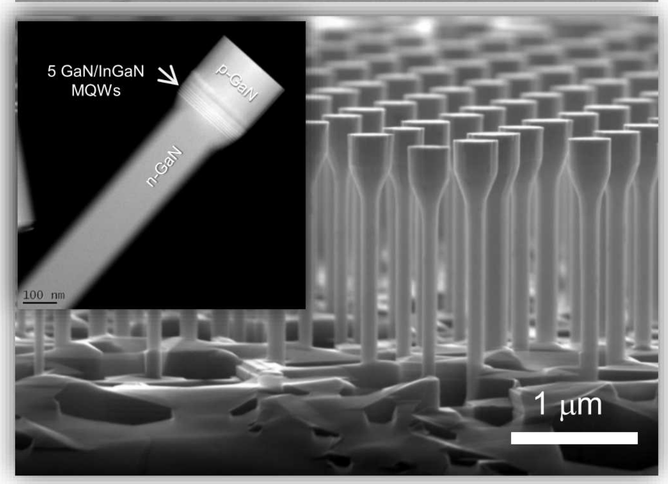


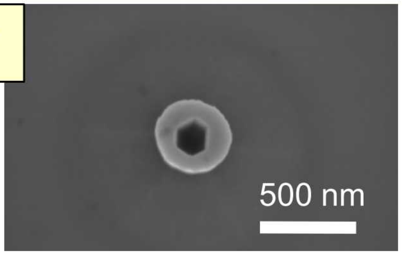


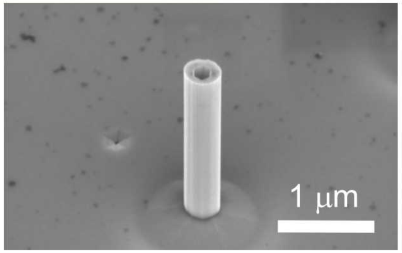


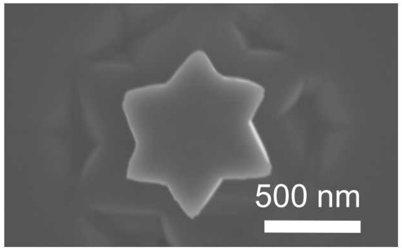


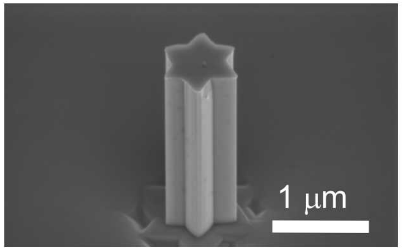


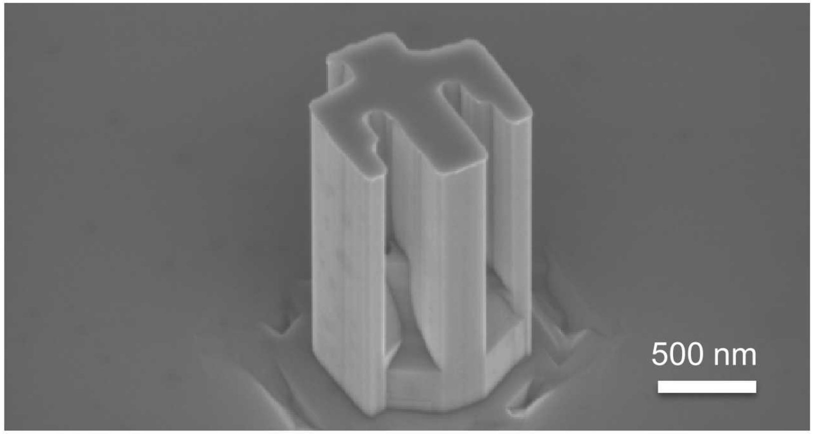








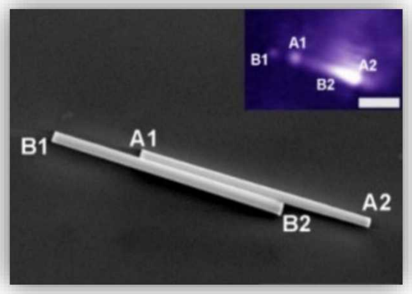


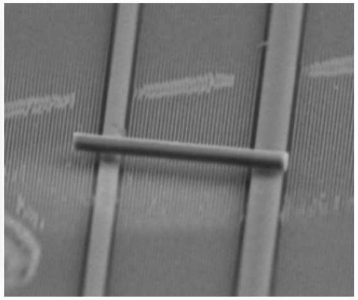


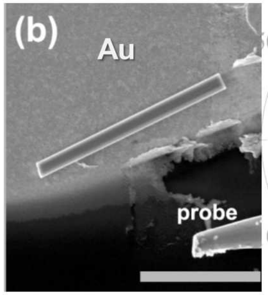
Understanding of the etch evolution enables design of a wide range of smooth faceted vertical nanostructures

Top down vertical nanostructures for photonics

Mode & polarization control in GaN nanowire lasers







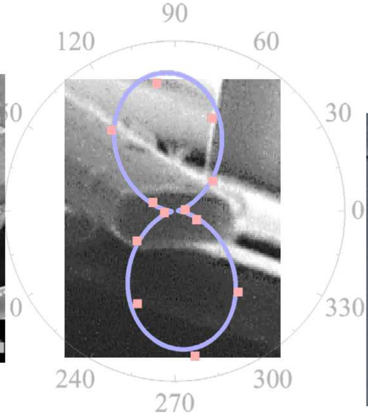
Q. Li et al., *Optics Express* **20** 17874 (2012)

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

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

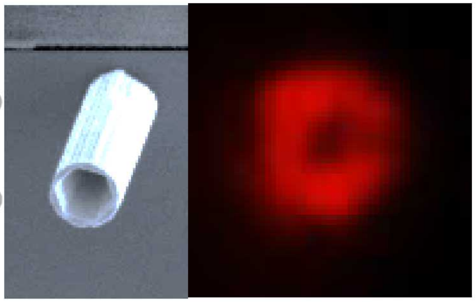
H. Xu et al, *Opt. Exp.* **22**, 19198 (2014)

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



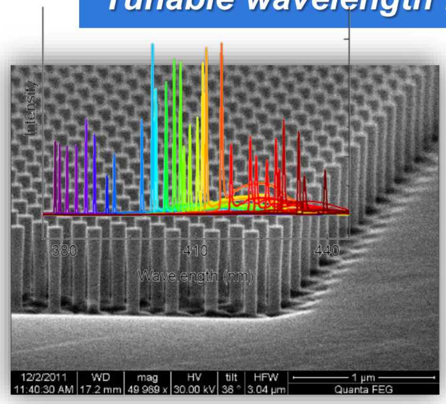
Li, Changyi, et al. *Nanoscale* **8**, 5682 (2016)

Beam shape control nanotube lasers

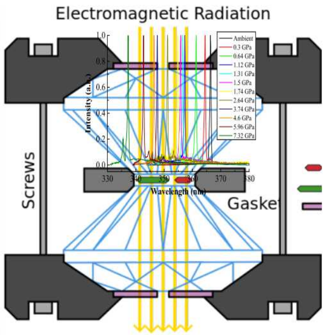


C. Li et al., *ACS Photonics*, **2**, 1025 **(2015)**.

Tunable wavelength nanowire lasers

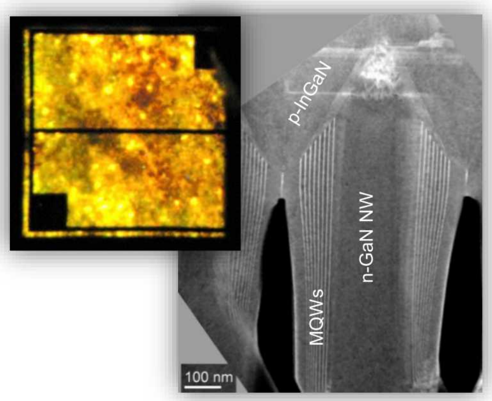


J.B. Wright et al., *Sci. Reports* 3, Art no. 2982 (2013) doi:10.1038/srep02982



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

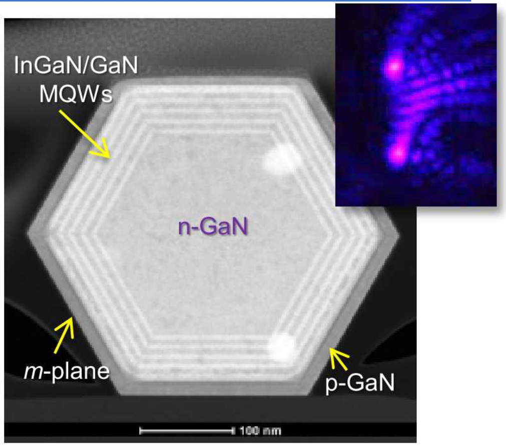
Nonpolar core-shell nanowire LEDs, solar cells, and lasers



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

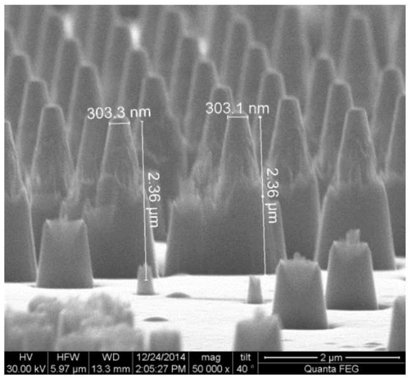
After AZ400K 65°C wet etch

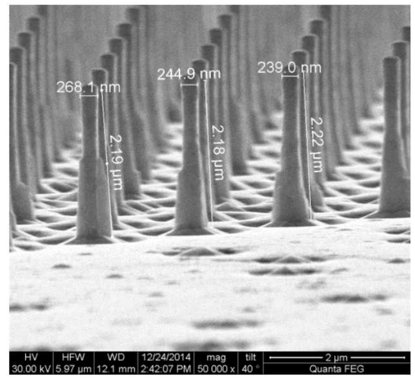
240-500nm diameter

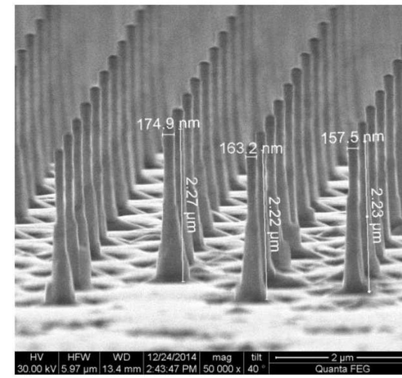
150-250 nm diameter

30% AlGaN

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

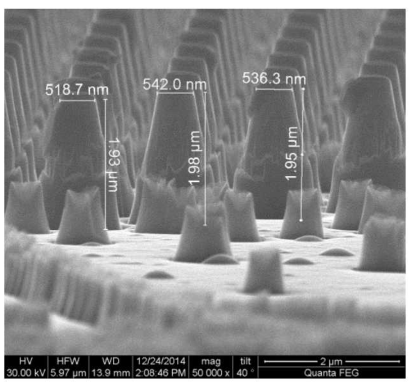


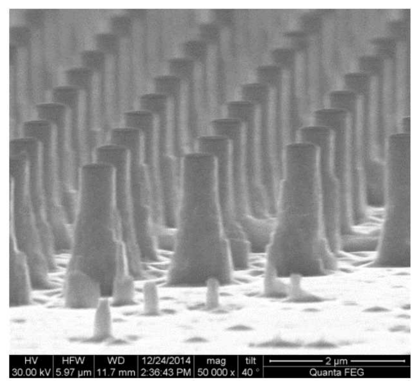


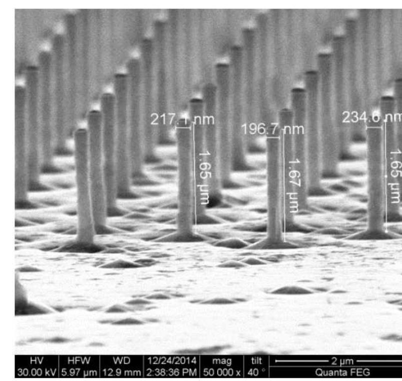


70% AlGaN

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





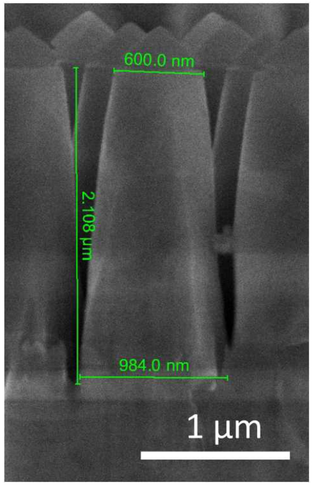


AlGaN samples grown by Andrew Allerman

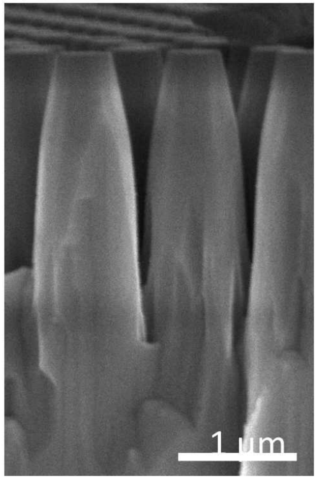
AlGaN exhibits less vertical sidewalls than GaN – why??

H_3PO_4 wet etching of tapered GaN nanowires

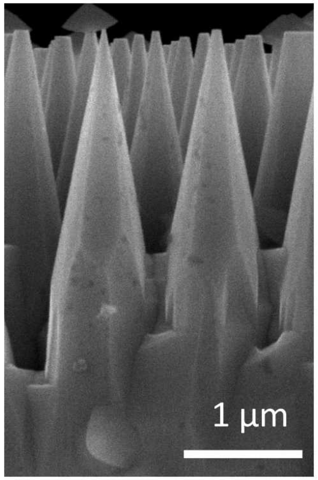
93-96 °C H_3PO_4



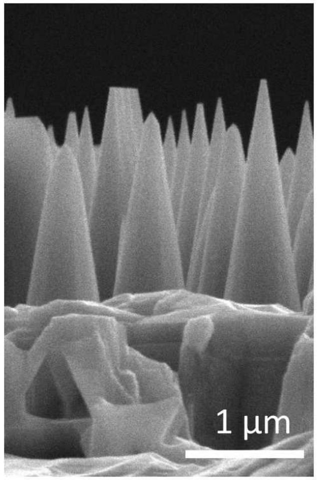
30 min ICP only



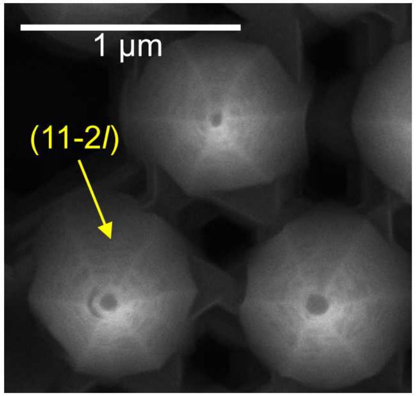
10 min H_3PO_4 (~95°C)



40 min



55 min



40 min, top view

- H_3PO_4 wet etching of ICP dry etched GaN nanowires leads to tapered nanowires
- {11-2*l*} type facets observed in contrast to {10-10} facets for KOH-based etch

Motivation: InGaN Quantum Dots (QDs) as emitters

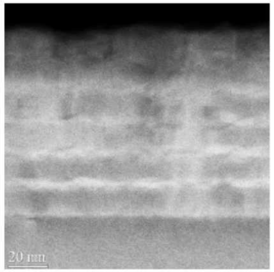
Potential advantages vs quantum wells

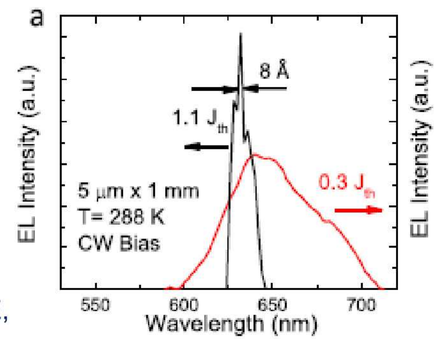
- Single photon emission
- Reduced polarization fields (reduced QCSE)

Schulz & Reilly, PRB 82, 033411 (2010)

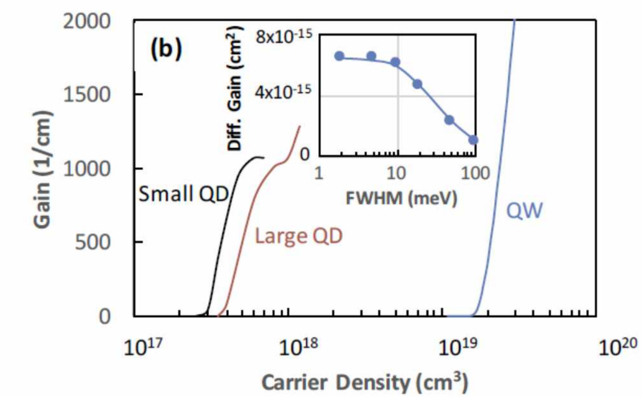
- Longer wavelength emission
- Lower lasing thresholds
- Higher efficiencies

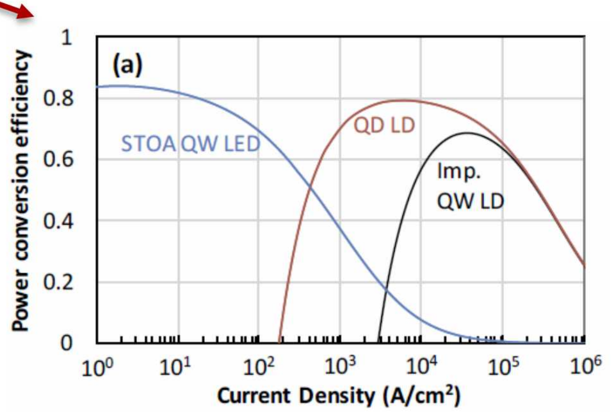
U. Mich. - Red electrically injected InGaN QD laser





Frost et al., IEEE JQE, **49,** 923 (2013).





Jonathan J. Wierer, Jr., Nelson Tansu, Arthur J. Fischer, and Jeffrey Tsao, "III-nitride quantum dots for ultra-efficient solid-state lighting," *Laser and Photonics Reviews*, **10,** 612 (2016) / **DOI** 10.1002/lpor.201500332

Challenge: Find methods to synthesize QDs to meet the required sizes, inhomogeneous broadening, and densities

(In)GaN Photoelectrochemical (PEC) Etching

- GaN relatively inert to wet etching, particularly (0001) c-plane
- PEC etching: photogenerated holes oxide surface which is then dissolved

in 1 M H_2SO_4

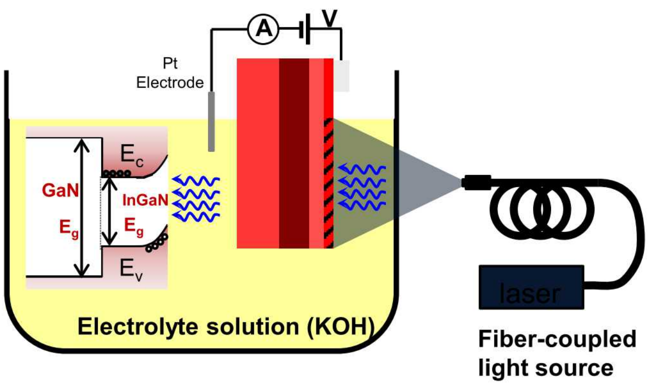
$$GaN + 3h^+ \rightarrow Ga^{3+} + 0.5N_2$$

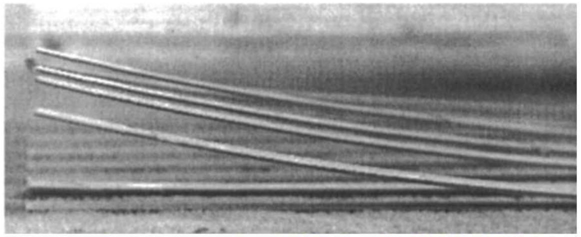
in 1 M KOH

$$GaN + 6\,OH^- + 3h^+ \rightarrow GaO_3^{3-} + 0.5N_2 + 3H_2O$$

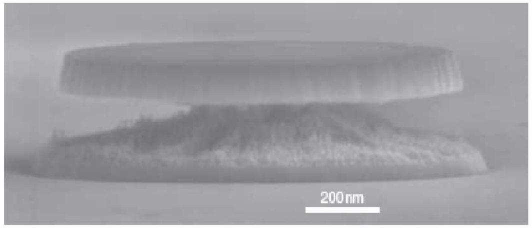
Huygens et al., J. ECS **147**, 1797 (2000)

- Laser or lamp excitation (Xe arc lamp, tunable ps Ti:S)
- KOH (~0.1M) typically used as electrolyte for GaN
- Band gap selective (etch InGaN over GaN) based on wavelength used

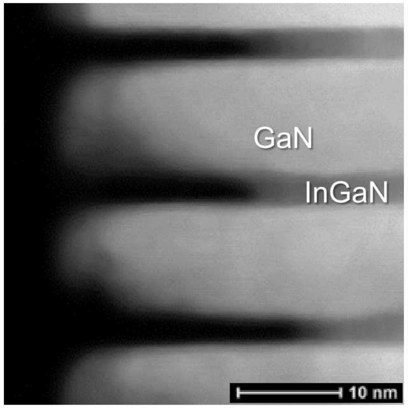




Stonas et al., JVST B **19**, 2838 (2001)



Tamboli et al., Nat. Phot. **1**, 61 (2007)

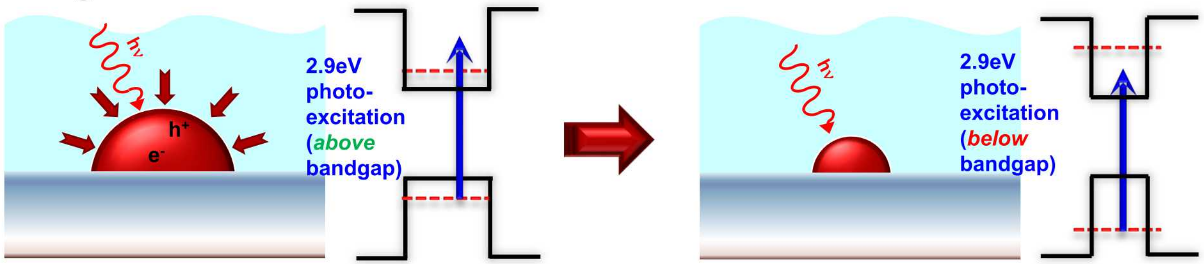


Xiao et al, Elec. Acta 162, 163 (2015)

Controlled fabrication of QDs via PEC etching

Quantum Size Control: Use size quantization to control QD size

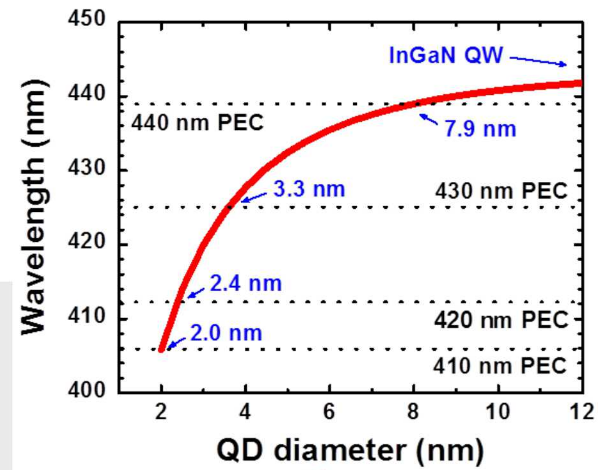
"Large" nanostructure | ***Quantum* nanostructure**



Absorption: PEC etching occurs

No Absorption: etching *self-terminates*

Bandgap for idealized spherical $In_{0.13}Ga_{0.87}N$ QDs embedded in GaN

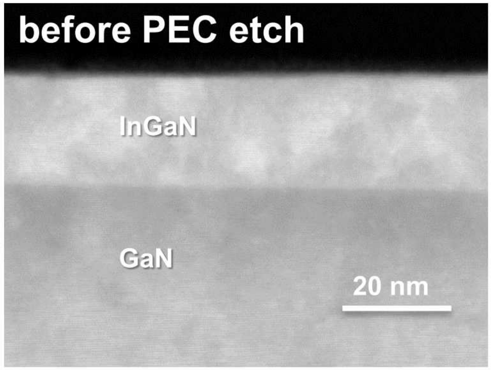


- For QDs, band gap depends on size
- As PEC etch proceeds,
  - QD size gets smaller, band gap goes up
  - Etch should terminate for $E_g > E_{photon}$ pump (no more carriers needed for etch)
- Self-terminating etch process
- Final QD size (band gap) depends on PEC etch wavelength used
- "Monodisperse" QD distributions ??
- Earlier work on "size selective photocorrosion" to shrink size of colloidal CdS QDs using monochromatic light[1,2]

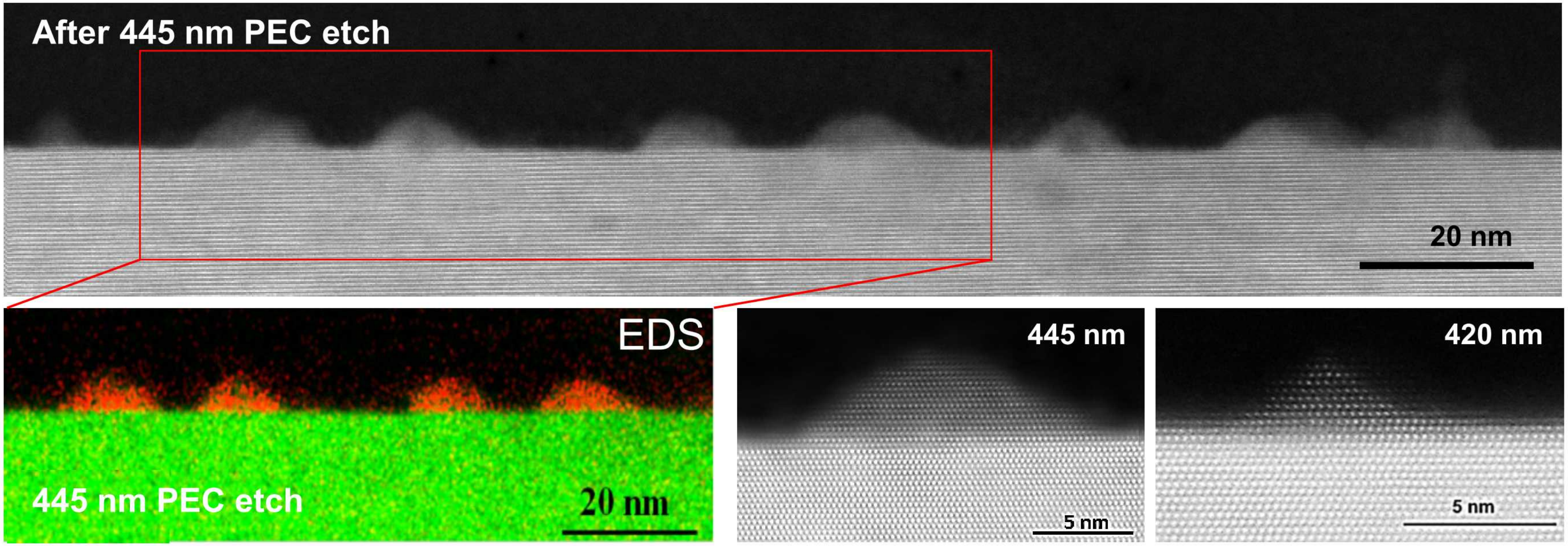
[1]Matsumoto et al., J. Phys. Chem. **100**, 13781 (1996)   [2]Torimoto et al., J. ECS **145**, 1964 (1998)

QSC-PEC etched uncapped InGaN layer – Scanning TEM measurements

Uncapped InGaN QW



- Cross-sectional high-angle annular dark-field (HAADF) scanning TEM images
- Samples etched at 420 nm and 445 nm
- Energy dispersive (EDS) x-ray mapping
  - QDs on surface are InGaN (Red = In, Green = Ga)
- InGaN QDs are epitaxial to the underlying GaN
- No underlayer, no cap → PL is not very bright

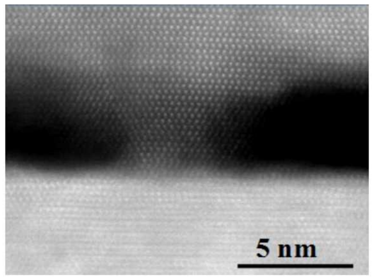


X. Xiao et al., Nano Lett. **14**, 5616−5620 (2014)

LT Photoluminescence from QSC-PEC etched InGaN QDs

Sandia National Laboratories

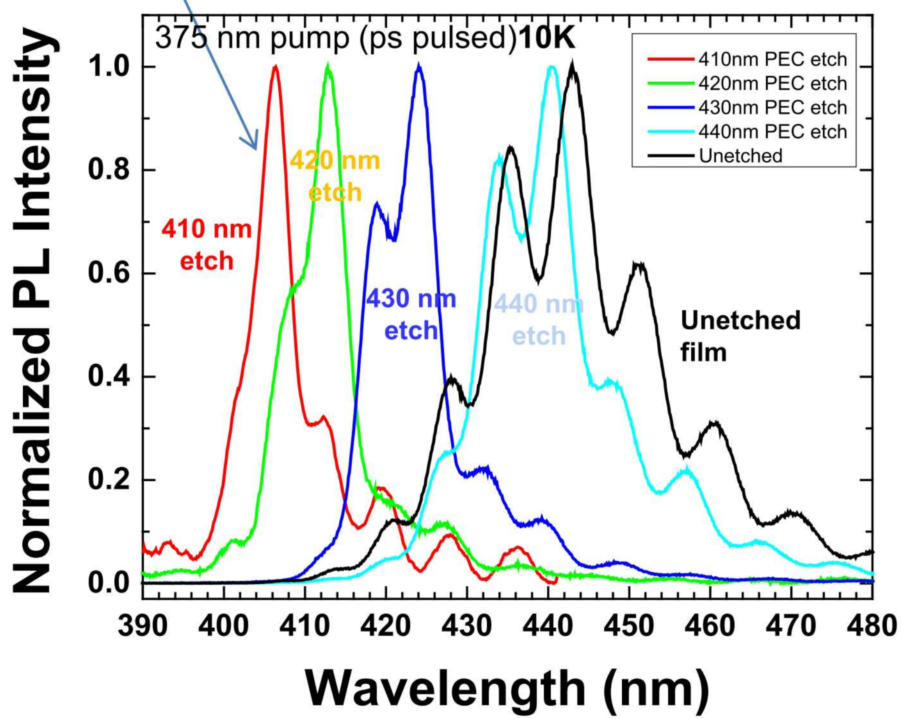
Capped InGaN QDs



Photoluminescence (PL) data:

- Etched QD PL **wavelength correlates** (but doesn't exactly coincide) **with PEC etch wavelength**
- PL linewidth **decreases with decreasing etch wavelength**: 24 nm (film) → 6 nm (QDs etched at 410 nm)
- **Strong evidence for quantum-size controlled etch!**

As narrow as **6 nm** FWHM is consistent with a narrowing of the QD size distribution

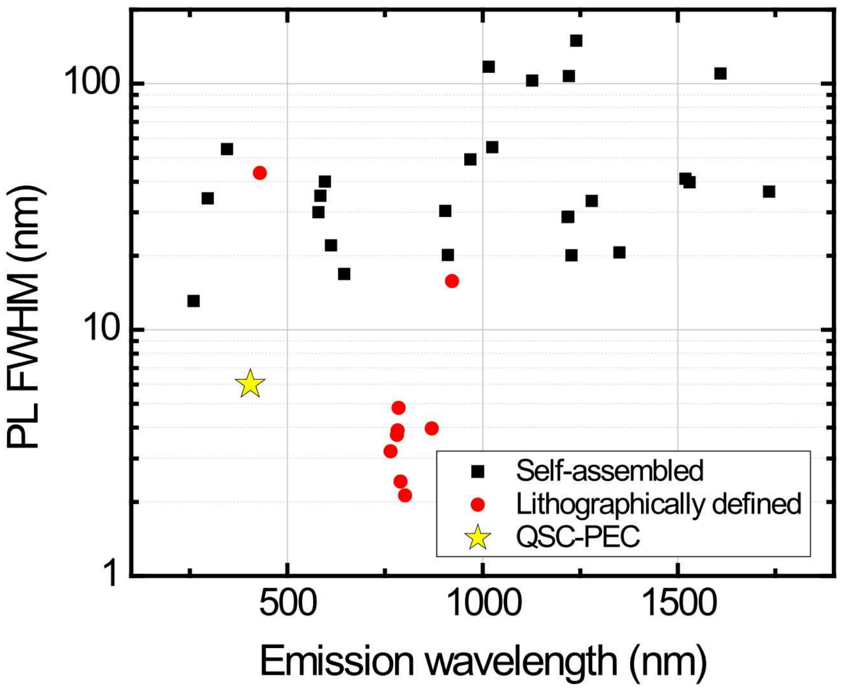


X. Xiao et al., Nano Lett. **14**, 5616−5620 (2014)

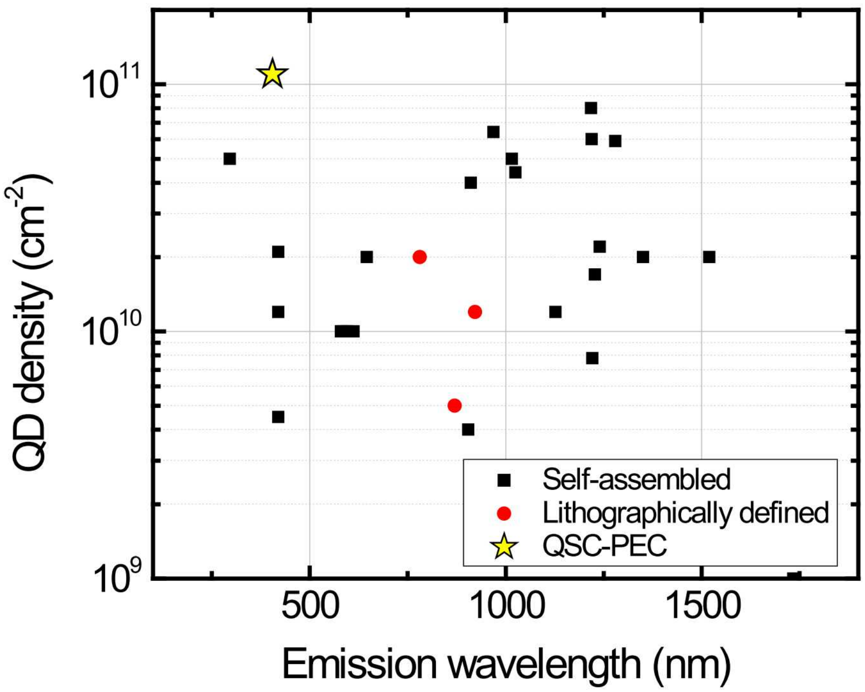
(Partial) Survey of III-V/N QD literature

Sandia National Laboratories

FWHM



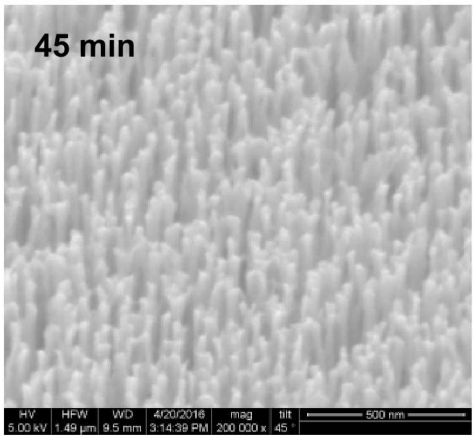
QD Density

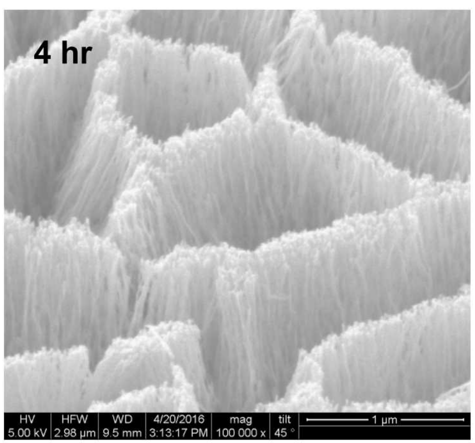


Compared to previous grown and lithographically etched QDs, QSC-PEC etched InGaN QDs have <u>narrow FWHM PL</u> and <u>high density</u>

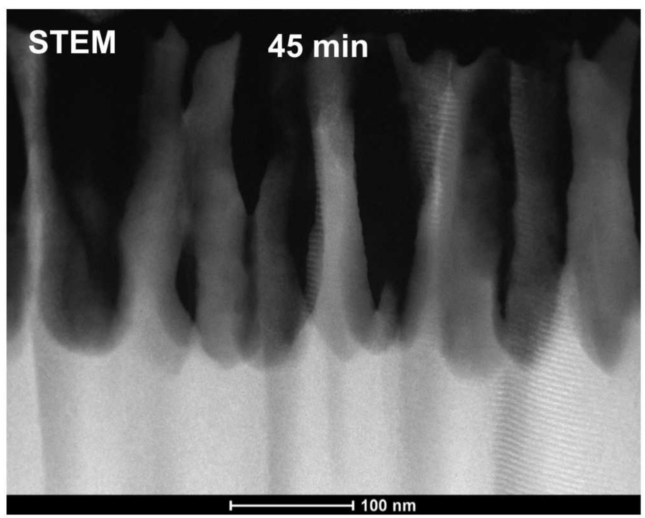
PEC etched GaN nanowires with very high aspect-ratios

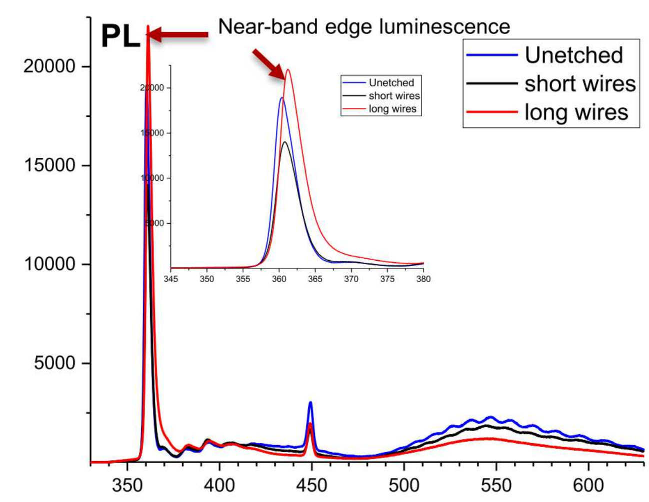
PEC etch: 370 nm, 4 mW, 1V, 2M H_2SO_4





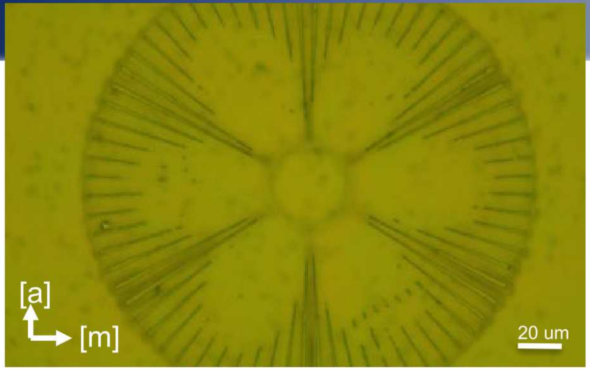
- GaN epilayer PEC etched at 370 nm results in dense array of thin GaN nanowires
- Cross-sectional STEM shows single-crystalline GaN nanowires; not related to dislocation cores, as previous reports showed
- Vertical etch through entire GaN film with little diameter change – self limiting lateral etch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

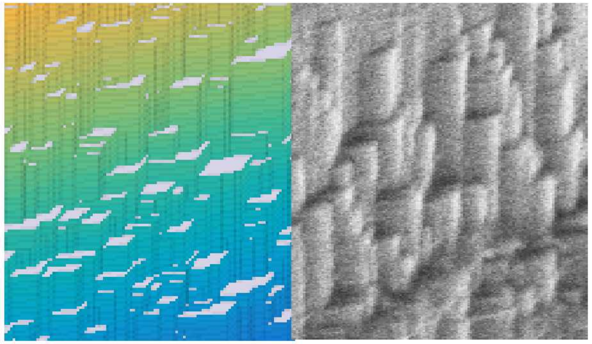


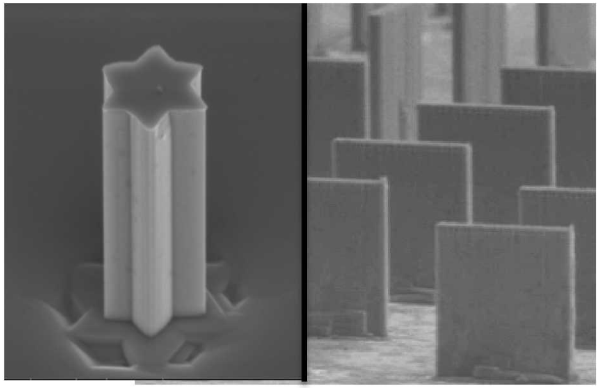


Conclusions

- **Wet chemical etching is an ideal technique for III-nitride nanostructure fabrication due to its extremely high anisotropy**
  - Implementation of Wulff-Jaccodine method for **prediction of pillar etch geometry and facets**
  - **Elucidated mechanism for facet evolution** from tapered to straight nanostructures
  - Phosphoric acid vs. KOH leads to appearance of different facets. Possibility for other, different 3D wet etches?
- Demonstrated **complex cross-sectional geometries** for vertical nanostructures with possible atomic-scale sidewall smoothness, for **III-nitride based nano-devices**
- **Quantum size controlled** fabrication of quantum dots demonstrated







Acknowledgments

Qiming Li – Top-down nanofabrication

Daniel Koleske, Jeffrey Figiel, Andrew Allerman –MOCVD growth, processing & support

Ping Lu – In-situ TEM and scanning TEM

Changyi Li (Ph. D student), Igal Brener, Willie Luk, Weng Chow, Jeremy Wright, Huiwen Xu (Ph. D student), Ganesh Subramania, Sheng Liu, Antonio Hurtado, Ganesh Balakrishnan, Steven Brueck, Daniel Feezell– Nanowire lasers

Arthur Fischer, Xiaoyin Xiao, Jeffrey Tsao, Michael Coltrin, Phil Miller – PEC Etching

Funding Acknowledgment: DOE Basic Energy Sciences (BES) DMSE, Sandia's Solid-State-Lighting Science Energy Frontier Research Center (DOE BES), and Sandia's LDRD program

Contact: e-mail: gtwang@sandia.gov

BACKUP SLIDES

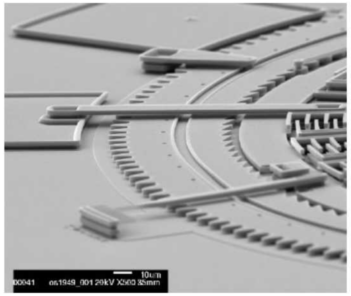
Problem: Lack of 3D nano-microfabrication processes for III-nitrides and III-V compound semiconductors

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

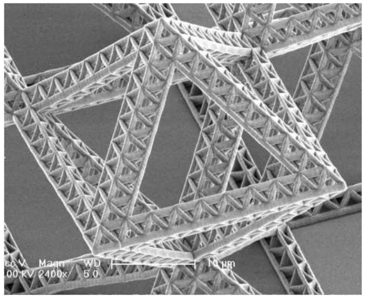
N/MEMS



Torsional Ratcheting Actuator

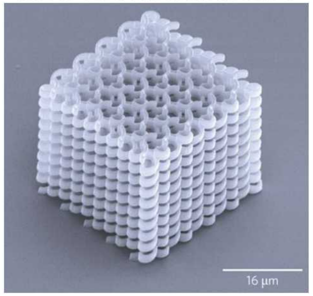
SNL

Nanolattice/truss



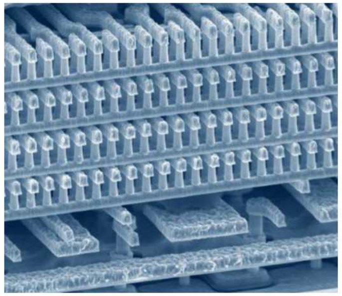
J. Greer, Caltech (2014)

3D Photonic Crystals and Metamaterials



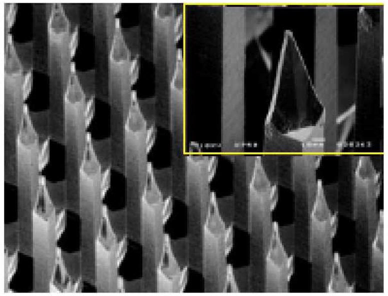
Farsari et al. *Nat. Phot.* (2009)

3D FinFET/NAND



Matrix Semiconductor (2012)

3D Nanoneedles



Shikida et al. (2004)

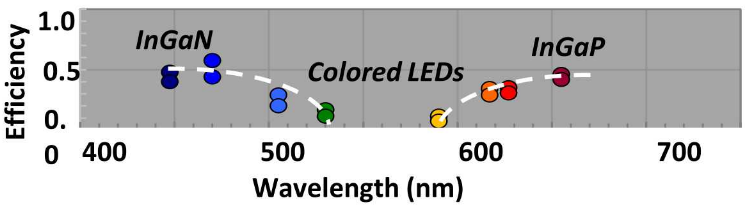
Methods to realize tailored 3D nanostructures are significantly underdeveloped for GaN and even classic III-V semiconductors (e.g. GaAs), hindering development of novel and next generation nano- and micro- enabled semiconductor structures and devices for solid-state lighting, high-speed and high power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

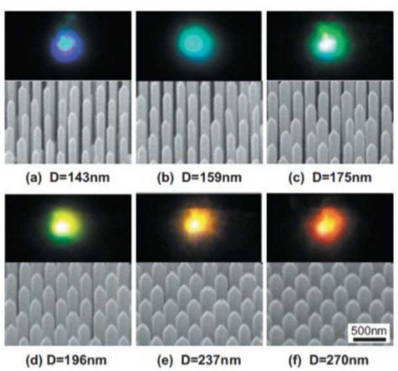
Why III-nitride nanowires for SSL?

Advantages due to enhanced strain accommodation in nanowires

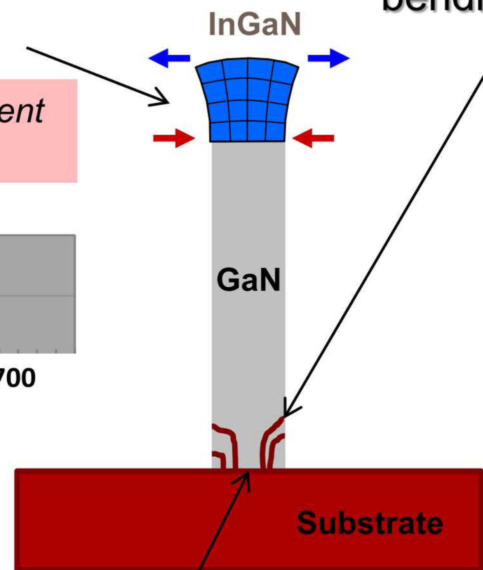
elastic strain relaxation at surface

<u>benefit:</u> heterostructures with high In content (e.g. green-yellow-red gap)





Sekiguchi et al., APL **96**, 231104 (2010) – Sophia U.

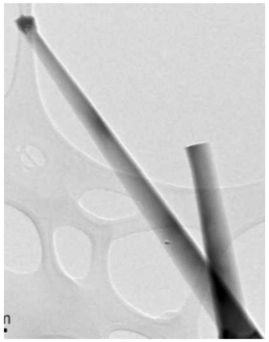


small interfacial area

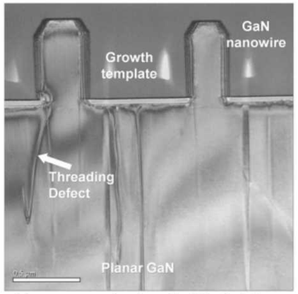
<u>benefit</u>: can grow on cheaper, lattice mismatched substrates; integration with Si devices

bending of dislocations (TDs) toward surface

<u>benefit:</u> reduced TDs, higher IQE

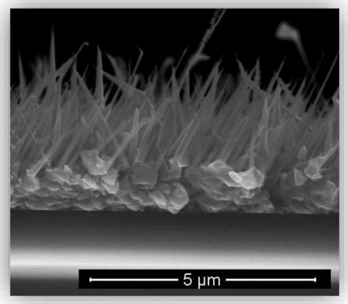


VLS-grown TD-free GaN NWs - Sandia

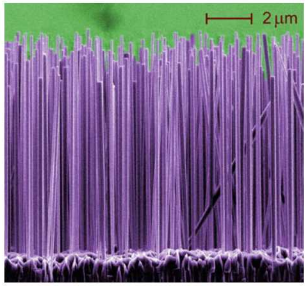


Hersee et al., J. Mat. Res. **17**, 2293 (2011) - UNM

Bending & termination of TDs at nanowire base



GaN NWs on tungsten foil - Sandia

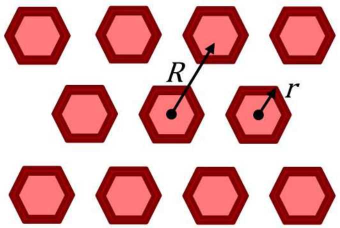


GaN NWs on Si - NIST

Why III-nitride nanowires for optoelectronics?

vertical device integration

<u>benefit:</u> higher device area per chip (cost/droop)

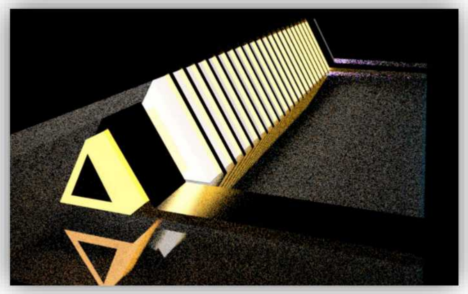


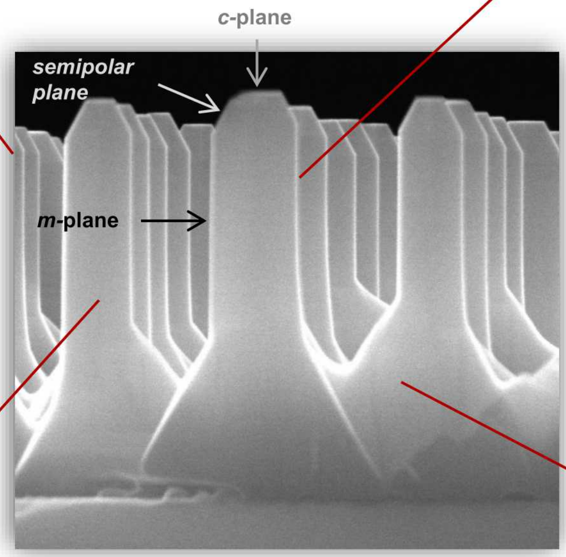
$$\frac{A_{sidewall}}{A_{substrate}} = \frac{6rh}{2.6R^2} \cong \mathbf{4.6F \cdot AR}$$

*example: 4.6·0.5·3=**6.9× increase!***

nanolasers

<u>benefit:</u> ultracompact, low power coherent light source

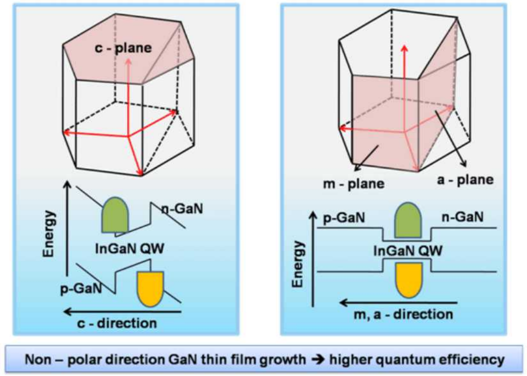




Radial GaN/InGaN MQW NW (Sandia)

access to nonpolar & semipolar planes

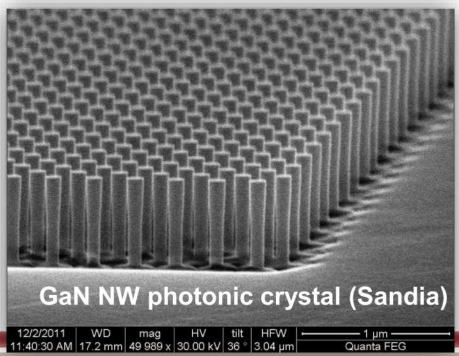
<u>benefit:</u> higher IQE, reduced wavelength shift



http://csel.snu.ac.kr/research/LED.php

2D arrangements (photonic crystals)

<u>benefit:</u> higher light extraction, IQE, wavelength tuning



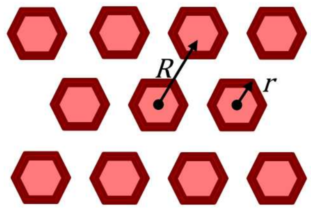
III-N Nanostructures for low-cost, reduced droop LEDs

Sandia National Laboratories

Vertical device integration

benefit: higher effective device area (cost/droop)

Nonpolar sidewall nanowires

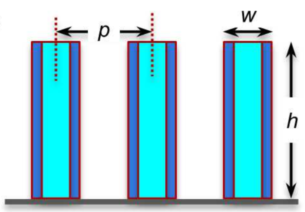


AR = aspect ratio
FF = fill factor

$$\frac{A_{sidewall}}{A_{substrate}} = \frac{6rh}{2.6R^2} \cong \mathbf{4.6AR \cdot FF}$$

ex: AR=3, FF=0.5 → ***6.9× increase!***

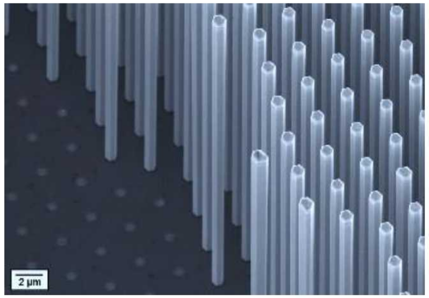
Nonpolar sidewall nanowalls



$$\frac{A_{sidewall}}{A_{substrate}} = \frac{2h}{w} \cdot FF = 2AR \cdot FF = \frac{2h}{p}$$

ex: p=0.5 μm, h=3 μm → ***12× increase!***

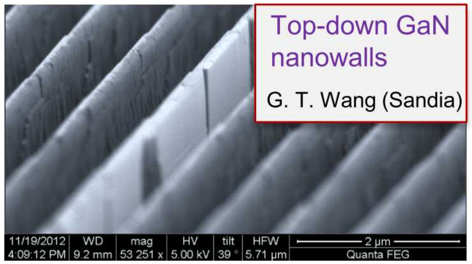
Microrod LEDs (Osram Opto)



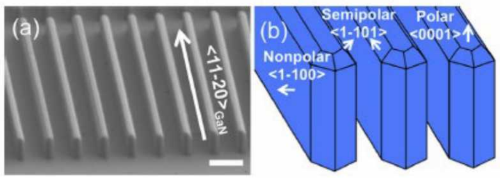
Microwire LED Blue IQE~65%

Cpd Semiconductor Mag: *What's The Best Business Model For Nanowire LEDs? (Dec. 14)*

Complex 3D growth and injection



InGaN/GaN MQWs on m-plane nanosheets

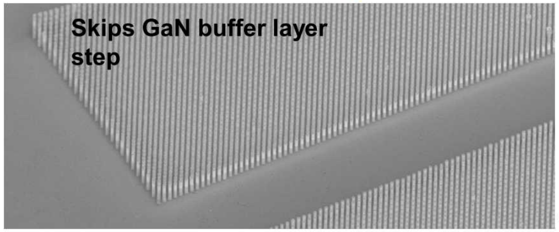


Dapkus (USC), *APL* **100** 033119 (2012)

Use of alternative substrates

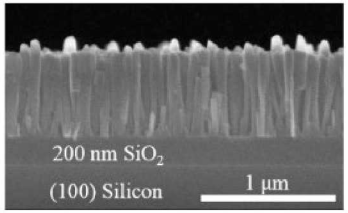
benefit: lower cost, new form factors

Core-shell nanowire LEDs grown on 8" Si



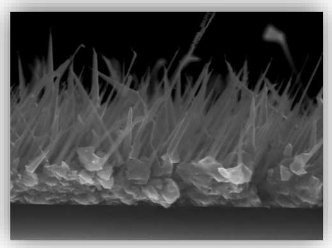
Aledia, Inc.

Nanowire LEDs grown on SiO_2



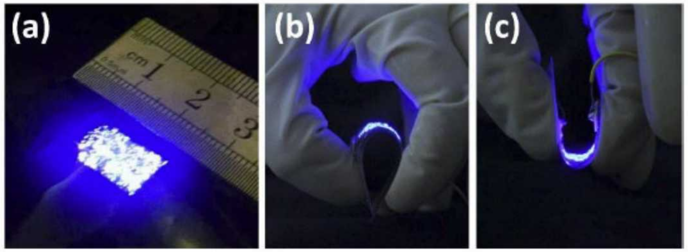
Bhattacharya (Michigan) *Opt. Exp.* **23** A650 (2015)

GaN NWs on tungsten foil



G. T. Wang (Sandia)

Flexible core-shell NW LEDs by MOCVD



CNRS (Grenoble), *NL, just accepted 8/31/15*

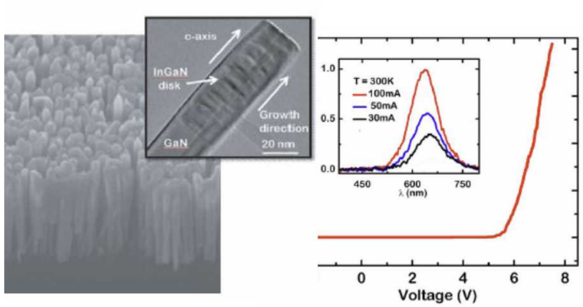
III-N Nanostructures for the Green-Yellow-Red Gap

Sandia National Laboratories

benefit: strain accommodation allows heterostructures with high In content (e.g. green-yellow-red gap)

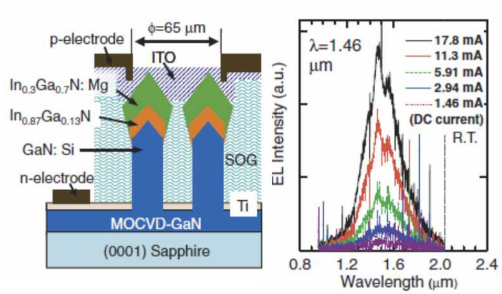
Axial *c*-plane InGaN disc/dot-in-a-wire grown by MBE: long wavelength emission demonstrated

Red emitting InGaN disks-in-wire ~52% IQE



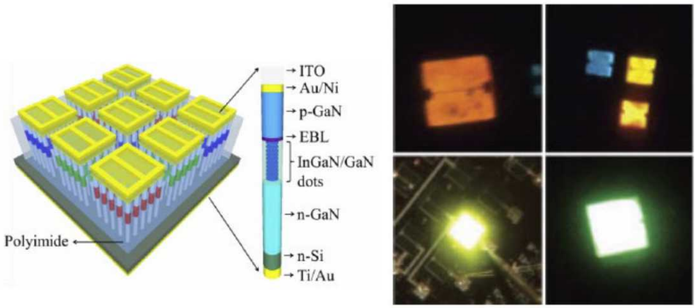
Bhattacharya (U. Michigan) *APL* **102** 071101 (2013)

Near IR InGaN LEDs at 1.46 μm



Kishino (Sophia U.), *APE* **5** 031001 (2012)

Phosphor-free RGB nanowire arrays on Si



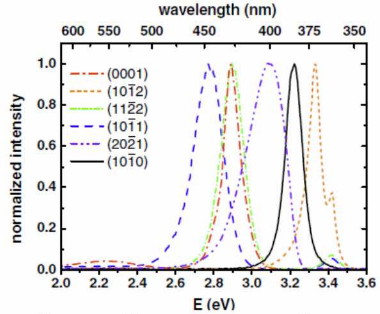
Z. Mi (McGill U.), *Opt. Exp.* **22** A1768 (2014)

Can similar bottom-up axial heterostructures be replicated with MOCVD?

Uniform injection of NW arrays an issue

{10-11} Semipolar nanostructures: potentially higher In incorporation

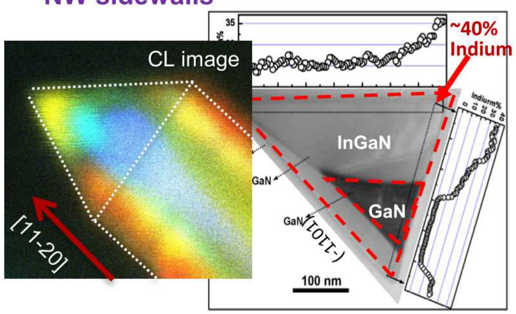
InGaN MQW emission by facet orientation



$$(10\bar{1}1) < (11\bar{2}2) = (0001) < (20\bar{2}1) < (10\bar{1}0) = (10\bar{1}2).$$

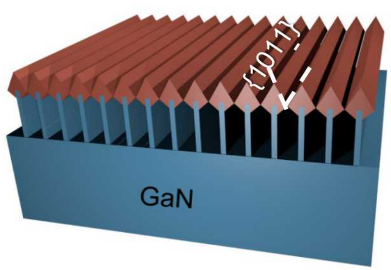
Wernicke (TU Berlin), *SST* **27** 024014 (2012)

High In incorporation on (10-11) NW sidewalls



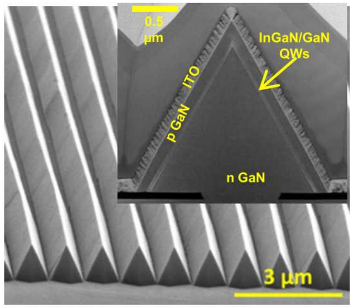
G. T. Wang (Sandia), *APL* **97** 181107 (2010)

InGaN pseudo-templates based on semipolar nanostripes?



G. T. Wang (Sandia)

(10-11) semipolar nanowall LEDs



Feezell (U. New Mexico)

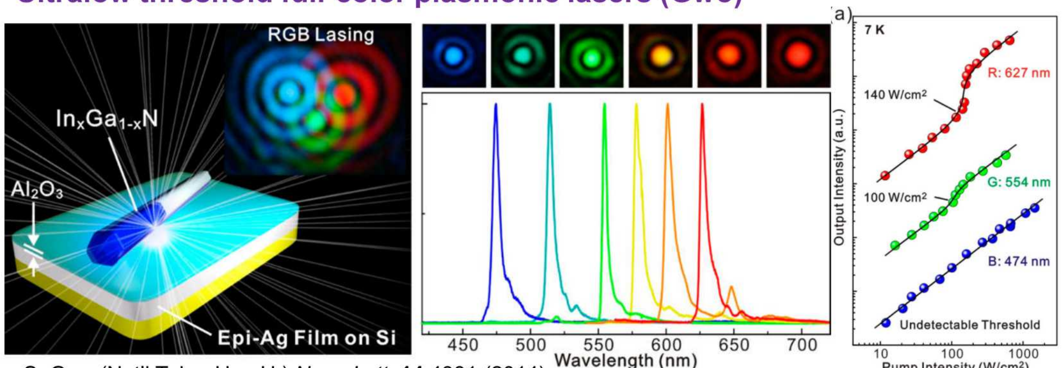
See also work by Wunderer (U. Ulm)

Corner effects (nonuniform In incorporation), material quality?

III-N Nanowire and Quantum Dot Lasers

<u>Potential benefits</u>: long wavelengths, low thresholds, higher efficiencies, wavelength tuning, nanophotonics

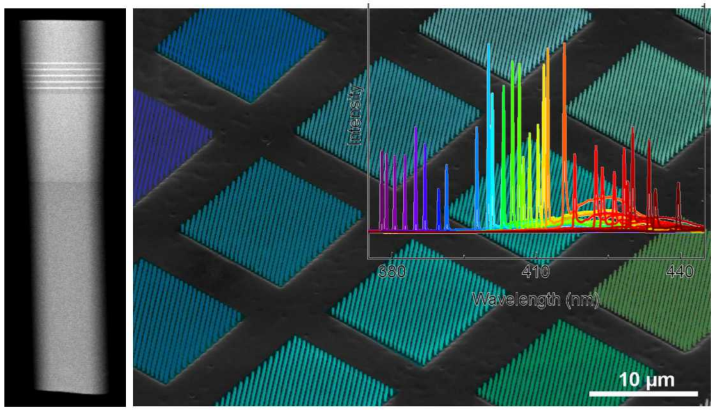
Ultralow threshold full-color plasmonic lasers (Gwo)



S. Gwo (Nat'l Tsing-Hua U.) *Nano Lett.* **14** 4381 (2014)

Ultralow continuous wave threshold across visible spectrum (single NWs on Ag)

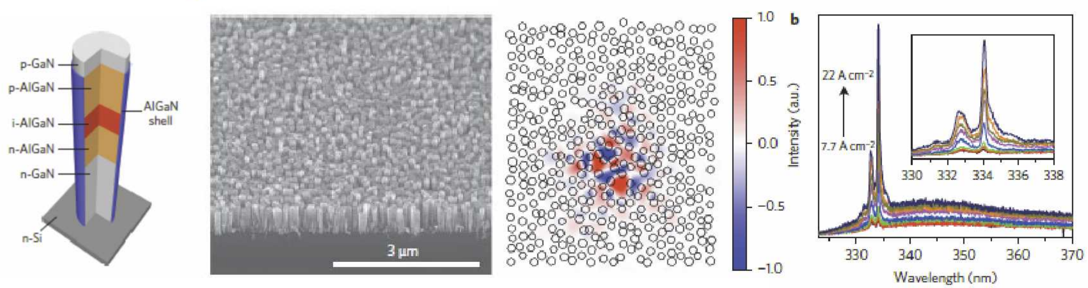
Top-down nanowire photonic crystal laser pixels



J. B. Wright et al. (Sandia) *Sci. Rep.* 3, Art. #: 2982 (2013)

60 nm λ tuning demonstrated purely by PC geometry

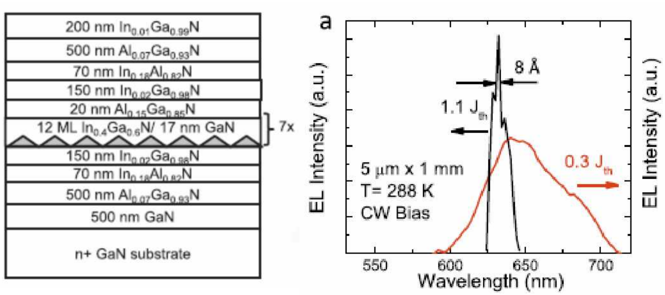
Ultralow threshold electrically injected AlGaN nanowire array UV random laser on Si by MBE



Z. Mi (McGill), *NNANO.2014.308* (2015)

Electrically injected lasing at 263 nm @ 0.6 kA/cm^2 threshold, deepest UV reported to date

Red Edge-Emitting QD Lasers by MBE



Bhattacharya (U. Michigan) *IEEE J. Quant. Electr.* **49** 923 (2013)

~36% IQE at 630 nm, 2.5 kA/cm^2 threshold

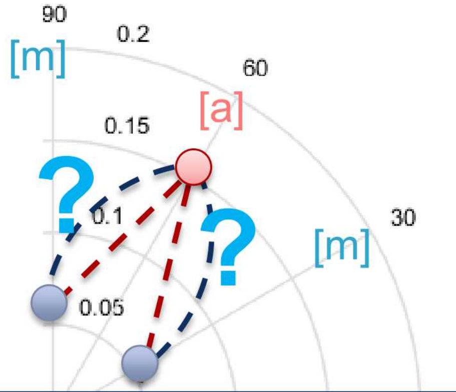
Aboslute EQEs and Output Powers?

Electrical Injection for single NWs?

MOCVD Compatible Processes?

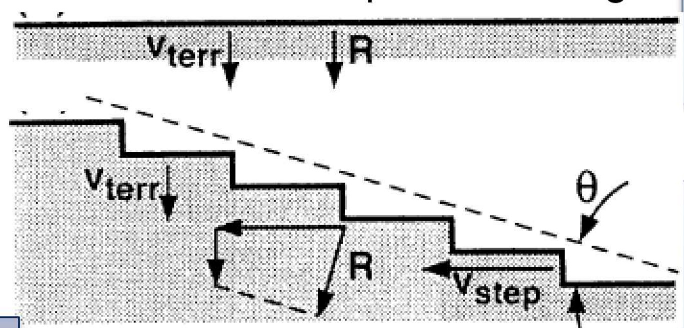
How Does the Etch Rate Depend on Orientation?

Sandia National Laboratories



What is the shape of this curve ?

Illustration of step-flow etching



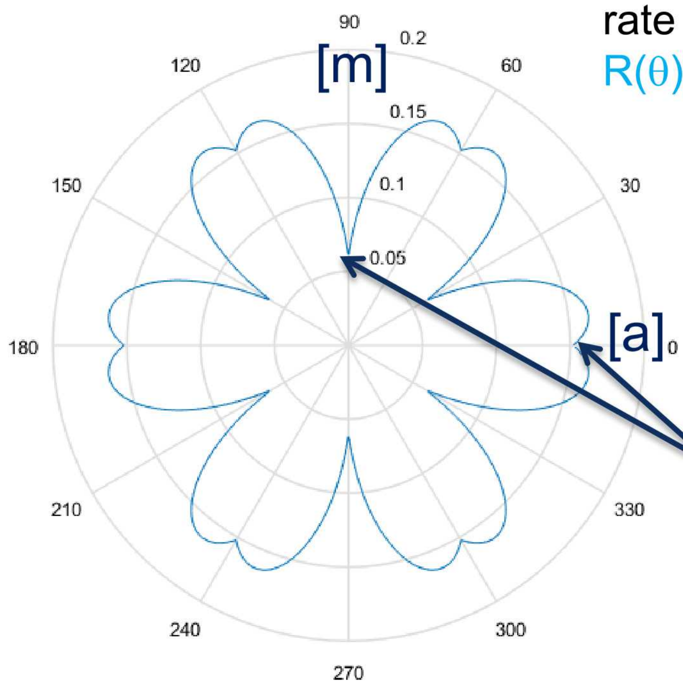
Wind et al., Surf. Sci. 460, 21 (2000)

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

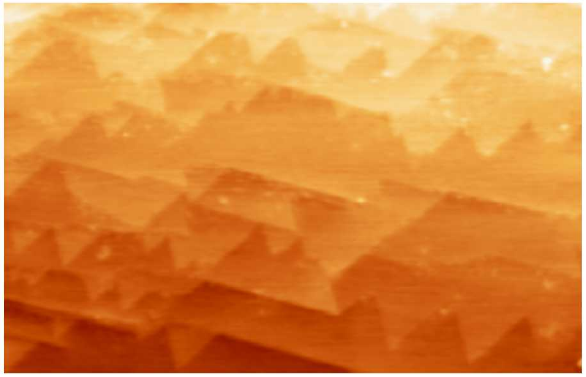
$R(\theta) = m\cos(\theta\pi/(\pi/3)) + a\sin(|\theta\pi/(\pi/3)|)$, for θ: $-\pi/6 < \theta < \pi/6$

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

Conclusions

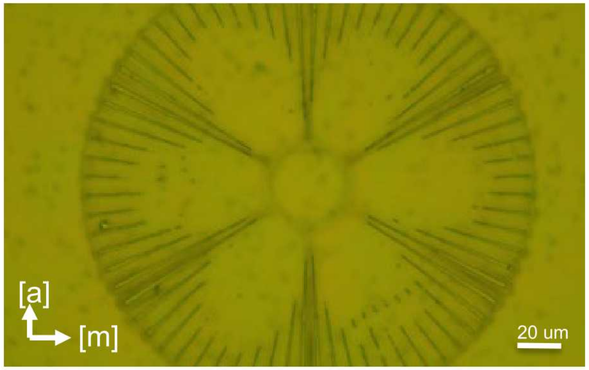
Atomic anisotropy

- Probed by AFM of etched c-plane surface - inert (slow) c-plane GaN etch is due to the bonding configuration of the m-plane aligned steps
- Still open questions on classification of etch sites and chemical reaction pathways



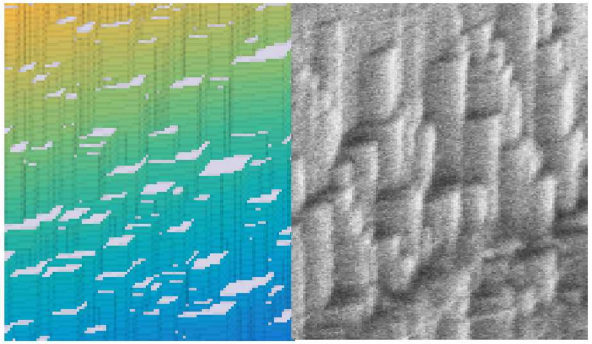
Facet scale anisotropy

- Direct orientation resolved etch rate measurements for the m-a set of planes

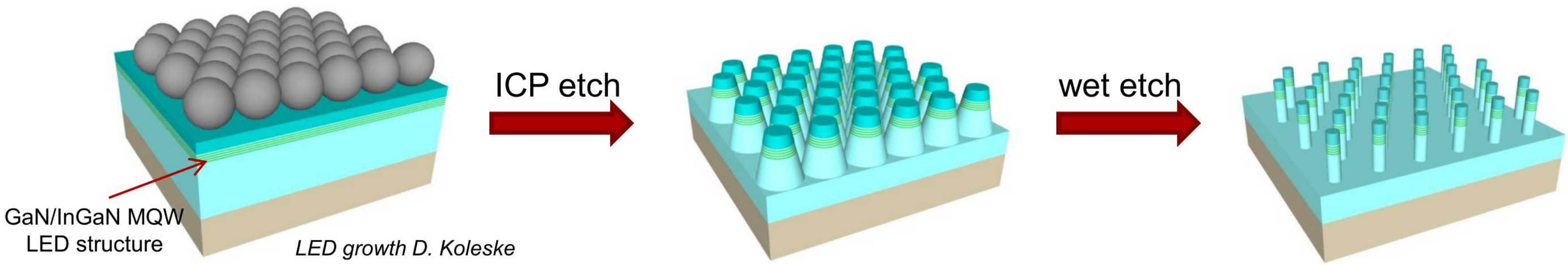


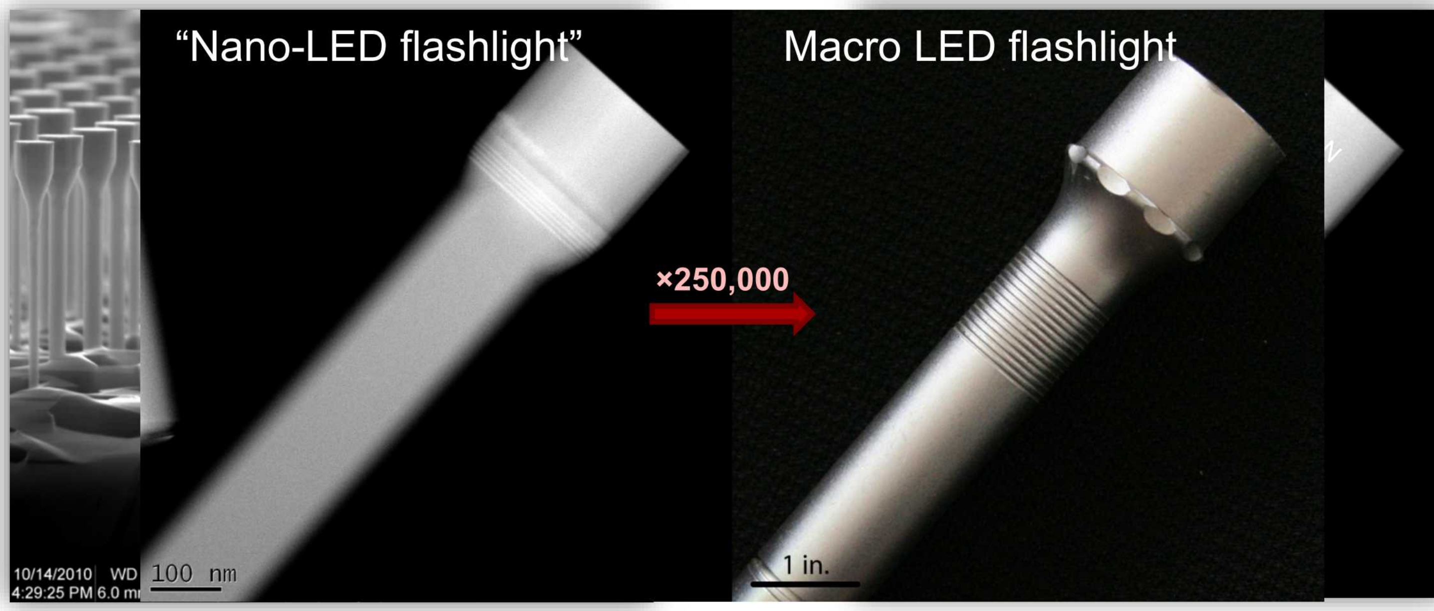
Nanostructures

- Wet chemical etching is an ideal technique for III-nitride nanostructure fabrication due to its extremely high anisotropy



Axial GaN/InGaN nanowire LEDs

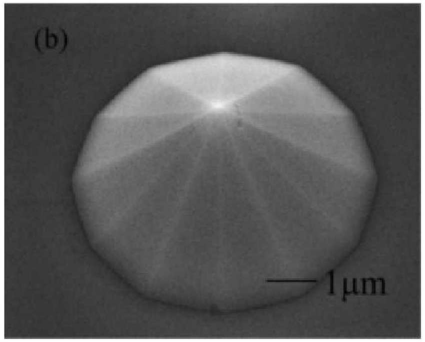


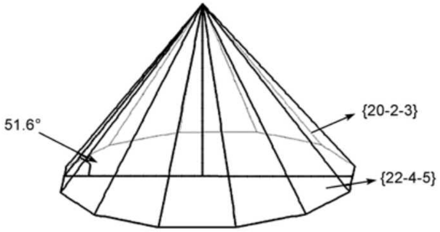


Q. Li et al., *Optics Express* **19**, 25528 (2011)

Prior H_3PO_4 Wet etching of planar GaN

N-polar GaN

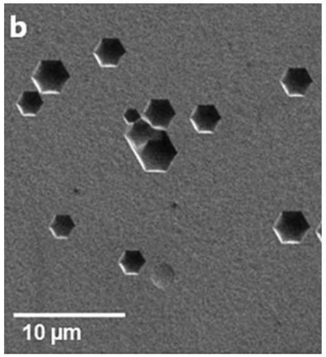


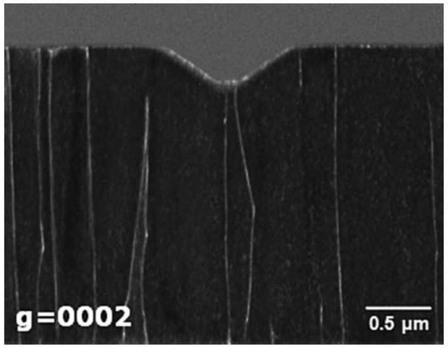


Qi et al., Sci. China, Tech. Sci., 53, 769 (2010)

- 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



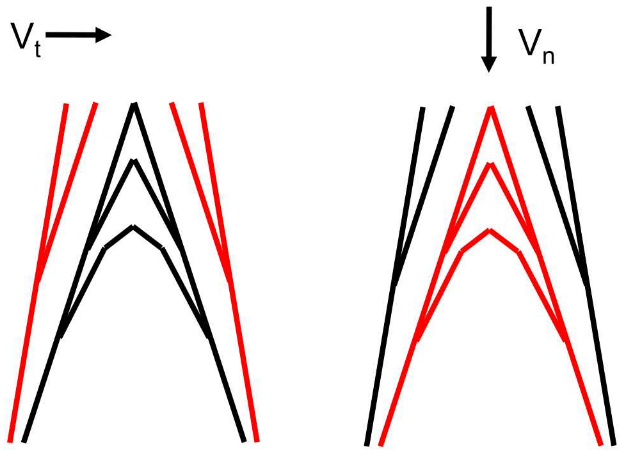


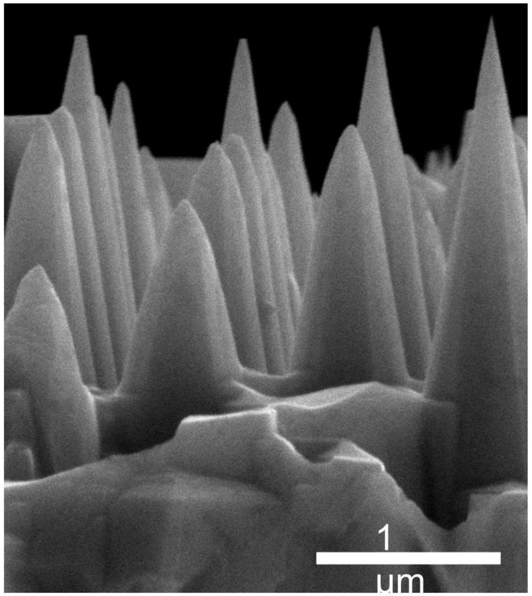
M. Reiner et al., PSSB, 252, 1121 (2015)

- 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

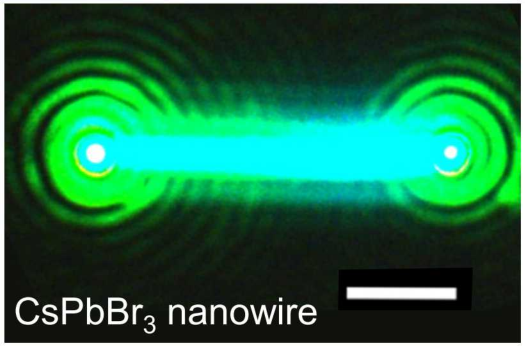




Semipolar facets form due to V_n/V_t ratios. Initially, V_t dominates where it is dominated by concentration (kinetics). When V_n dominates, an increase in semipolar angle occurs, and this is driven more by temperature and surface energy (thermodynamics).

Nanowire Lasers

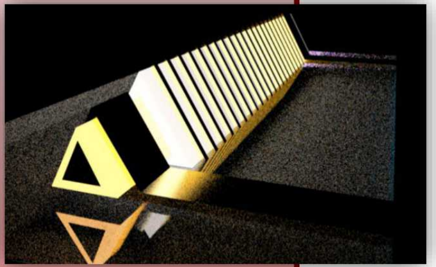
- Nanowire forms a freestanding, low loss optical cavity
- Optically pumped nanowire lasers reported:
  - ZnO, CdS, GaAs, GaSb, GaP, GaN, etc.
- Most commonly Fabry-Perot type lasing from end facets
- Promising nanophotonic elements - compact and low power due to small mode volume



S. W. Eaton, *PNAS* **113**, 1193 (2016)

Need to understand & control optical properties

- **Mode control** – single vs. multi-mode behavior
- **Polarization control** – linear vs. elliptical
- **Wavelength tuning**
- **Beam shaping**
- **Beam steering**

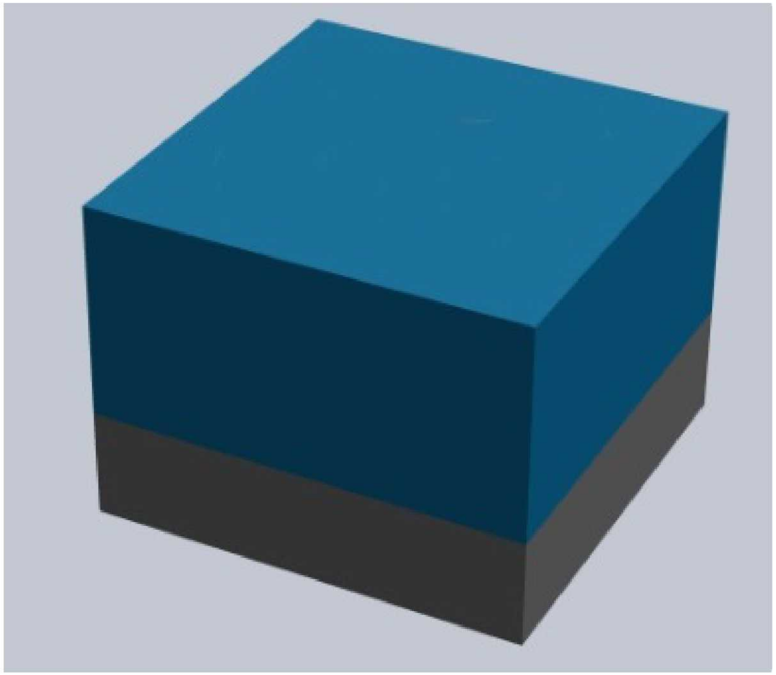


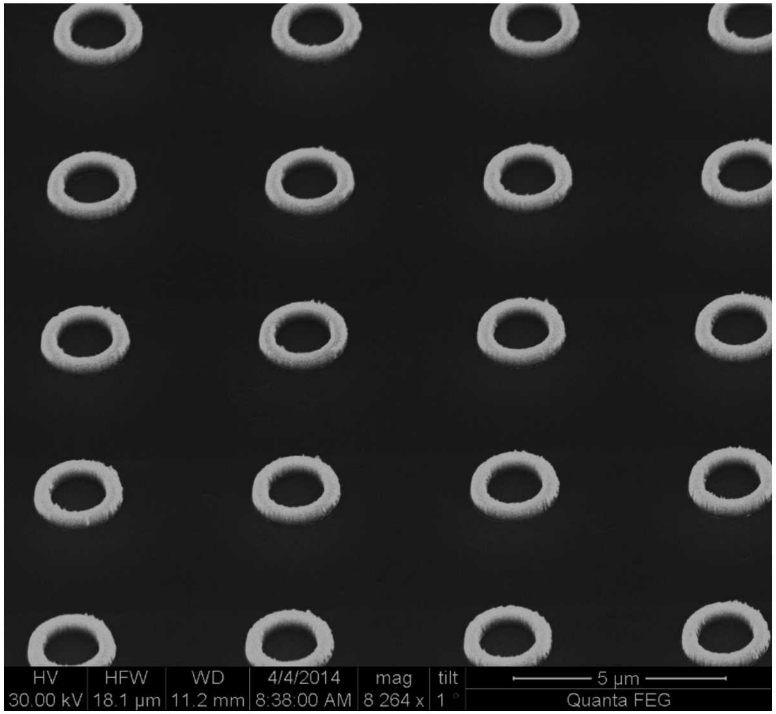
1) S. Arafin, X. Liu, Z. Mi, “Review of recent progress of III-nitride nanowire lasers,” *J. Nanophotonics* **7,** 074599-1 (2013)
2) C. Couteau et al., “Nanowire Lasers,” *Nanophotonics* **4**, 90 (2015)

Cross-sectional shape control - GaN nanotubes

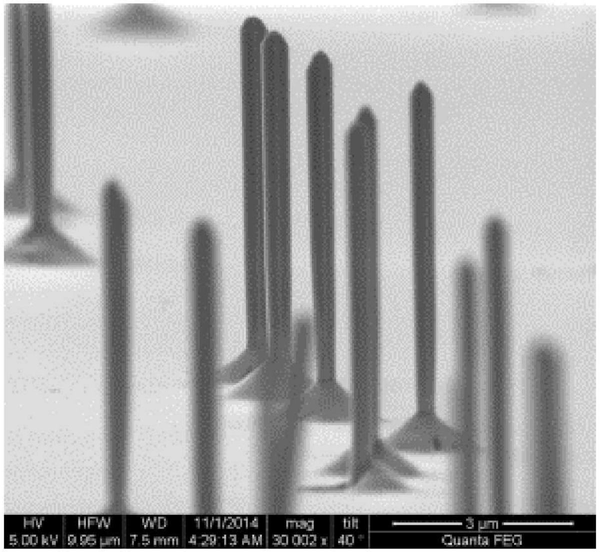
EBL Patterning and PMMA Lift-off

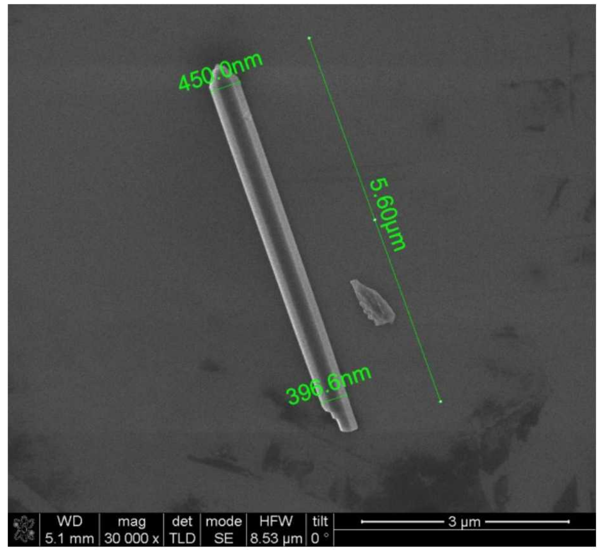
ICP dry etch

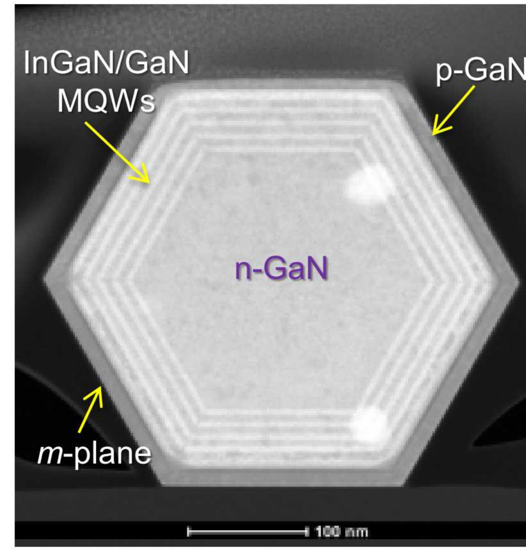




Hybrid top-down bottom-up fabrication of core-shell p-i-n InGaN/GaN core-shell NWs

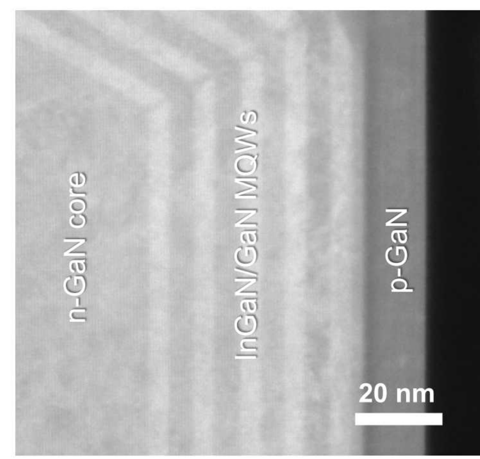






Core-shell radial p-i-n InGaN/GaN MQW nanowires following MOCVD regrowth on top-down fabricated n-type GaN nanowires

- 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

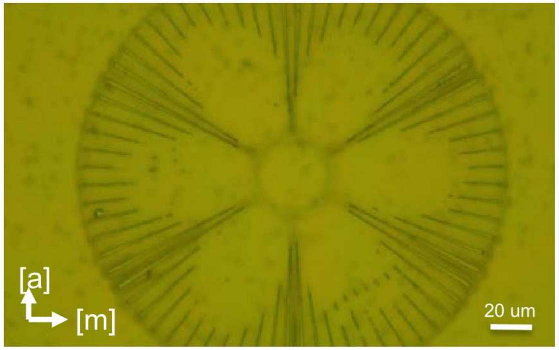


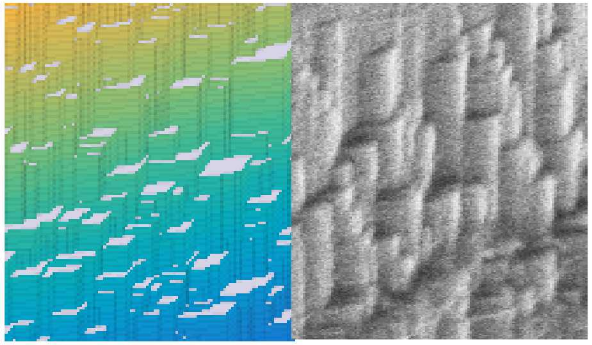
STEM by Ping Lu

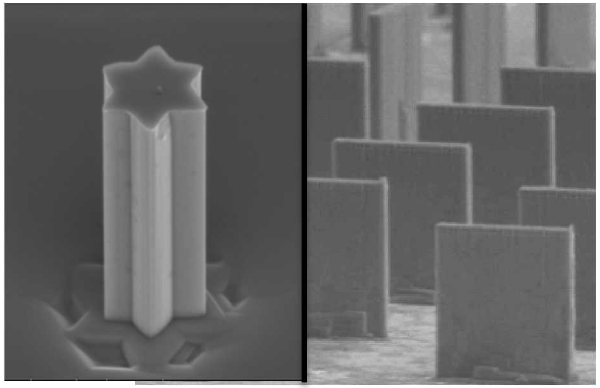
Summary – Top-down fabrication of III-nitride nanostructures for photonics

Sandia National Laboratories

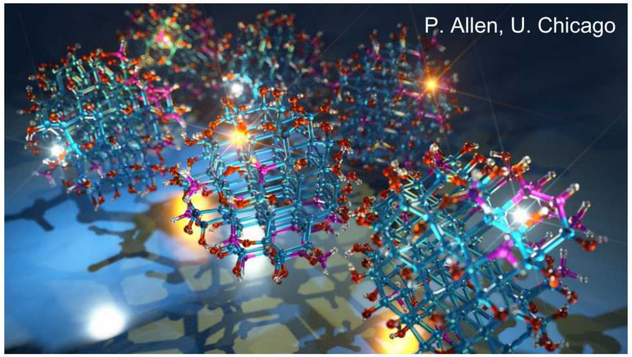
- **First direct orientation resolved wet etch rate measurements** for the nonpolar GaN set of planes
- Implementation of Wulff-Jaccodine method for **prediction of pillar etch geometry and facets**
- **Elucidated mechanism for facet evolution** from tapered to straight nanostructures
- Demonstrated **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**



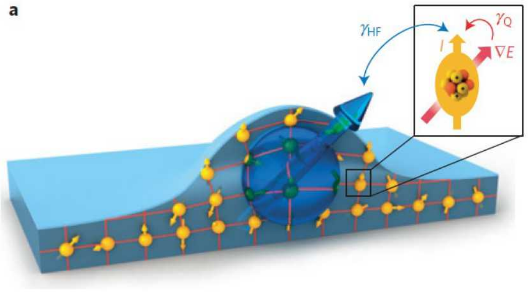




Quantum dots

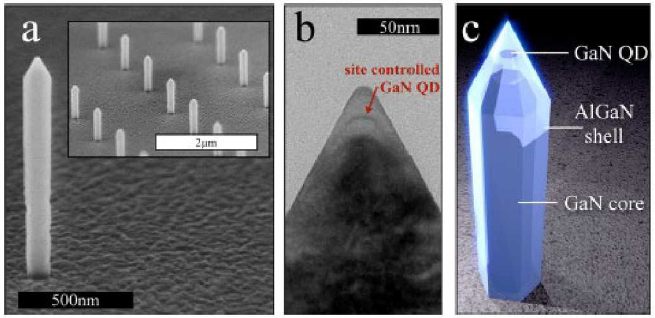


Electron spin qubit - In(Ga)As /GaAs QD



A. Bechtold et al., *Nat. Phys.*, **11** , 1005 (2015)

RT single photon emitter - GaN QD in a nanowire



M. Holmes et al., *Nano Lett.*, **14** , 982 (2014)

Quantum Dots (QDs): 0D structures produced by colloidal, epitaxial, or electrically defined of interest for:

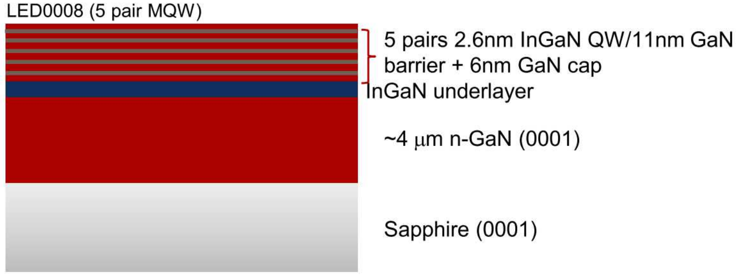
- Single electron devices - low power chips
- Spin quibits for quantum computing
- High efficiency laser and LEDs for integrated photonics/electronics
- Quantum emitters (single/dual photon sources) – for range of quantum computing schemes

Challenge: Find methods to realize epitaxial (on-chip) QDs to meet the required sizes (<10 nm), inhomogeneous broadening, placement, and densities

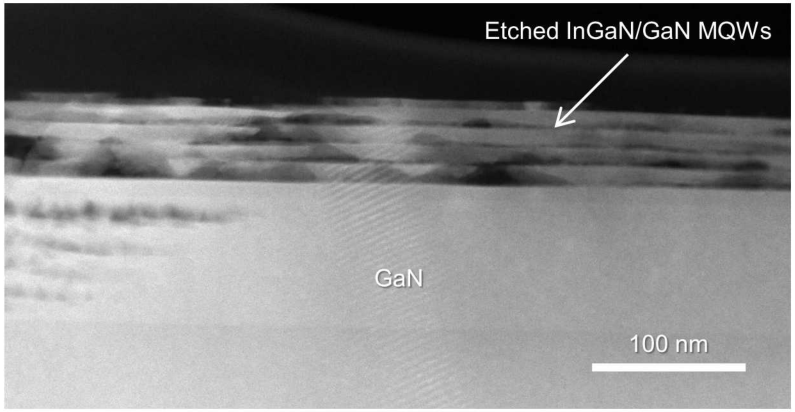
QSC-PEC Etching of InGaN/GaN Multiple Quantum Wells

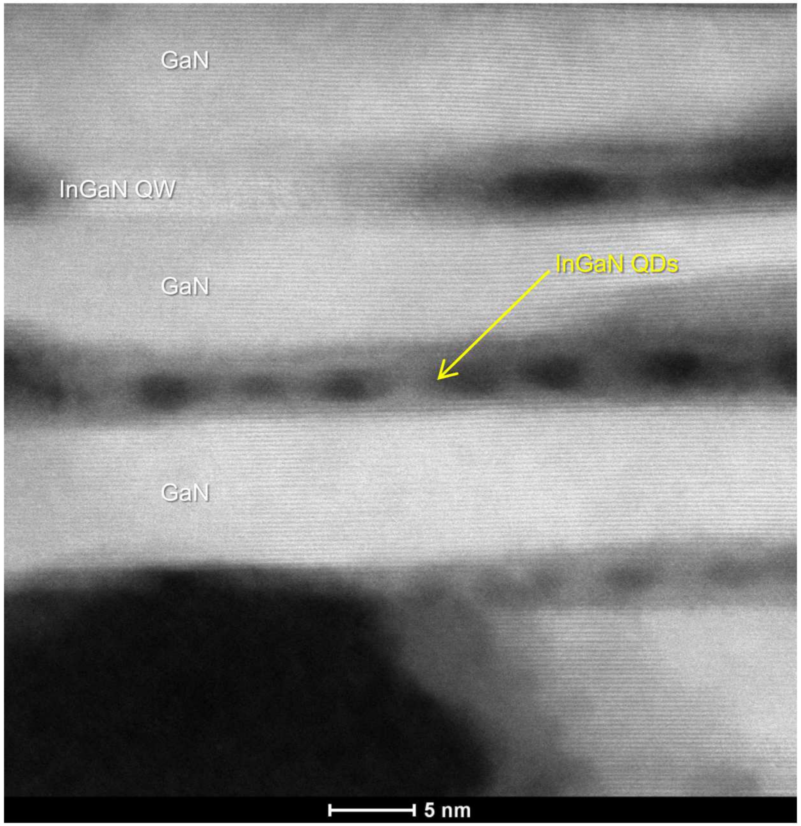
Sandia National Laboratories

- Cross-sectional STEM shows all InGaN layers etched, with GaN voids present
- InGaN QD density per layer appears low compared to QSC-PEC etched single InGaN layer, potentially explaining relatively low PL of etched MQW sample



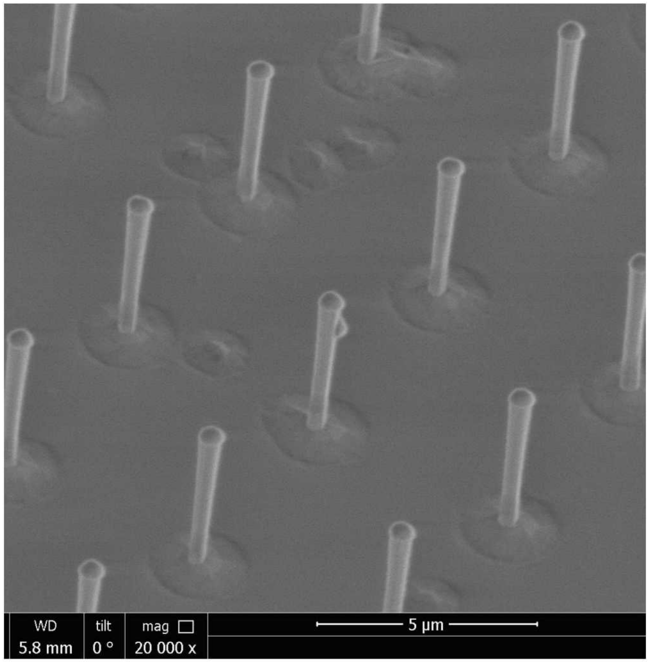
PEC etch: 420 nm, 20mW, 1.4V, 0.2M H_2SO_4, 45min



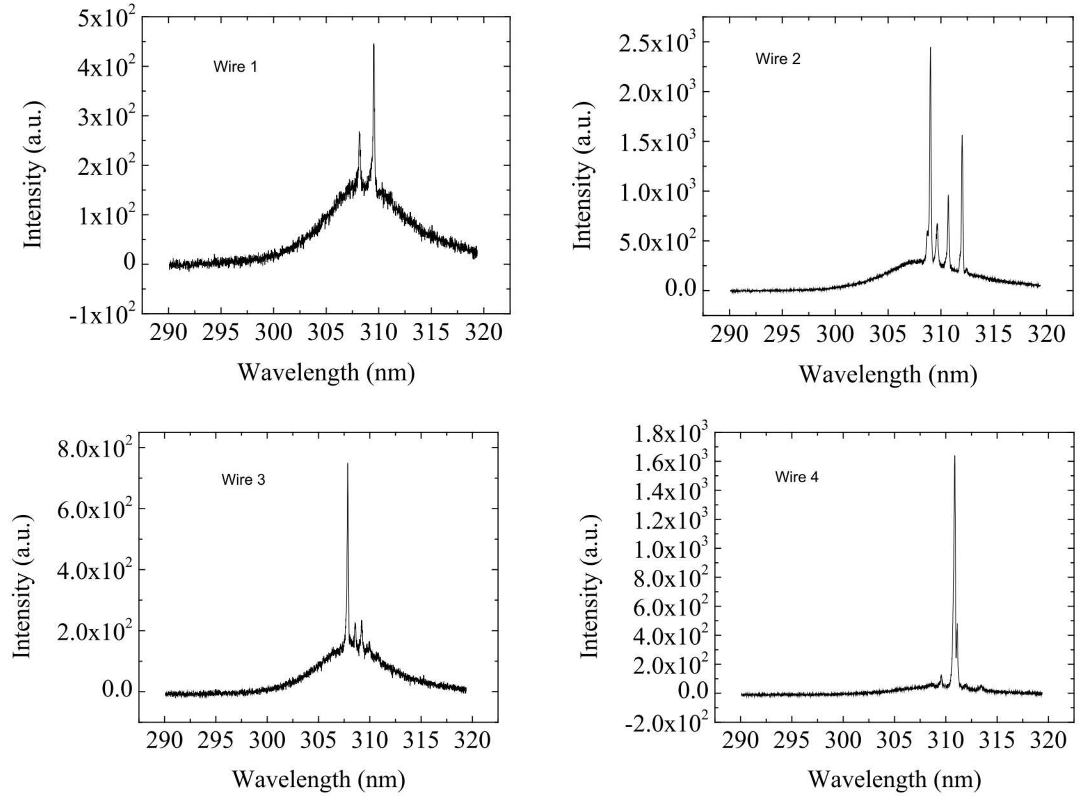


STEM by Ping Lu

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!?)