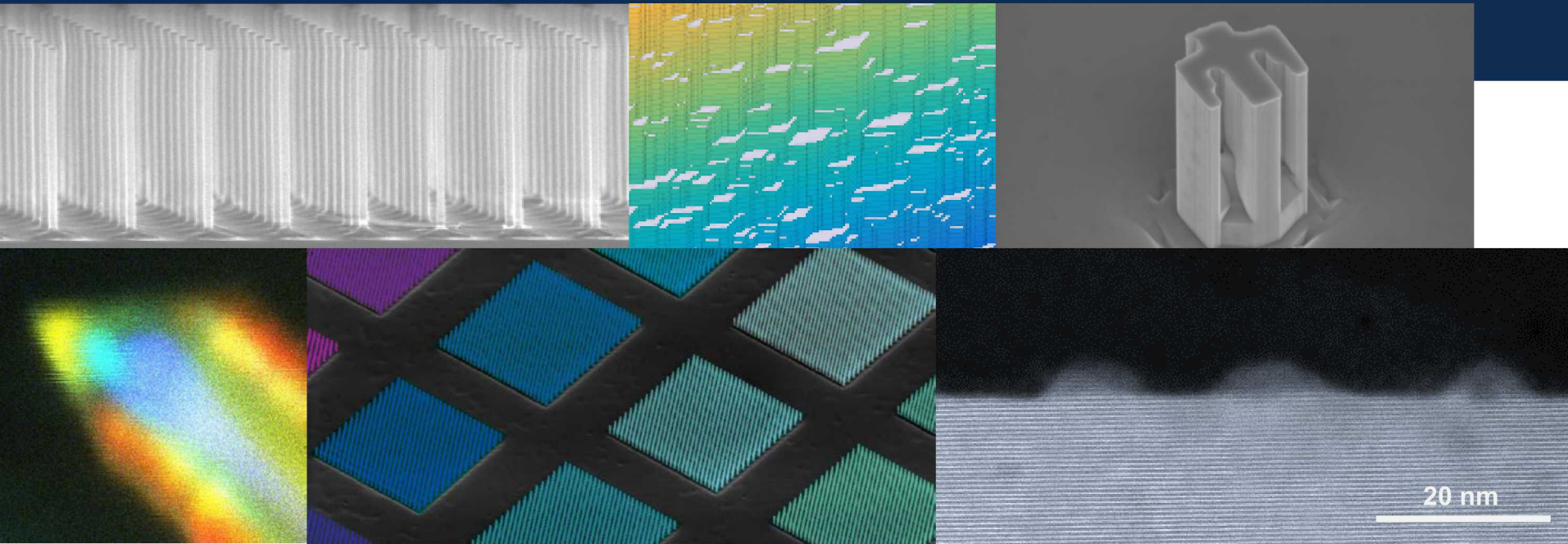




Fabrication of III-Nitride Nanostructures for Future Optoelectronics and Beyond

George T. Wang

Sandia National Laboratories, Albuquerque, NM, 87185, USA

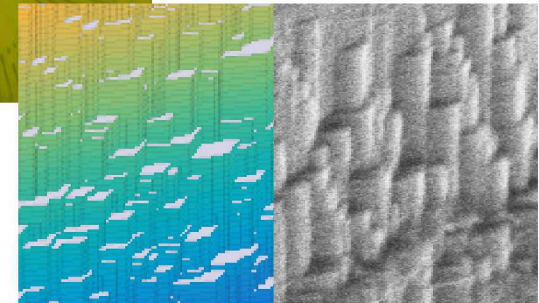
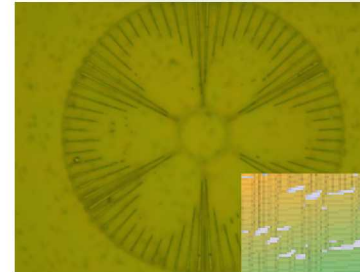
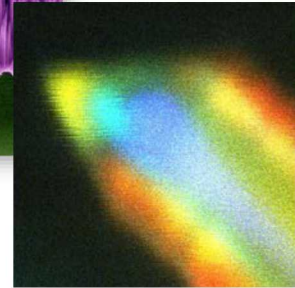
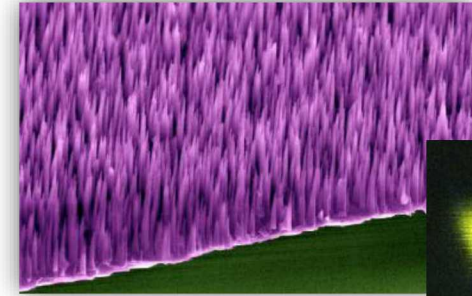
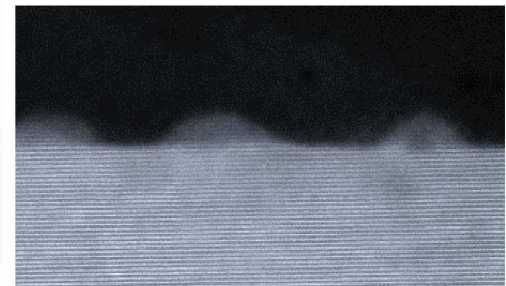
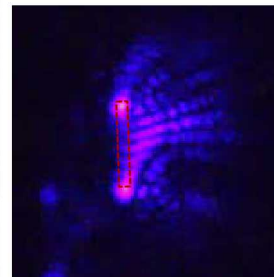
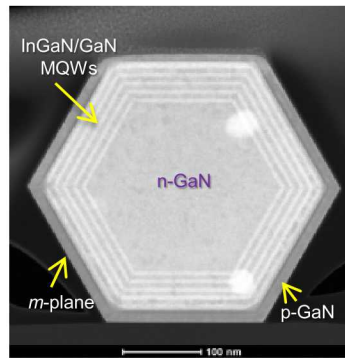
This work was supported by the DOE BES Materials Science and Engineering Division, DOE Energy Frontier Research Center for Solid-State Lighting Science, and the Laboratory Directed Research and Development program at Sandia National Laboratories. This work was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. Department of Energy, Office of Basic Energy Sciences user facility.



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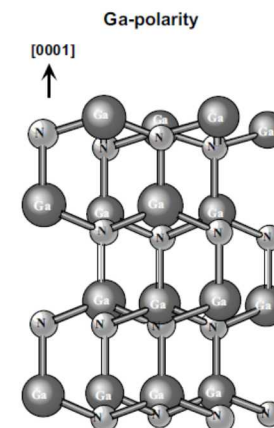
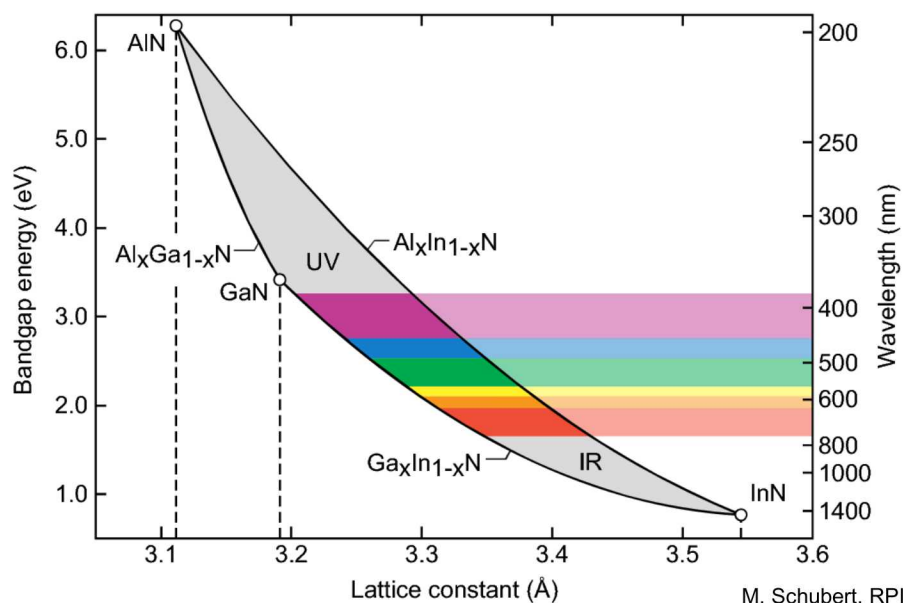
Outline - III-Nitride Nanostructures

- Why nanostructures?
- Bottom-up growth and characterization
- Top-down fabrication – wet etching of GaN
- III-Nitride nanowire photonics
- Quantum-size controlled etching of quantum dots



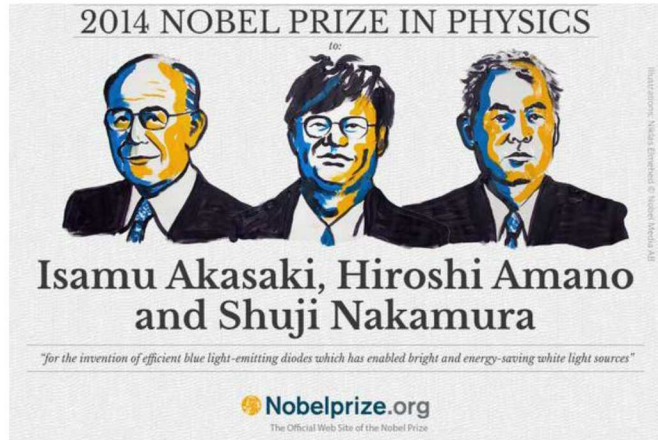
III-Nitride (AlGaInN) Semiconductors

- **Direct RT bandgaps: deep UV, entire visible, into IR: ~0.7-6.0 eV**
- Solid alloy system (tuneable bandgaps)
- High breakdown field, mobility, thermal conductivity, melting temperature
- Radiation resistant and chemically inert

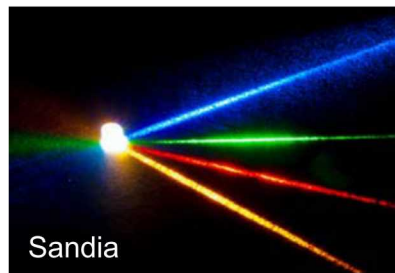


Handbook of Nitride
Semiconductors & Devices, H.
Morkoc (2009)

III-Nitride (AlGaInN) Semiconductors



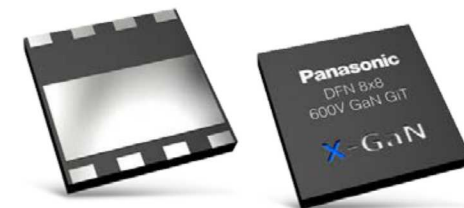
LEDs (UV to visible)



Lasers

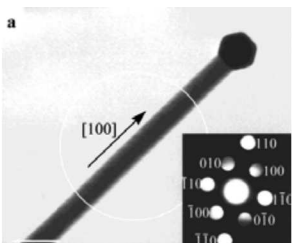
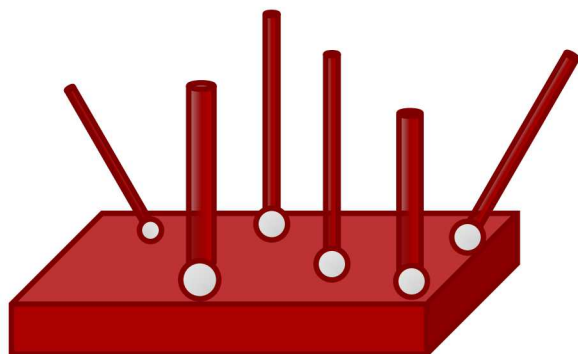


High-Speed & High Power Electronics



Bottom-up growth of GaN-based nanowires

Metal catalyzed (vapor-liquid-solid)



C. Lieber, 2000

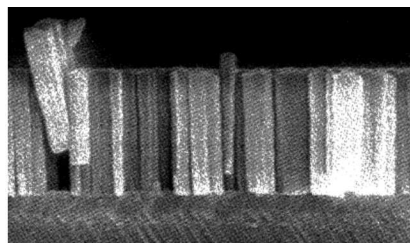
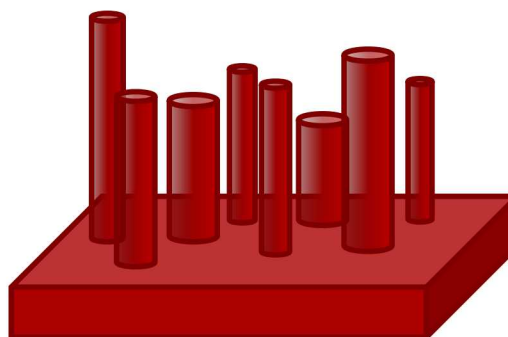


C.C. Chen, 2001

Methods: PLD, thermal evaporation, (MO)CVD

Historically popular (ease & low cost of entry), but falling out of favor due to limitations

"Self-catalyzed"

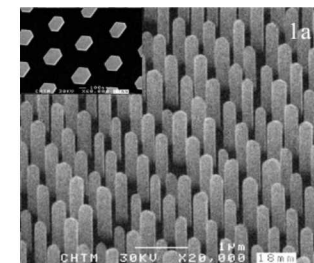
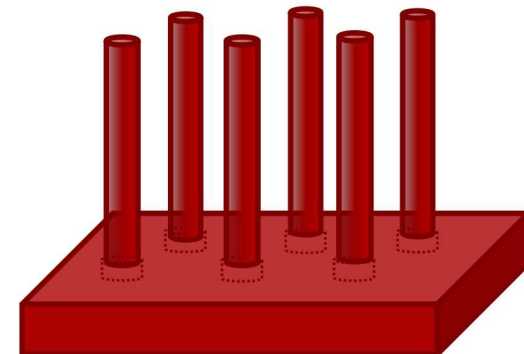


K. Kishino, 1997

Methods: (PA)MBE, HVPE, (MO)CVD

Cons include slow growth rates and random ordering

Selective area growth (SAG)

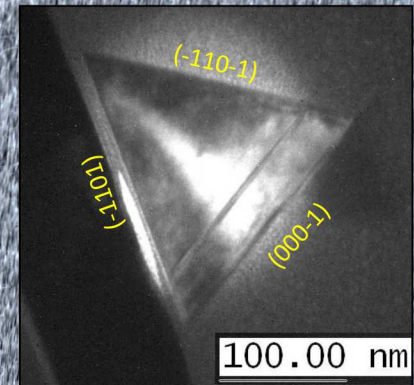
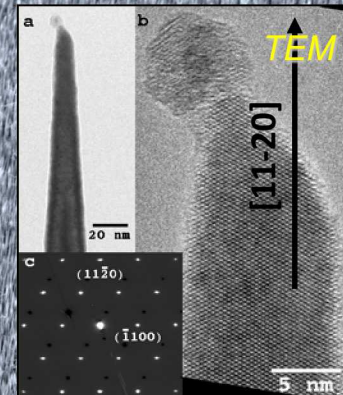
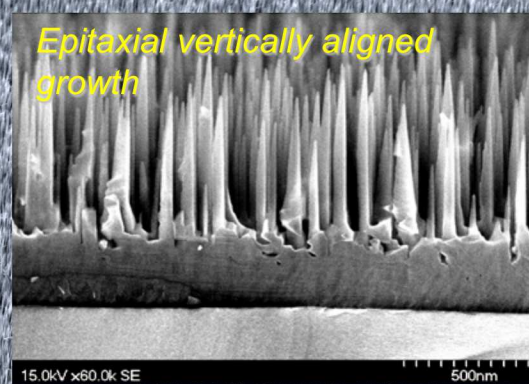
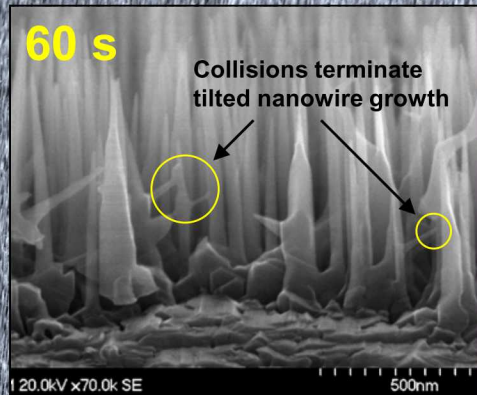


S. Hersee, 2006

Methods: (PA)MBE, MOCVD

Currently popular, but may require growth conditions that limit materials & architectural flexibility

“Bottom Up” aligned GaN nanowire growth



- Nanowires grown by Ni-catalyzed MOCVD (VLS)
- Demonstrated highly-aligned vertical growth over large areas on *r*-sapphire
 - Submonolayer Ni films necessary for high density and alignment
 - Collisions filter out tilted nanowires
- Primary $[11-20]$ growth orientation ($\perp$ to $(11-20)$ α -plane)
- Triangular faceted -- $(000-1)$ and equiv. (-1101) and $(-110-1)$
- TEM: Single crystal, dislocation free; c -plane stacking faults

G. T. Wang et al., *Nanotechnology* 17 5773-5780 (2006)

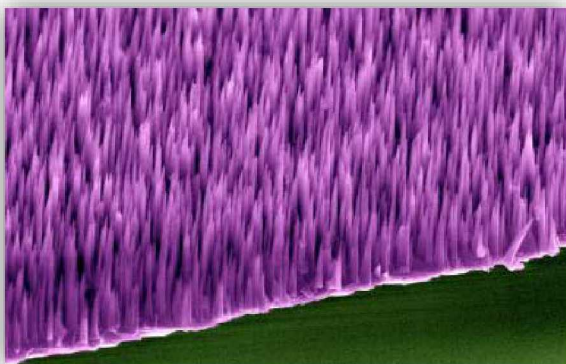
Q. Li, G. T. Wang, *Appl. Phys. Lett.* 93, 043119 (2008)

Q. Li, J. R. Creighton, G.T. Wang, *J. Crys. Growth* 310 3706-3709 (2008)

100 μm

Sandia bottom-up III-nitride nanowire work

Vertically-aligned growth



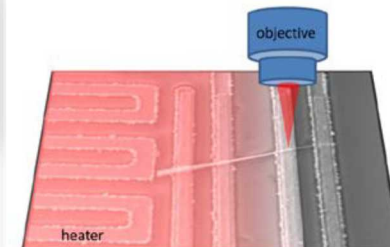
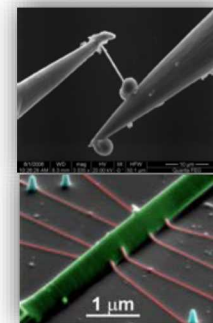
G. T. Wang et al., *Nanotechnology* **17** 5773-5780 (2006)
Q. Li, G. T. Wang, *Appl. Phys. Lett.* **93**, 043119 (2008)
Q. Li, J. R. Creighton, G.T. Wang, *J. Crys. Growth* **310** 3706-3709 (2008)

Nanowire-templated growth



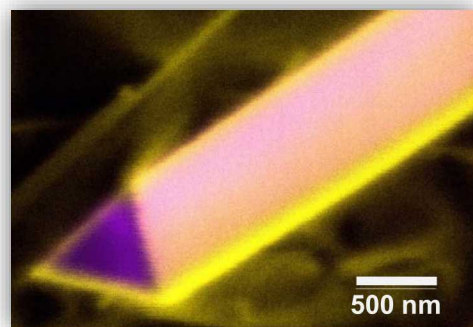
Q. Li, Y. Lin, J.R. Creighton, J. Figiel, G.T. Wang, *Adv. Mat.*, **21** 2416-2420 (2009)

[Thermo]Electrical characterization

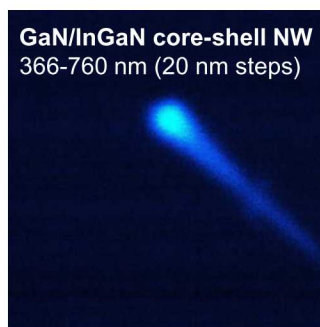


A. A. Talin, G. T. Wang, E. Lai, R. J. Anderson, *Appl. Phys. Lett.*, **92** 093105 (2008)
Y. Lin, Q. Li, A. Armstrong, and G. T. Wang, *Solid State Commun.*, **149**, 1608 (2009)
E. Song, et al., *Nanotechnology*, **27**, 015204 (2016)
F. Leonard, et al., *Nano Letters*, **15**, 8129 (2015)

Optical imaging and spectroscopy



GaN/InGaN core-shell NW
366-760 nm (20 nm steps)



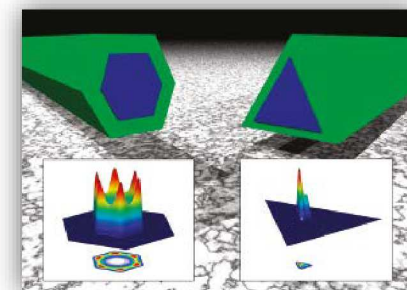
Q. Li, G. T. Wang, *Nano Lett.*, **10** (5), 1554 [GaN defect CL]
Q. M. Li, G. T. Wang, *Appl. Phys. Lett.*, **97**, 181107, 2010. [GaN/InGaN]
P.C. Uppadhya et al. *Semicond. Sci. Tech.* **25** 024017 (2010) [Ultrafast]
A. Armstrong, Q. Li, Y. Lin, A. A. Talin, G. T. Wang, *APL* **96**, 163106 (2010). [DLOS]

In-situ TEM



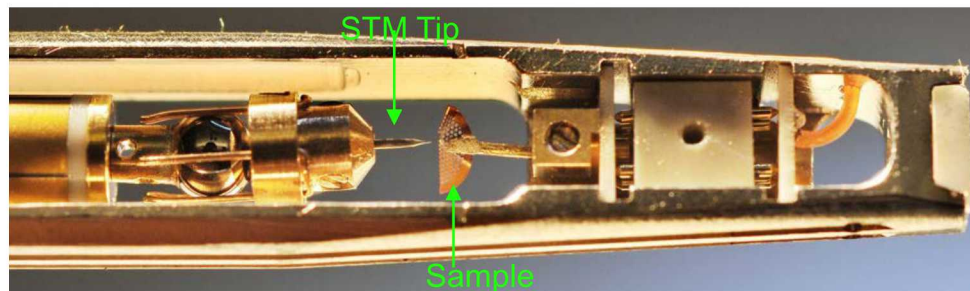
T. Westover et al., *Nano Lett.*, **9**, 257 (2009).
[in-situ NW breakdown]
J. Y. Huang et al., *Nano Lett.*, **11** (4), 1618 (2011). [in-situ nanomechanics]

Theory

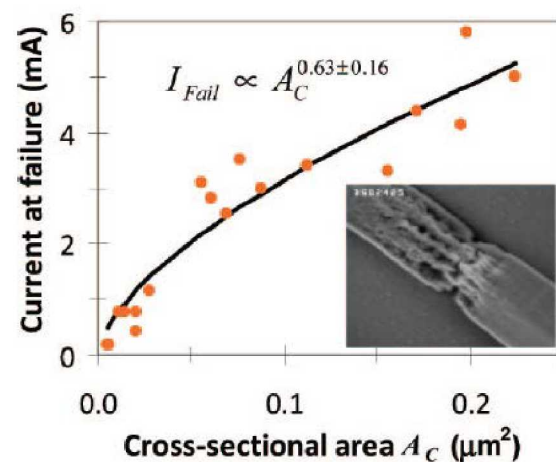
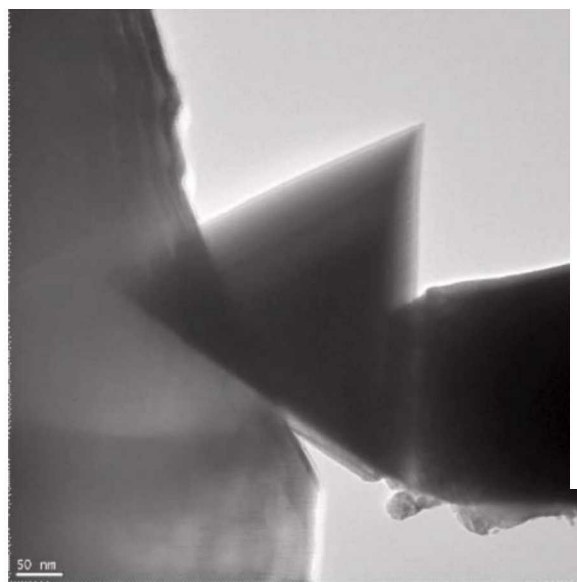
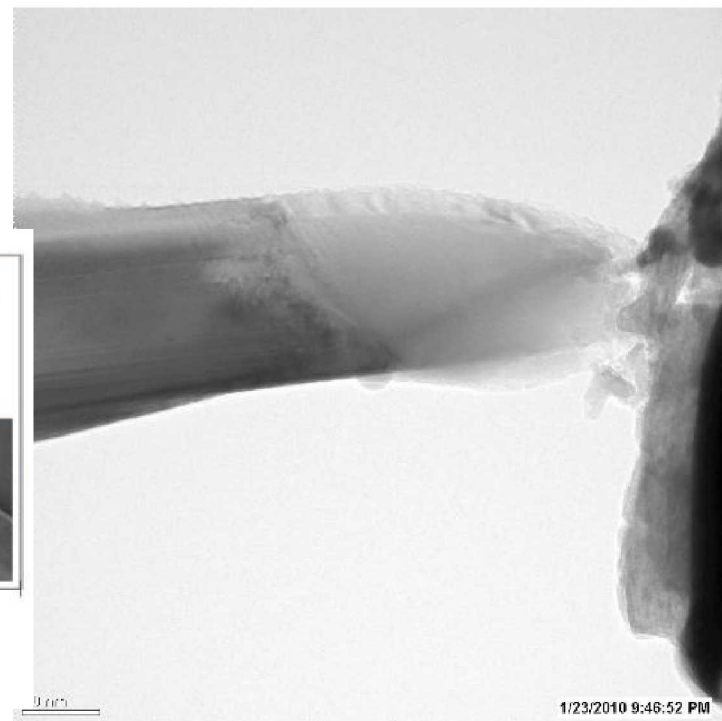


B. Wong et al., *Nano Lett* **11** (8), 3074, 2011

In-situ TEM studies – nanowire electrical breakdown



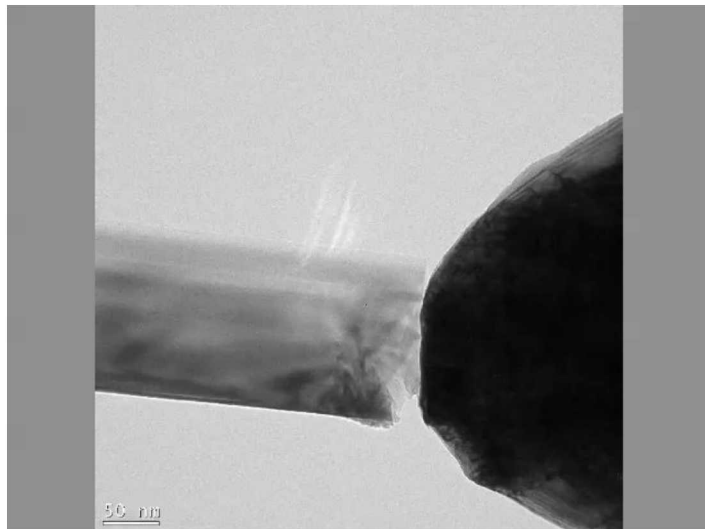
NW decomposition via Joule heating
(relevant for NW devices)



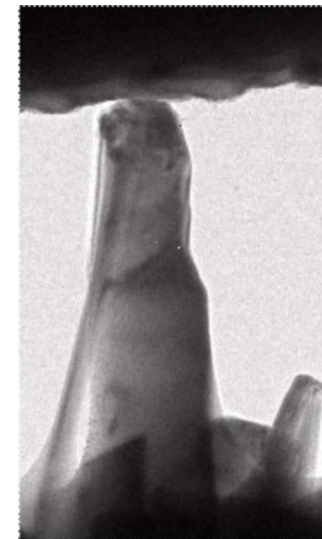
NW breakdown at 60V, 20 μA
(avg. breakdown $I \sim 3000 \text{ kW/cm}^2$)

T. Westover, R. Jones, J. Y. Huang, G. Wang, E. Lai, A. A. Talin, *Nano Lett.*, **9**, 257 (2009).

Real time *In-situ* TEM nanomechanics of GaN NWs



- Dislocation-free NW shows significant surface plastic deformation
- Mediated by dislocation nucleation & pile up, grain boundary sliding



- Plastic deformation often observed before fracture
- Plasticity is local, not global

Study provides unique insight into the nanomechanical properties which may impact nanowire device processing and operation

J. Y. Huang, H. Zheng, S. X. Mao, Q. Li, and G. T. Wang, *Nano Lett.*, **11** (4), 1618 (2011).

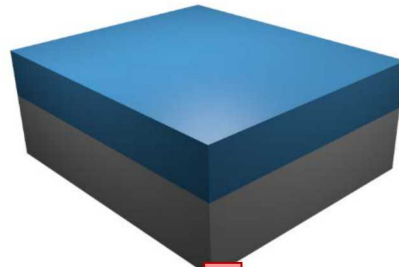
Motivation: Top-down approach for nanostructures

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

Steps

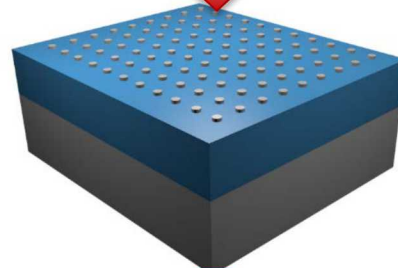
Advantages

Conventional
GaN film



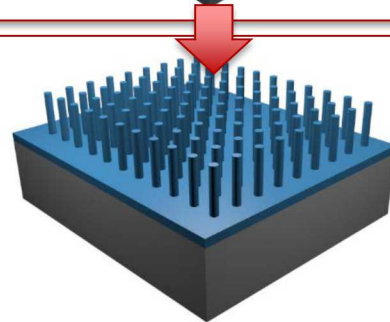
- Standard/optimized growth conditions (not limited by 1D growth window) give control over:
 - Dopant, impurity incorporation
 - Axial heterostructuring
- Can be characterized by standard methods

Lithographic
technique (e.g.
e-beam,
nanoimprint,
interferometric)



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

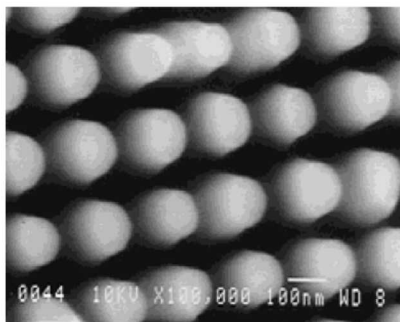
Anisotropic
etch



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

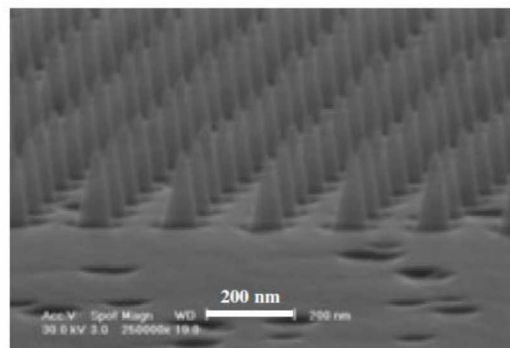
Previous top-down nanorod/nanopillar/nanopost work

InGaN/GaN MQW nanoposts/nanopillars



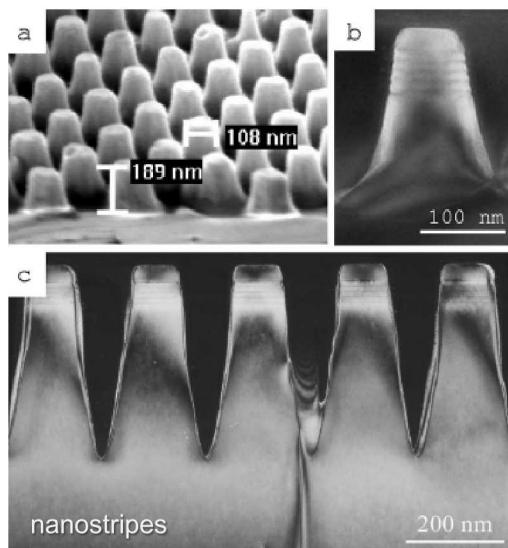
L. Chen et al., PSSa **188** 135 (2001) (Brown, Yale)

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



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

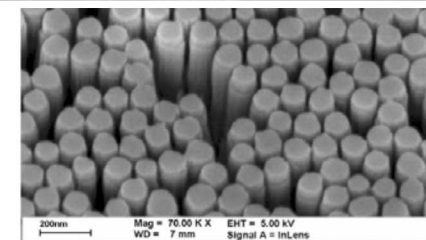
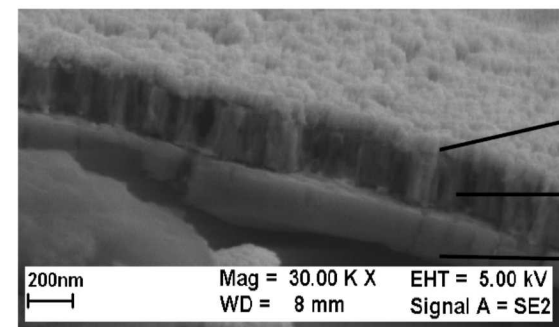
- E-beam Cr mask, Cl-based ICP-RIE etch
- Observed PL blue-shift w/decreasing diameter due to strain relaxation (reduction of QCSE)



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

Holographic lithography, SiO₂ mask, CHF₃ 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)

SiO₂ 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 ($< \text{\AA}/\text{min}$)

Significant etch rates, but extremely crystallographically anisotropic

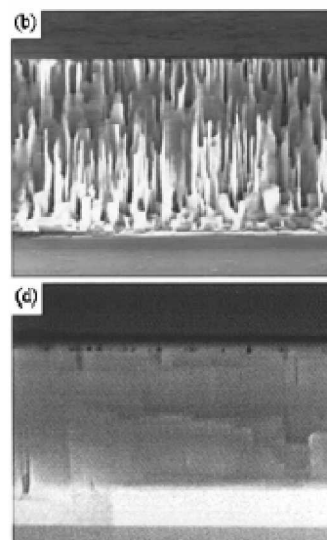
Table 1
GaN and AlN etching results in acid and base solutions

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
<i>n</i> -Methyl-2-pyrrolidone	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 ₂ O 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]).

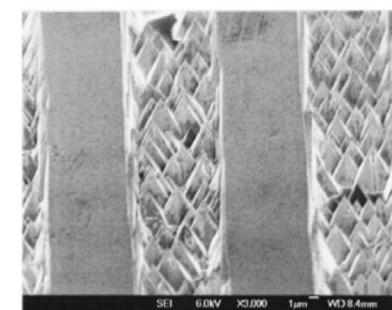
But actually...

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

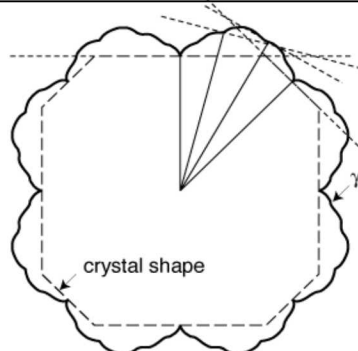
Zhuang and Edgar, *MSE R* **48** 1 (2005)

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 !

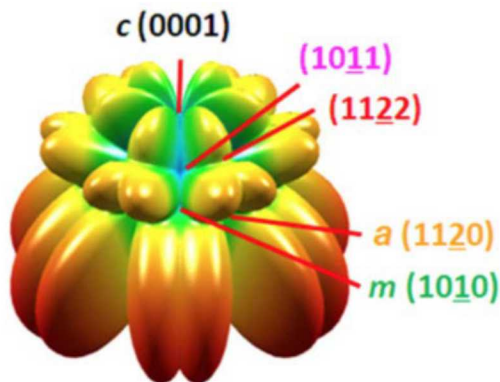
The appearance and evolution of facets

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



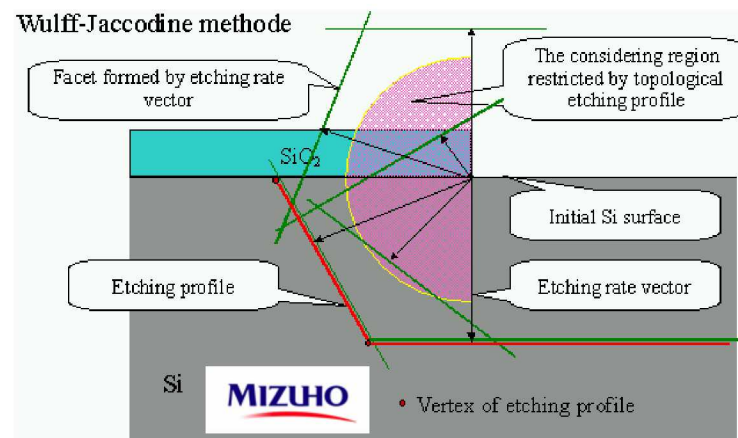
Wulff et al., Semicond. Z. Kristallogr 34, 449 (1901)

For MOVPE growth, use the *kinetic* Wulff plot



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

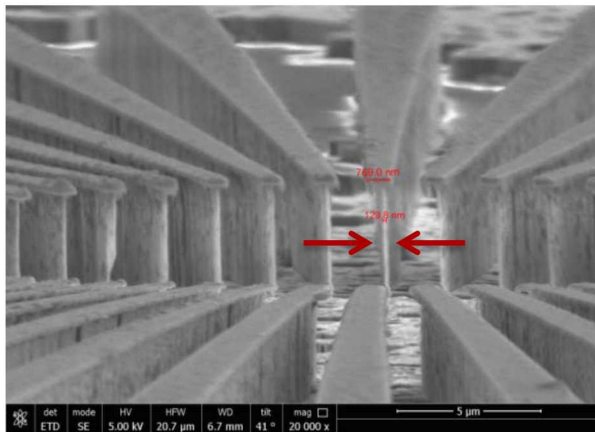
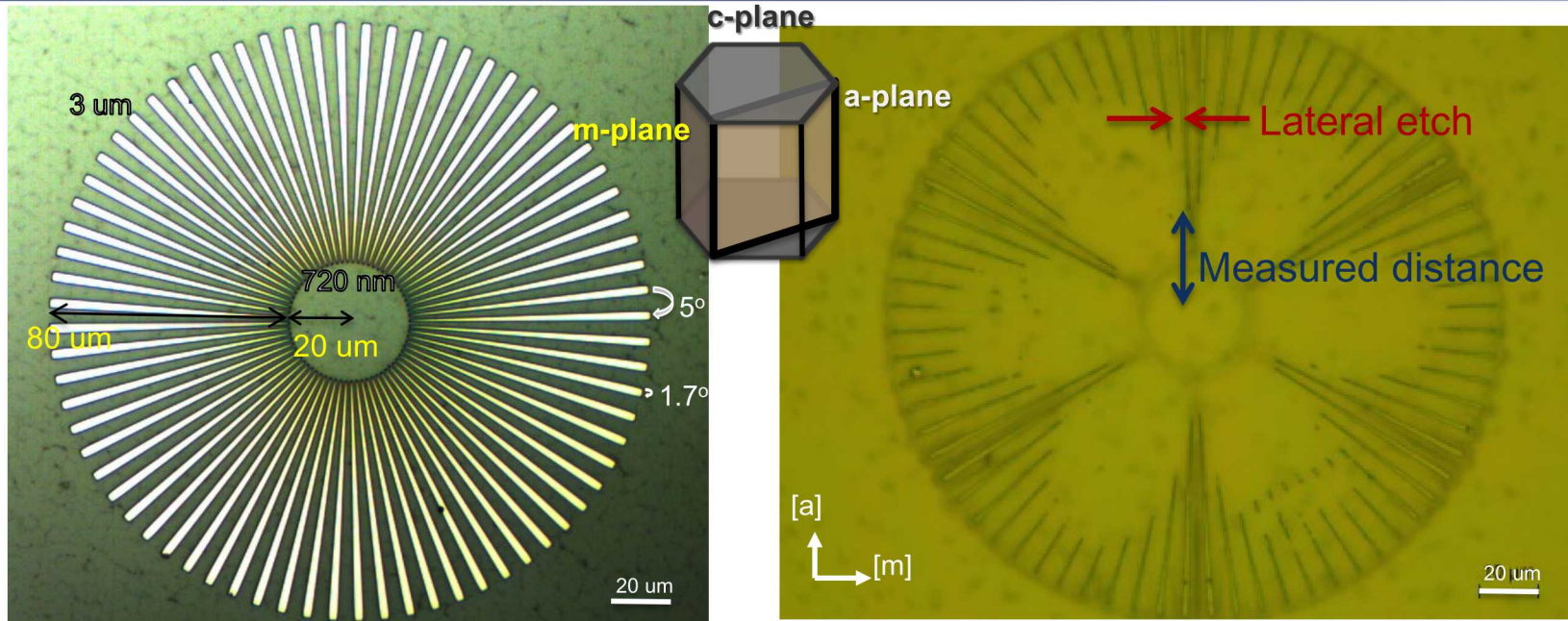
Same method used in commercial silicon wet etch simulators



Can we map the "Wulff plot" for etching?



Directly Measuring Orientation Resolved Etch Rates



1.7° $\downarrow$ 80 μm $\rightarrow$ 3 μm
 $\uparrow$
Lateral etch of 100 nm/min $\rightarrow$
Wedge retraction of 6.7 $\mu\text{m}/\text{min}$

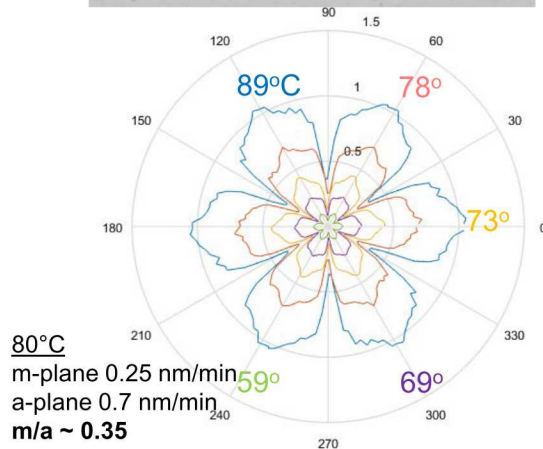
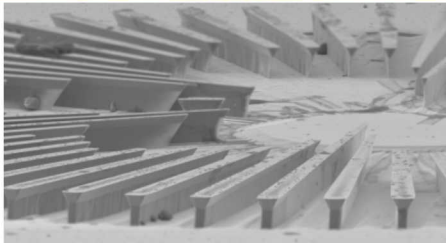
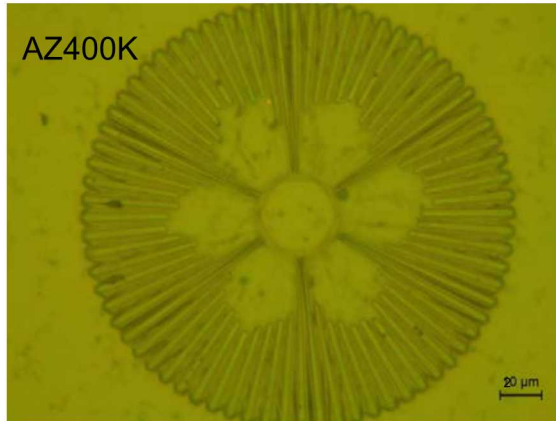
5% KOH in ethylene glycol

Etch rate is amplified
by a factor of 67

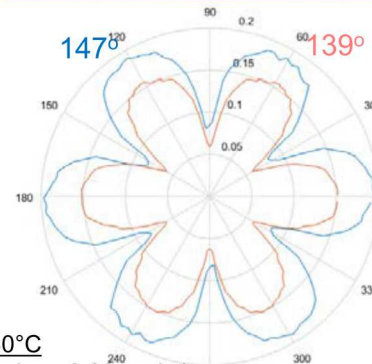
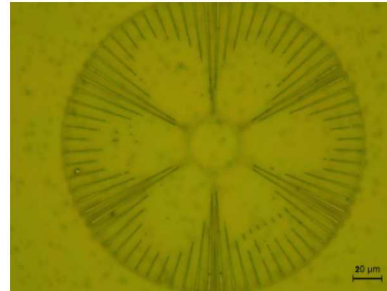
Direct measurement of orientation resolved etch
rates for the first time in GaN



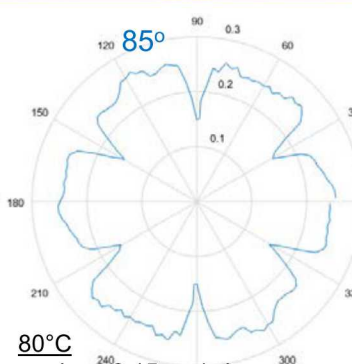
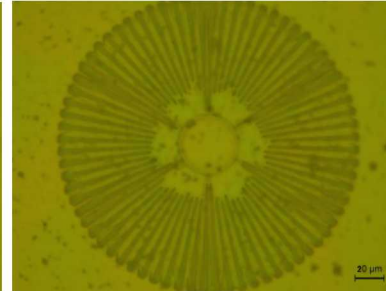
Direct Measurements of Orientation Resolved Etch Rates – Chemistries and Temperatures



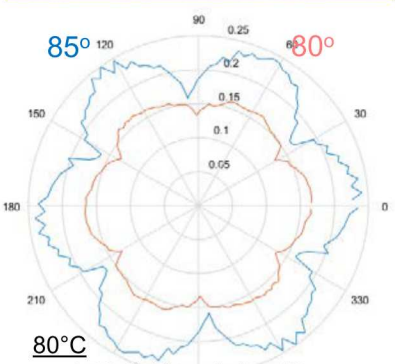
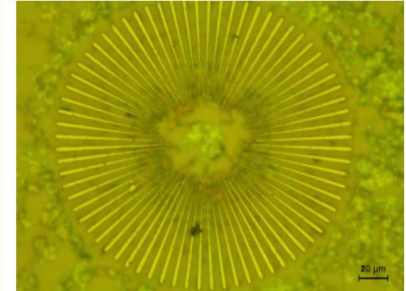
5% KOH in ethylene glycol



5% KOH in H₂O

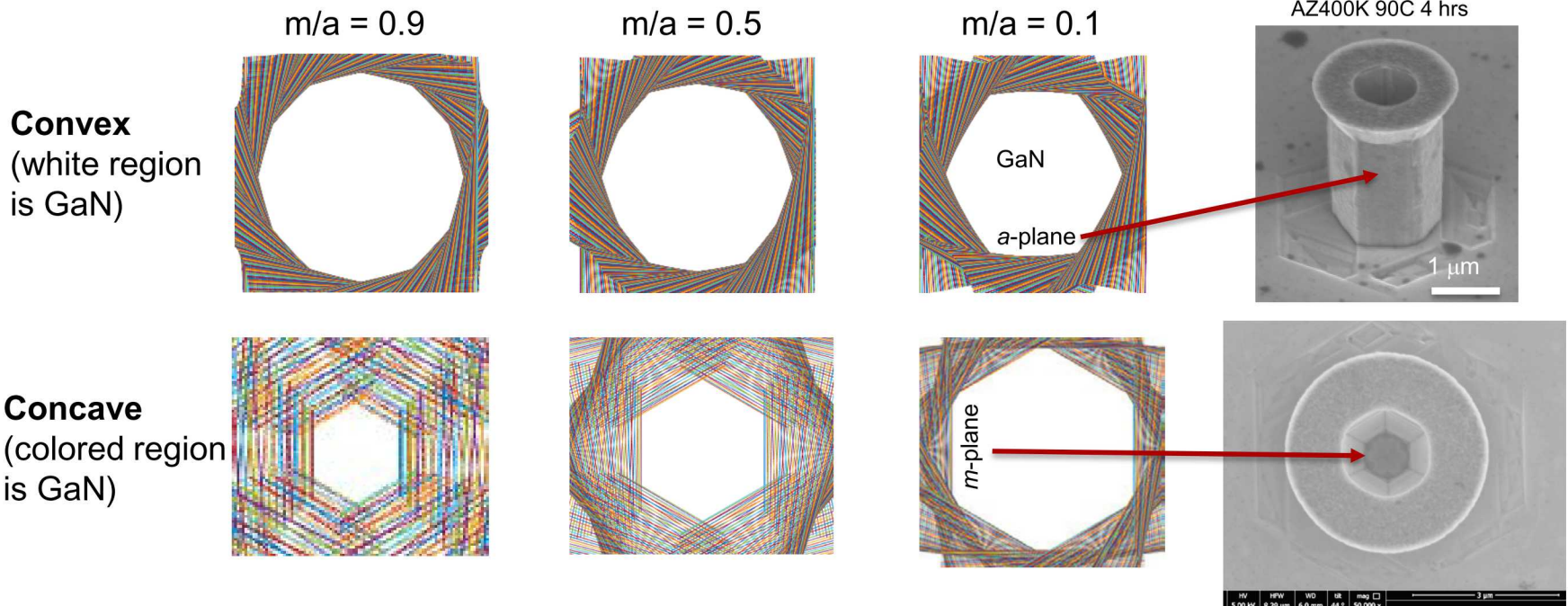
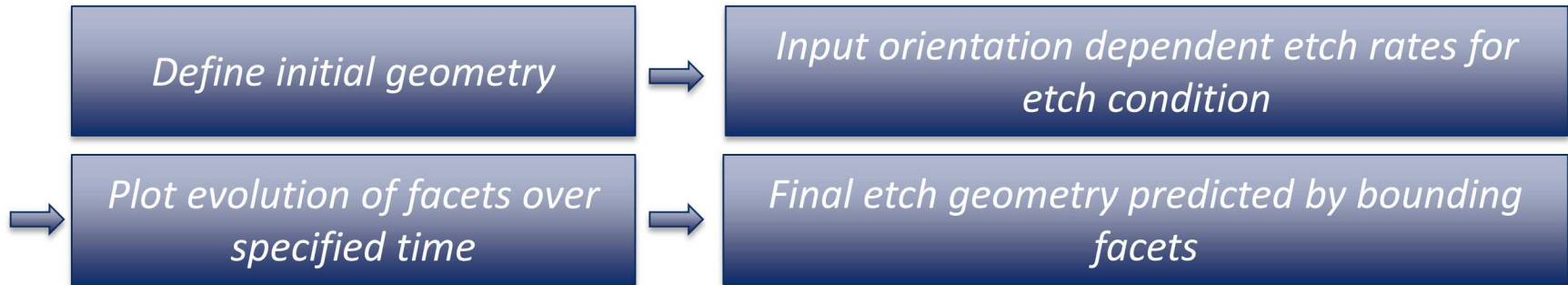


25% TMAH



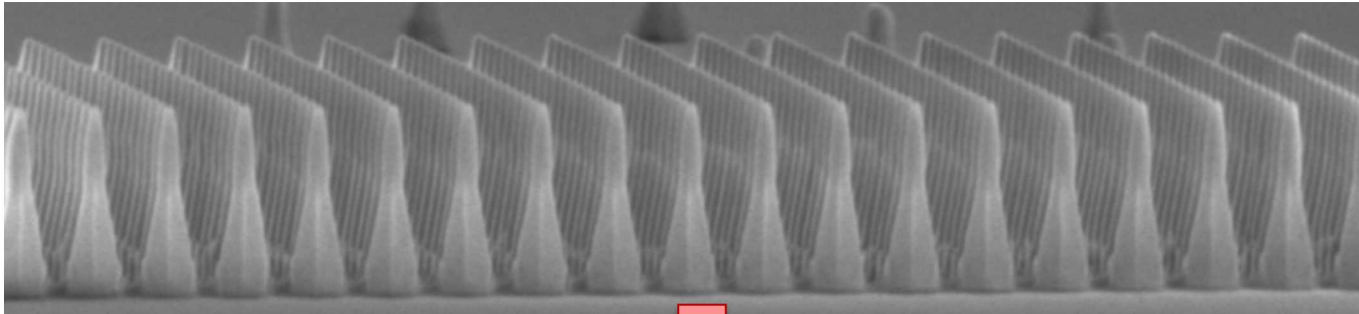
m-plane: Atomically smooth etch facet
a-plane: Transition from step-flow highly dependent on chemistry
m/a: 0.3 ~ 0.9

Prediction of Etched Geometry: Implementing the Wulff-Jaccodine Method

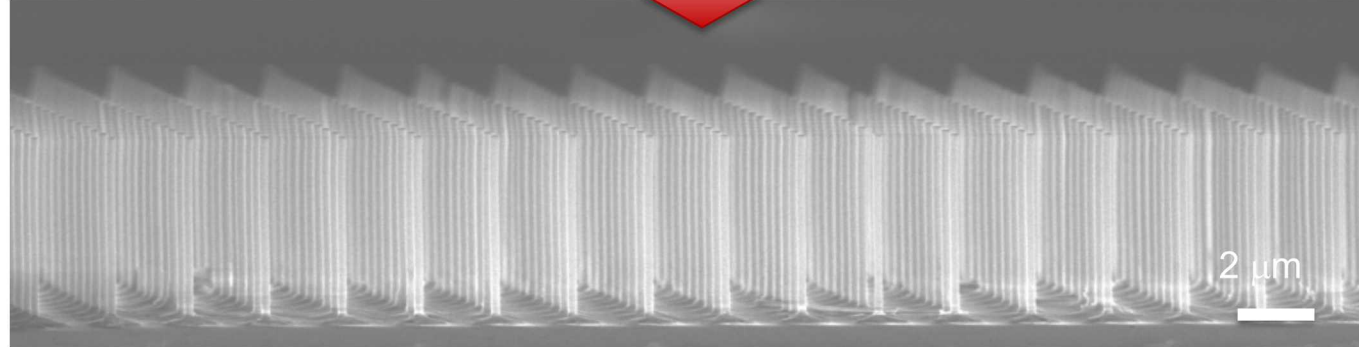


Fabricated top-down GaN nanostructures using two-step dry + wet etch approach

Dry etch (Cl_2 based ICP)



KOH-based wet etch (AZ400K)



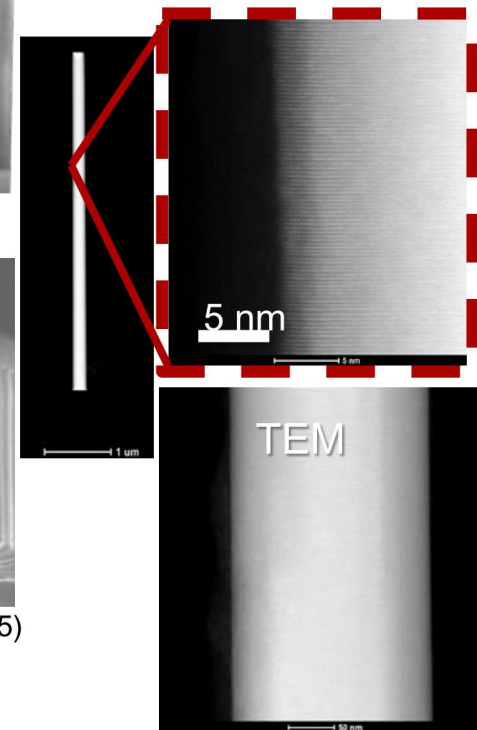
Diameter: 180 nm, Height: 4.5 μm, Pitch: 2 μm (AR: 25)

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

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

etc....

TEM shows smooth vertical sidewalls

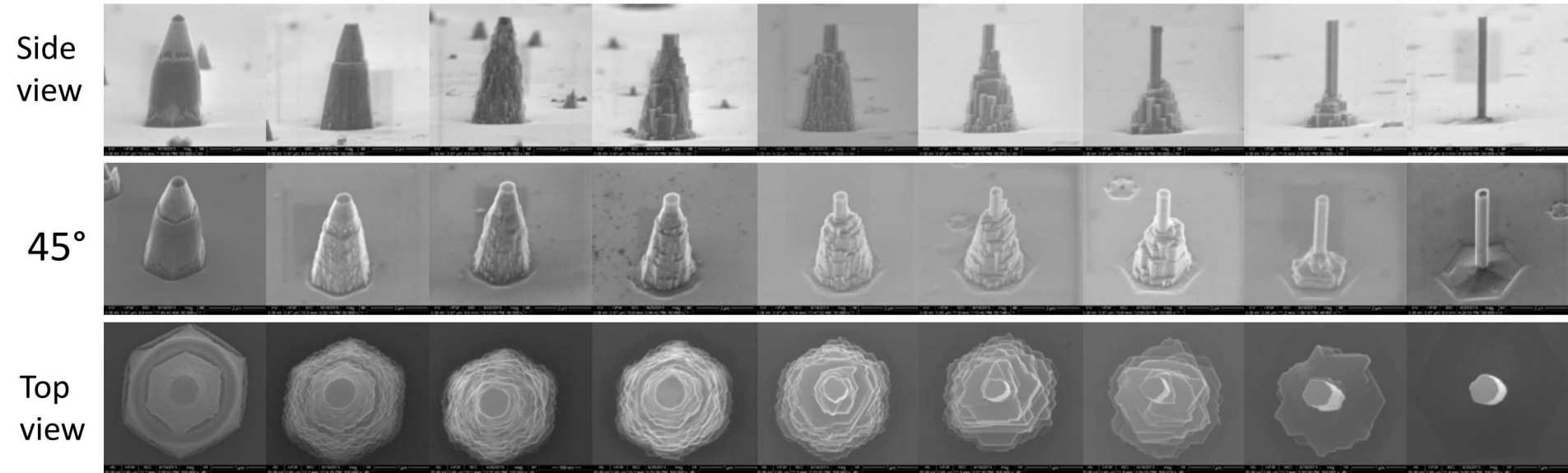


What is the wet-etch mechanism from *rough tapered* to *smooth vertical sidewalls*?



Wet etch evolution for nanowires

As ICP etched 1 min 2 min 5 min 10 min 15 min 20 min 30 min 52 min



AZ400K, 65°C

Wet etch proceeds “vertically” rather than horizontally

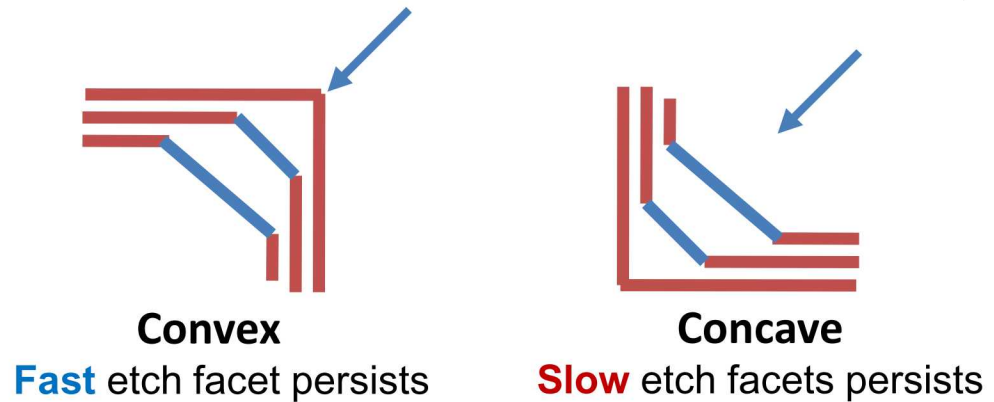
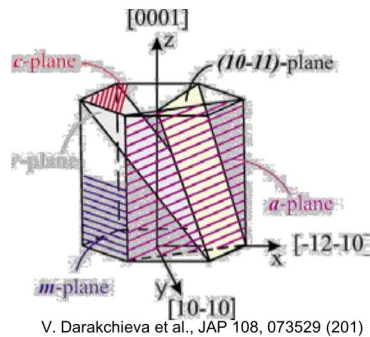
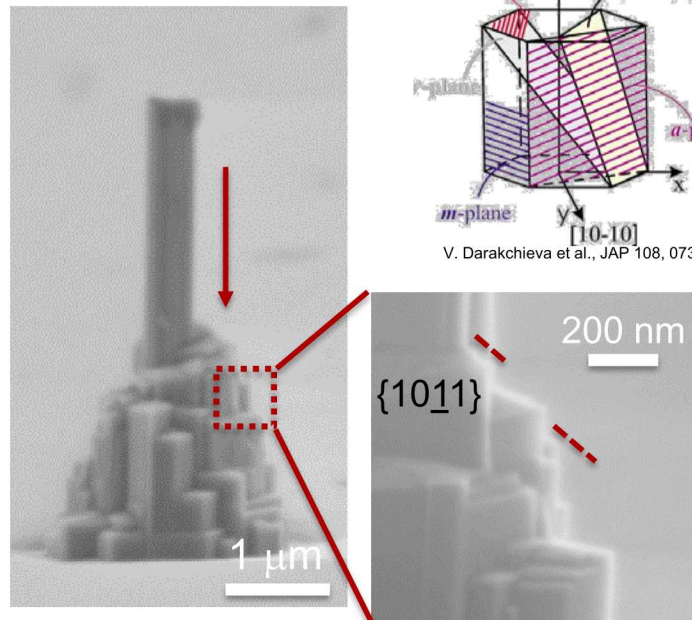


Mechanism/Basis for evolution of facets during GaN wet etching

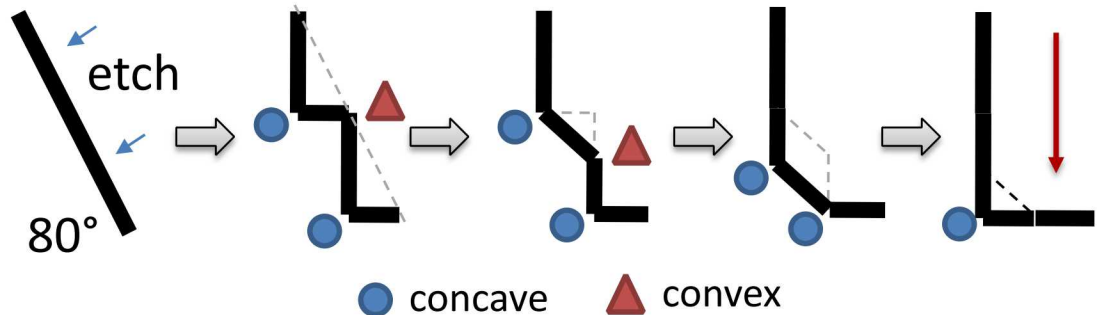
What is the mechanism from *tapered to smooth vertical sidewalls* through faceting?

Slow etching: c-plane, m-plane

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



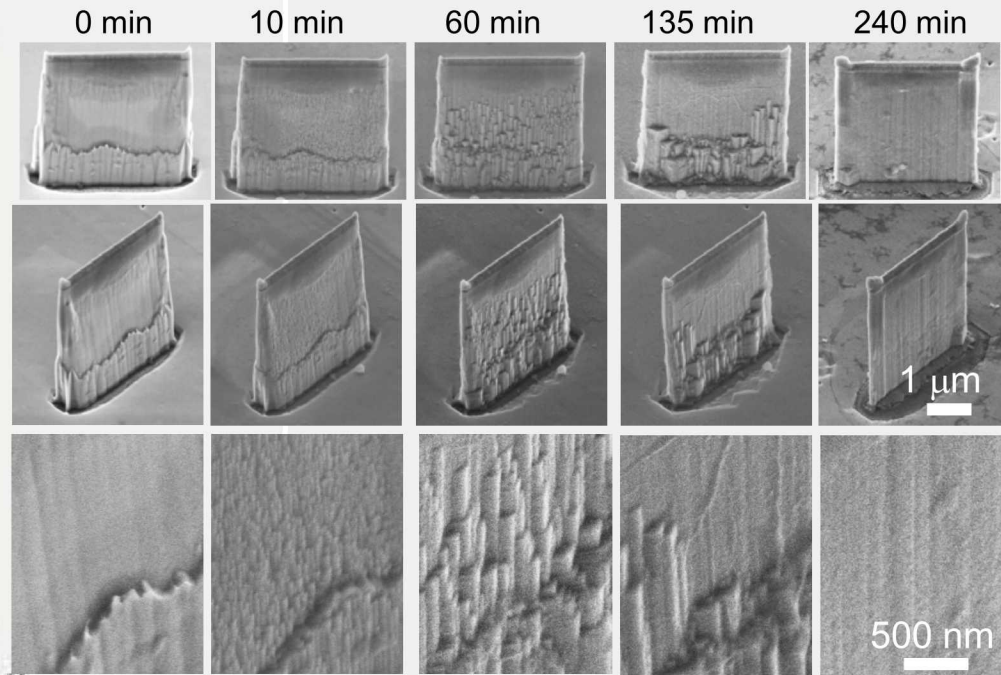
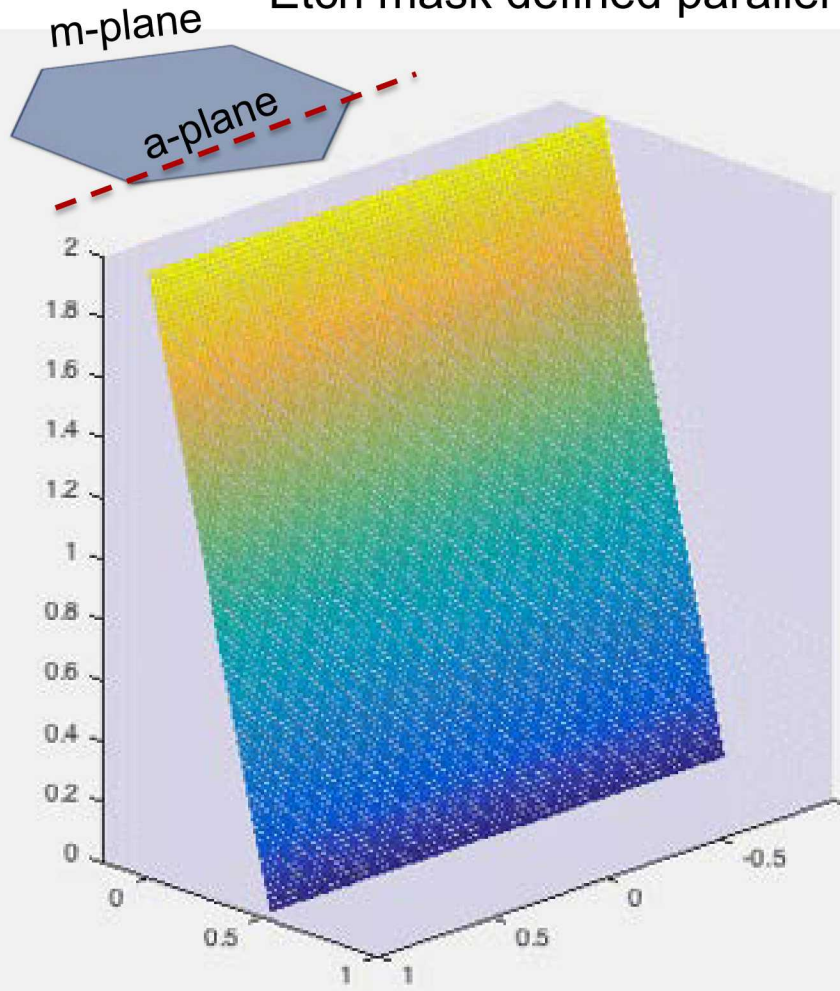
The facet etch sequence:



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

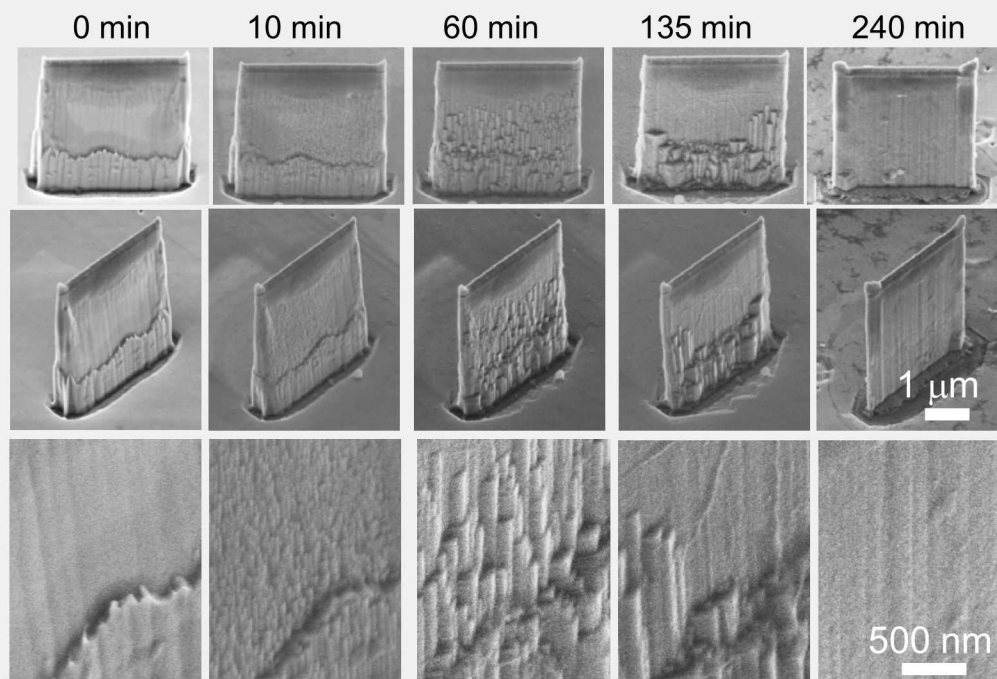
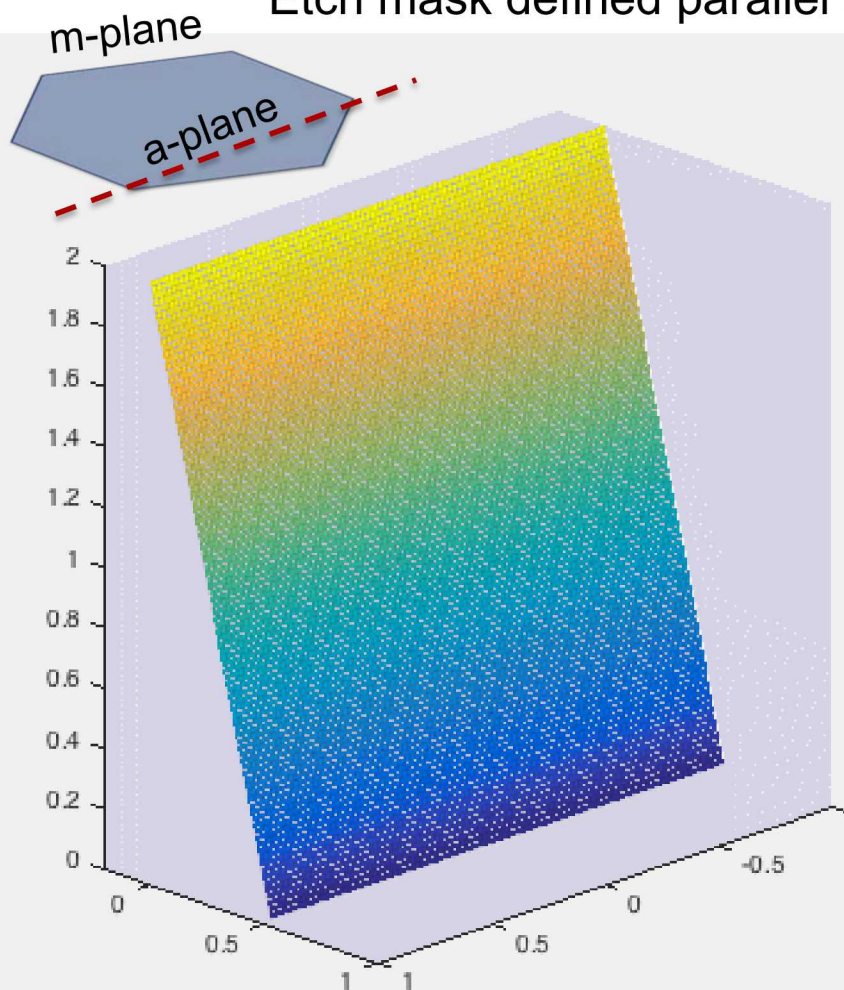


AZ400K, 65°C



Etch evolution of a -plane wall

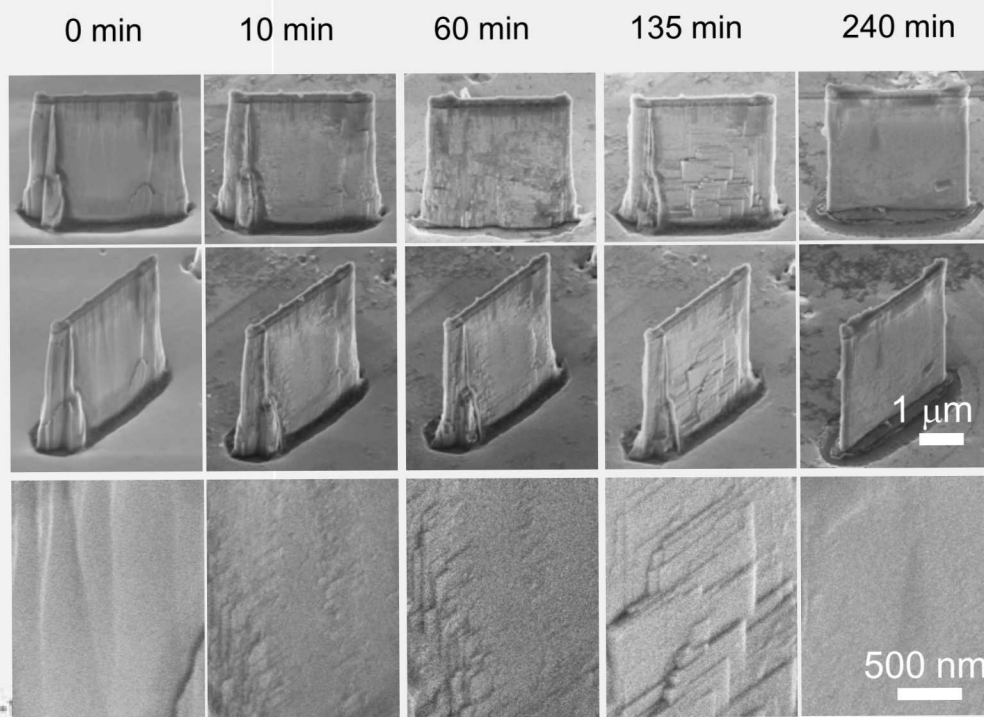
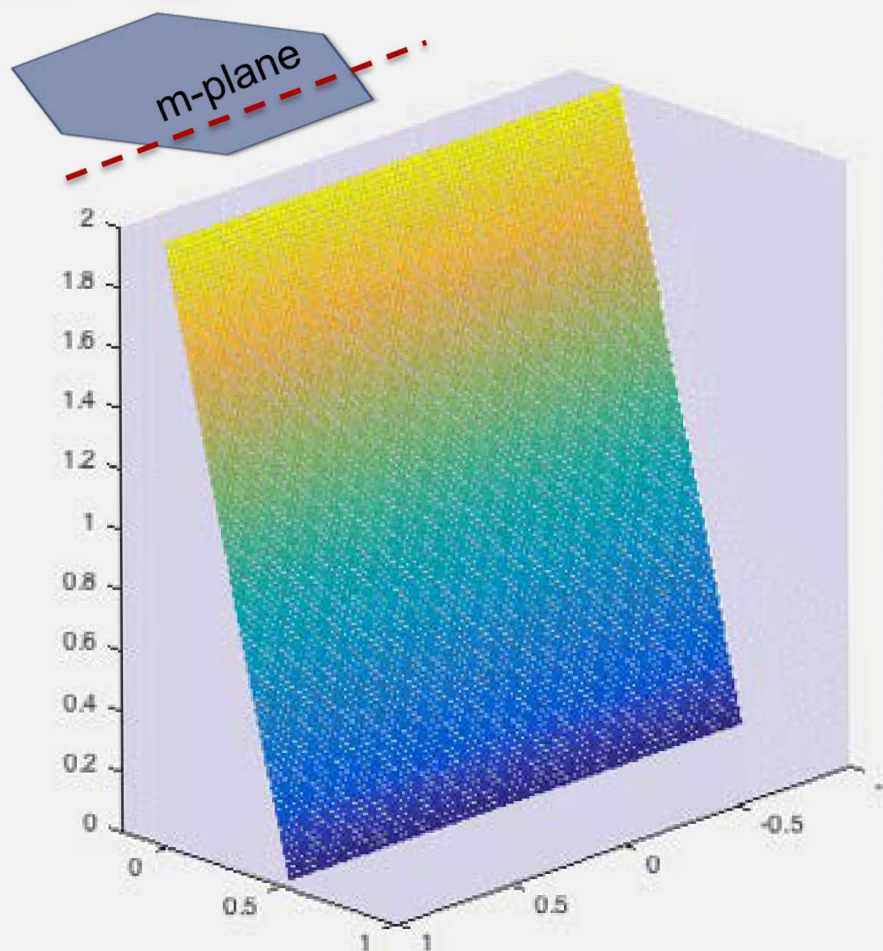
Etch mask defined parallel to a -plane



AZ400K, 65°C

Etch evolution of m -plane wall

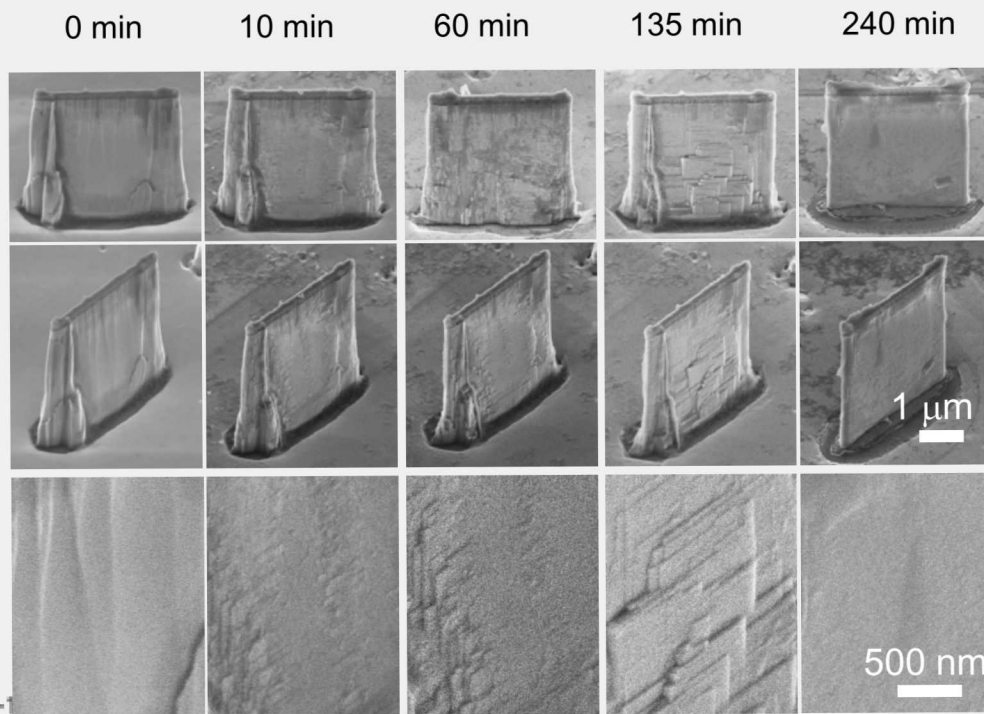
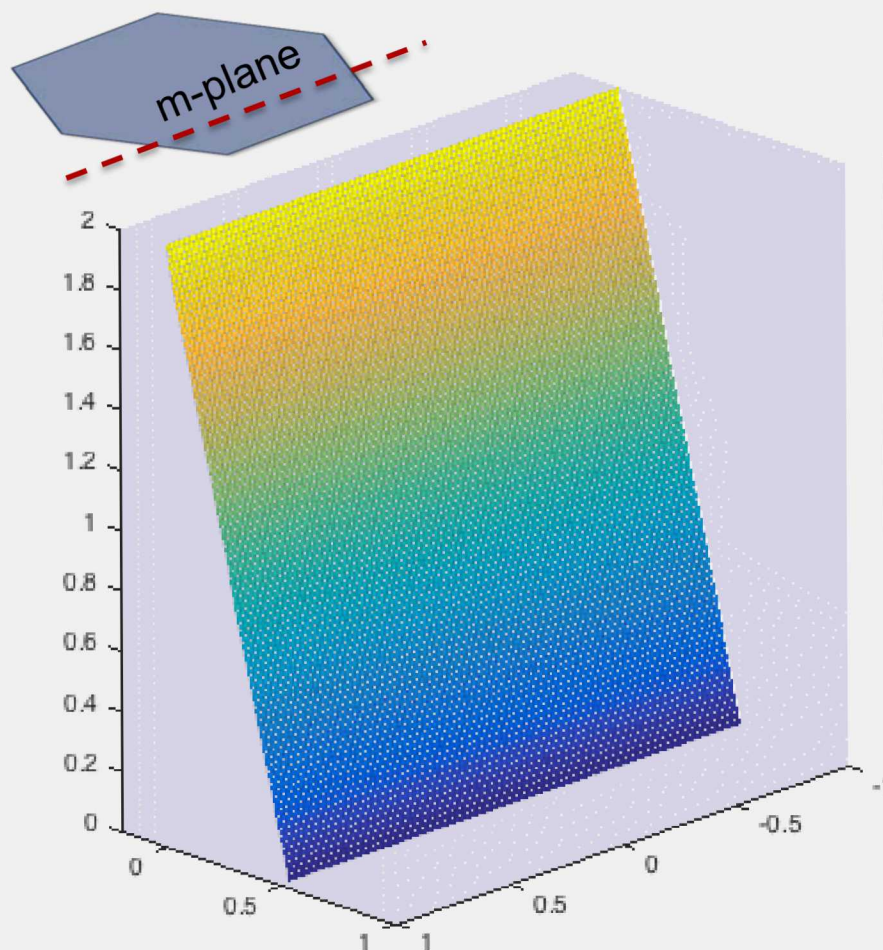
Etch mask defined parallel to m -plane



AZ400K, 65°C

Etch evolution of m -plane wall

Etch mask defined parallel to m -plane

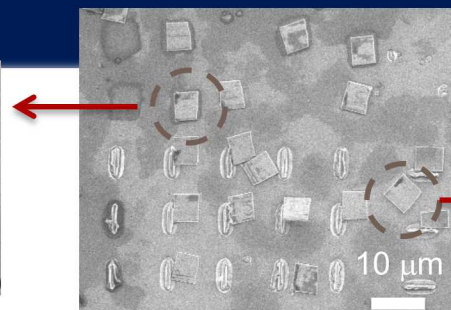
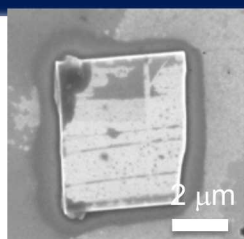


AZ400K, 65°C

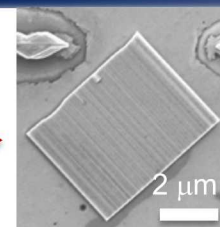


Measured etched nanowall morphology by AFM

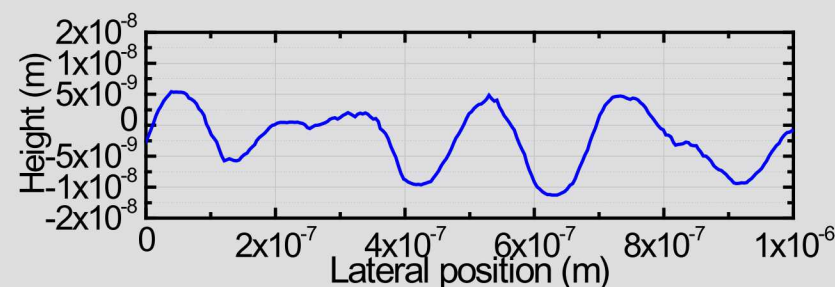
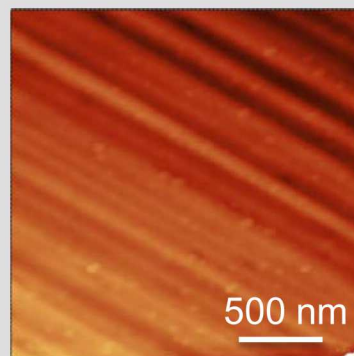
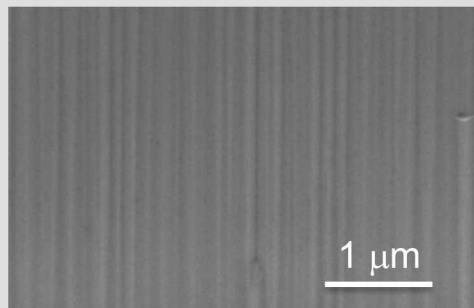
m-plane wall



a-plane wall

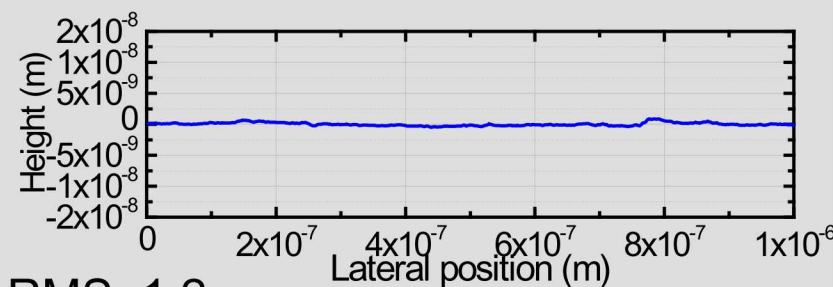
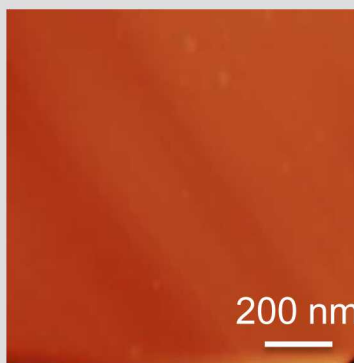
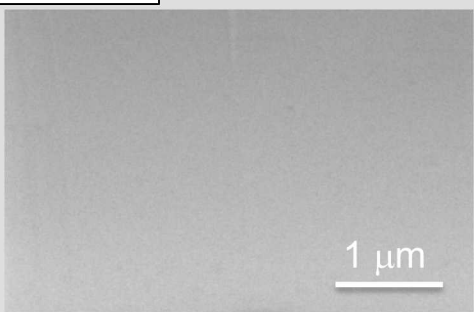


a-plane



RMS: 7.6 nm

m-plane

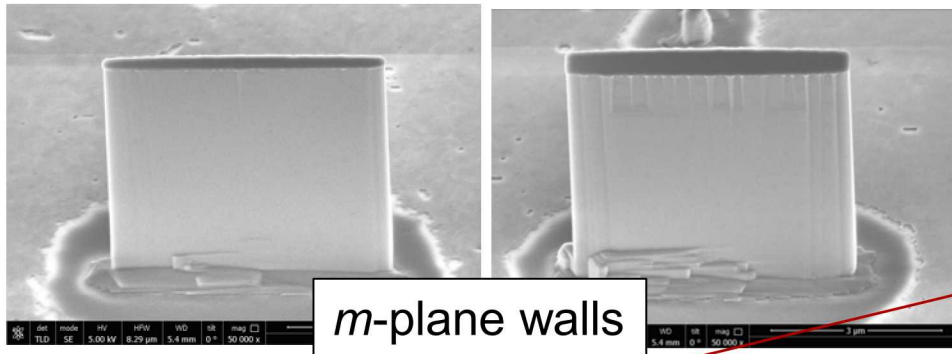


RMS: 1.2 nm

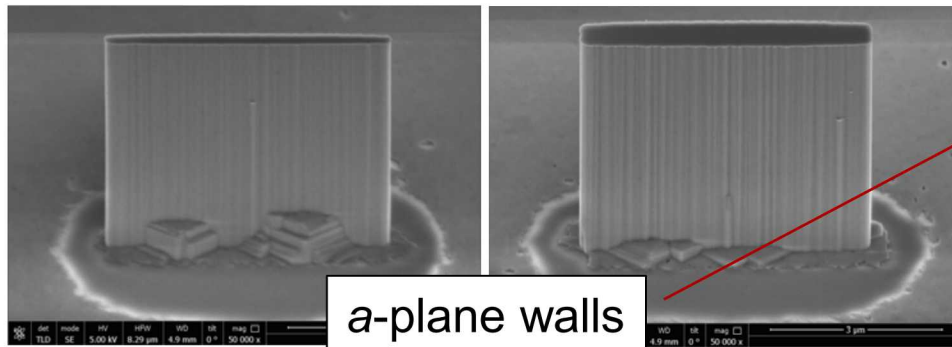
Achieved atomically smooth surfaces through a two-step top-down process!

Cavity modes in nanowalls

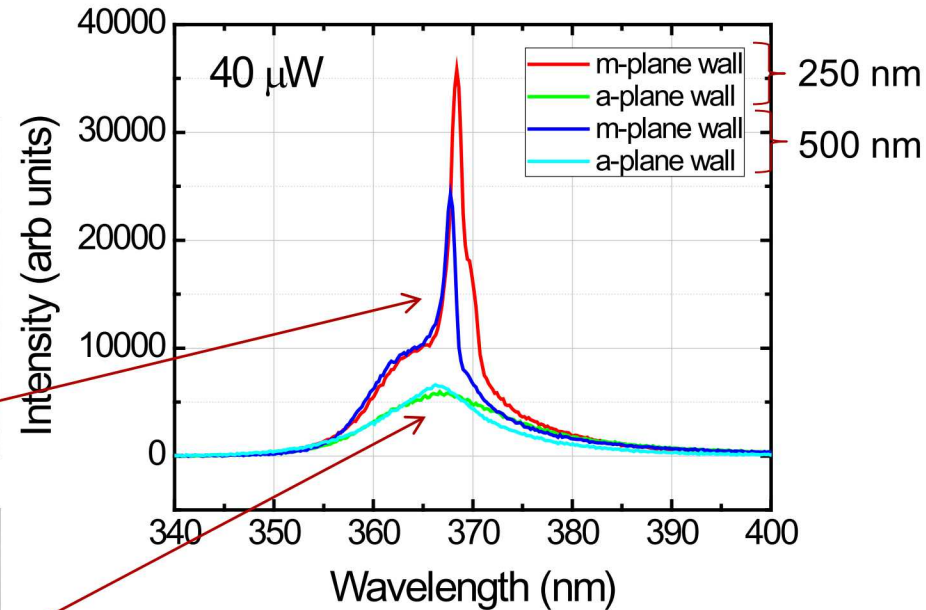
Optical pumping of GaN nanowalls
Nd:YAG, 266 nm pulsed laser, μ PL



m-plane walls



a-plane walls

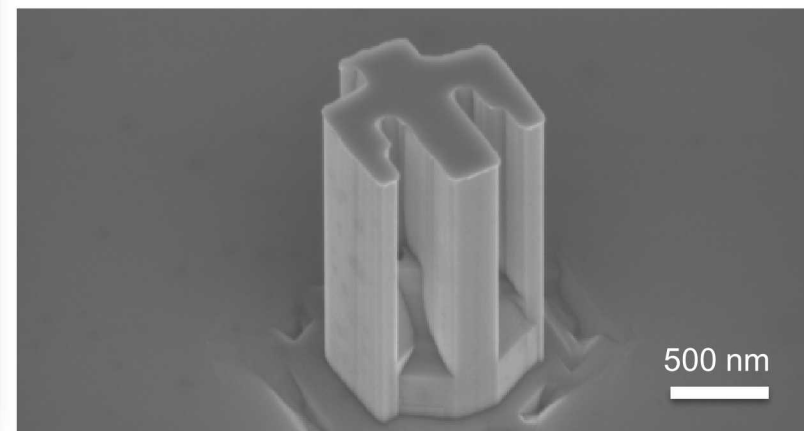
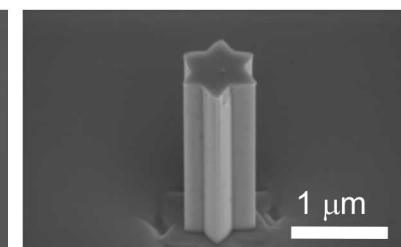
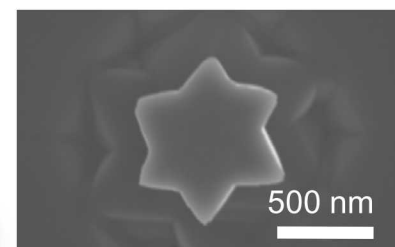
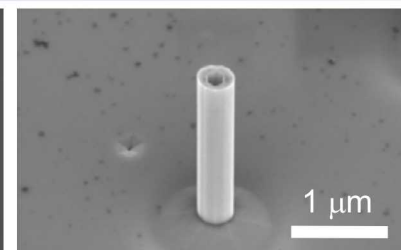
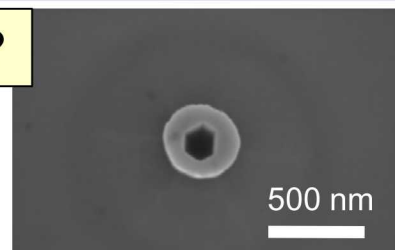
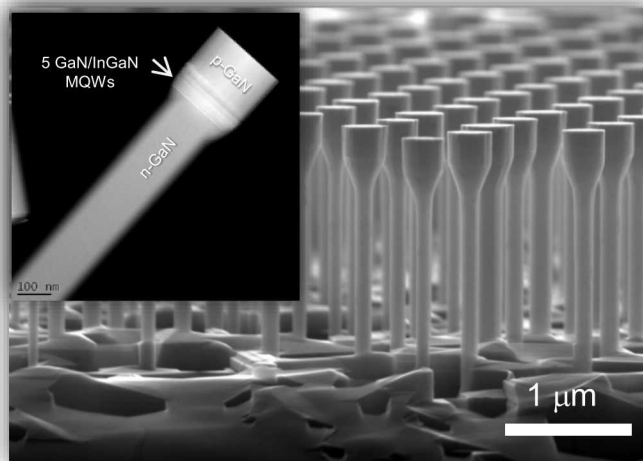
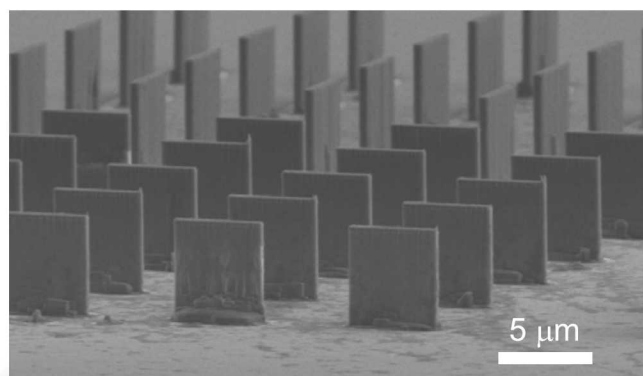
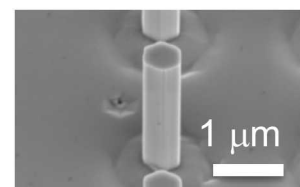
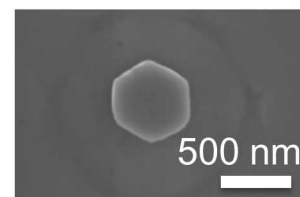
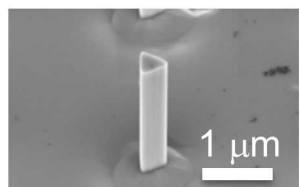


Optically pumped nanowalls shows luminescence coupled to cavity modes only with the smooth m-plane sidewalls

Etched surface morphology has important effects on optical properties of nanostructures

Controlled and complex cross-sections

Can we expand to more *complex geometries* ?

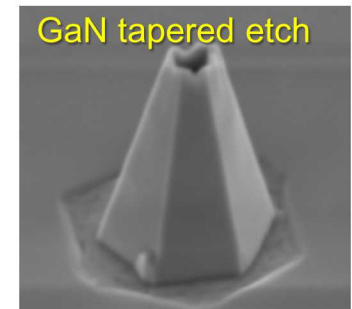
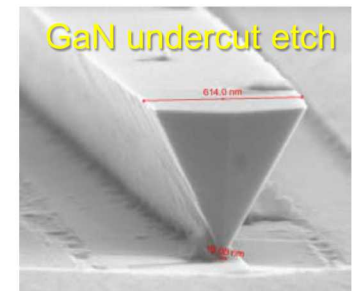
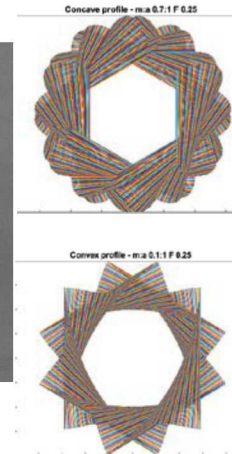
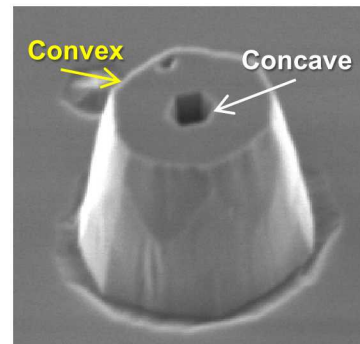
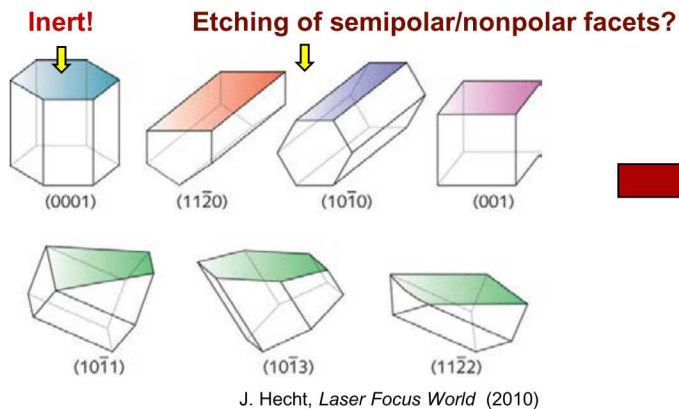


Understanding of the etch evolution enables design of a wide range of smooth faceted vertical nanostructures

The Future: 3D Etching of III-N Nanostructures

Explore and push the limits of 3D crystallographic and selective etching of lithographically defined test structures

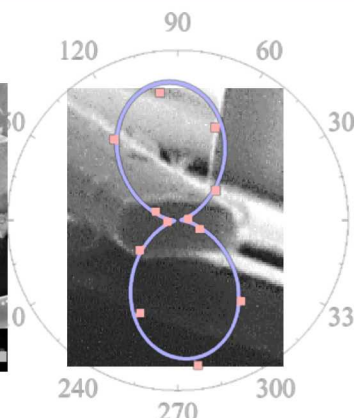
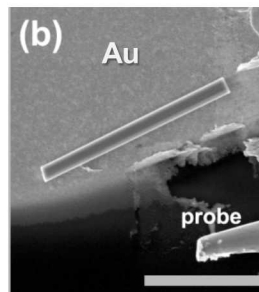
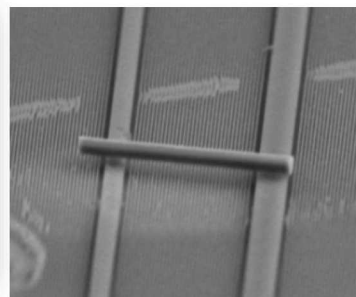
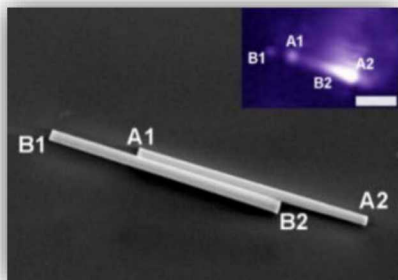
- Tapered, undercut, and lateral etches
- AlGaN and AlN



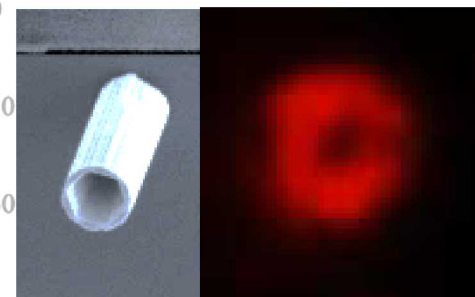
Goal: New capability for the rational design of complex, 3D tailored semiconductor nano- and microstructures with novel/enhanced photonic, [opto]mechanical, electronic, and electromagnetic properties

Top down vertical nanostructures for photonics

Mode & polarization control in GaN nanowire lasers



Beam shape control nanotube 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)

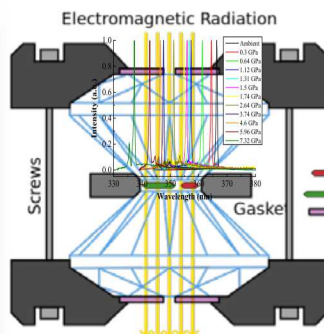
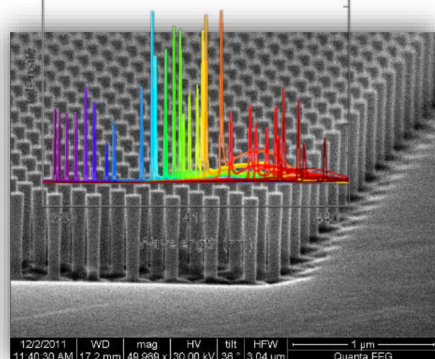
H. Xu et al., *Opt. Exp.* **22**, 19198 (2014)

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

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

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

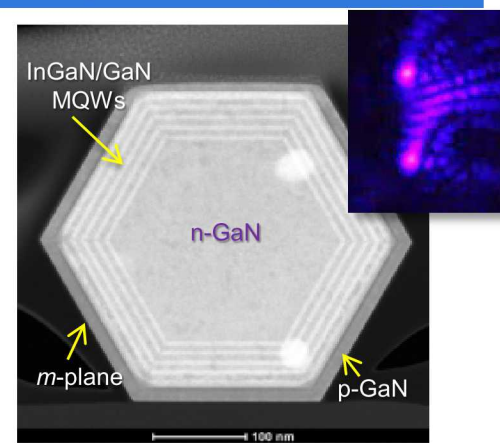
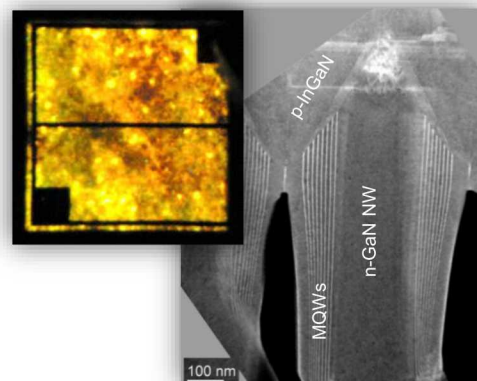
Tunable wavelength nanowire lasers



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)

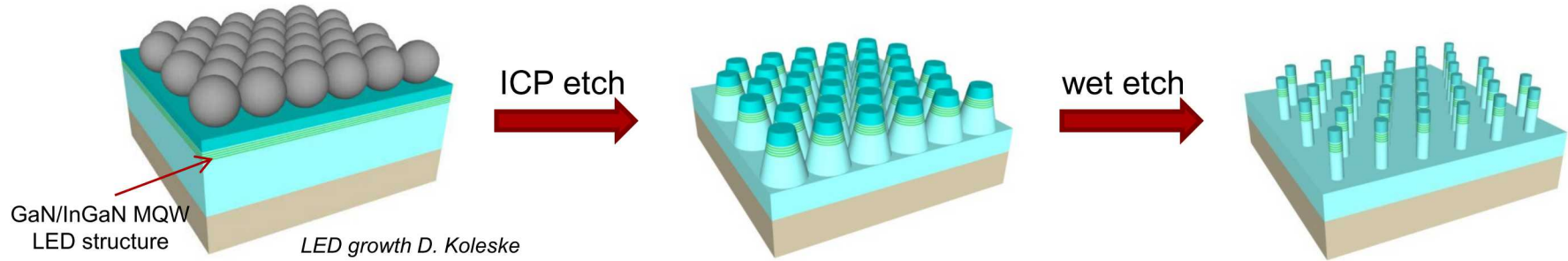
Riley, J.; *Nano Lett.* **14**, 4317 (2013).

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

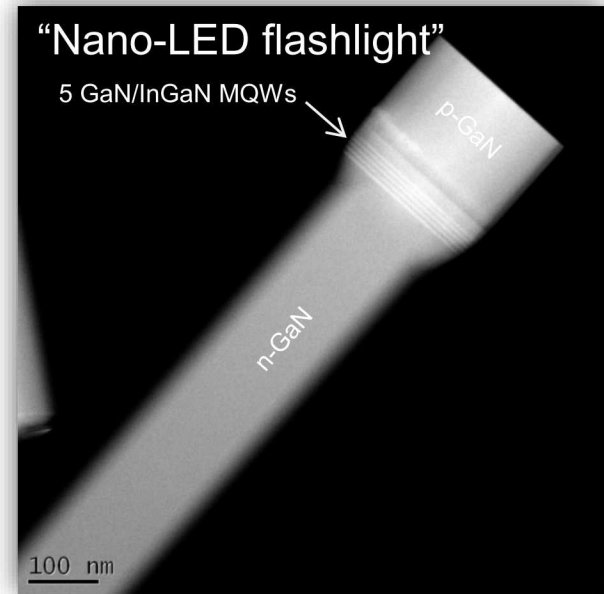
C. Li et al., *Nano Lett.*, **17**, 1049 (2017)

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

Etching of Axial Heterostructures - GaN/InGaN nanowire LEDs



×250,000

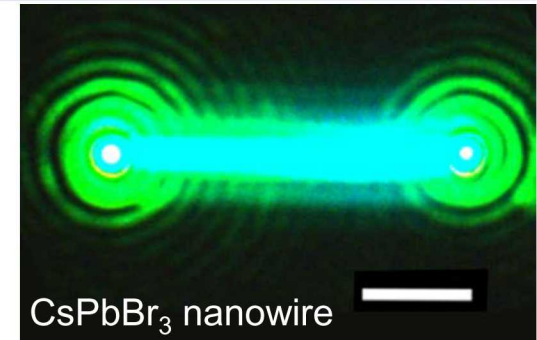


Q. Li et al.,
Optics Express 19,
25528 (2011)

Wet etch affected by doping (composition)

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

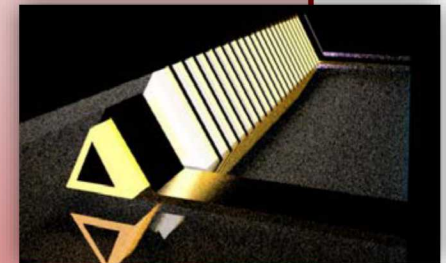


CsPbBr₃ nanowire

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**

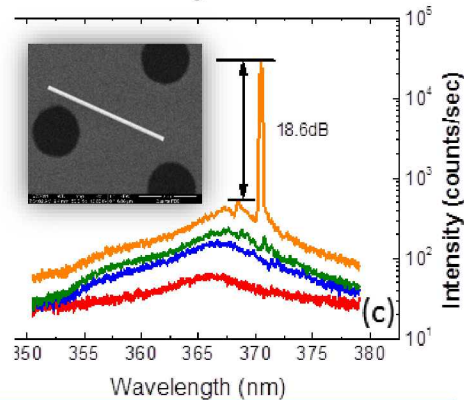


- 1) S. Arafin, X. Liu, Z. Mi, "Review of recent progress of III-nitride nanowire lasers," *J. Nanophotonics* **7**, 074599-1 (2013)
- 2) C. Couteau et al., "Nanowire Lasers," *Nanophotonics* **4**, 90 (2015)

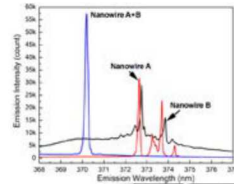
SNL Top-Down Nanowire Lasers – Mode, Polarization, and Wavelength Control

Single Mode Control

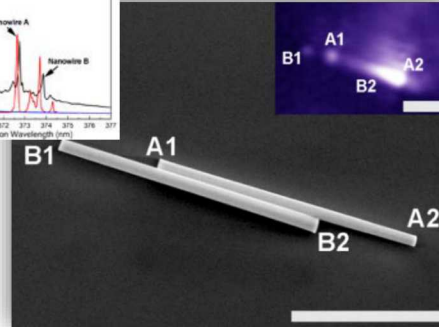
Geometry control



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



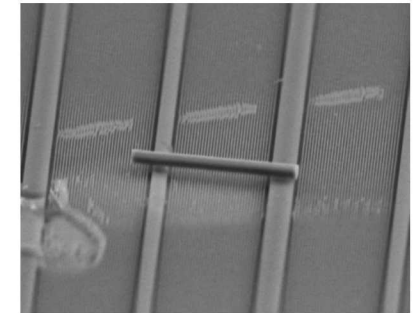
Coupled NW lasers



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

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

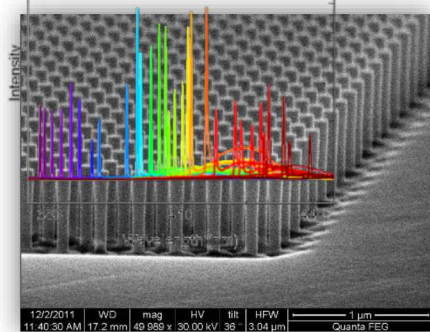
Distributed feedback NW lasers



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

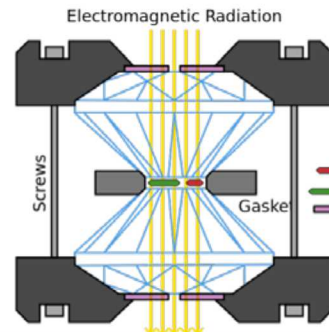
Wavelength Tuning Control

Nanowire photonic crystal



J.B. Wright et al., *Scientific Reports* **3**, Article number: 2982 (2013) doi:10.1038/srep02982

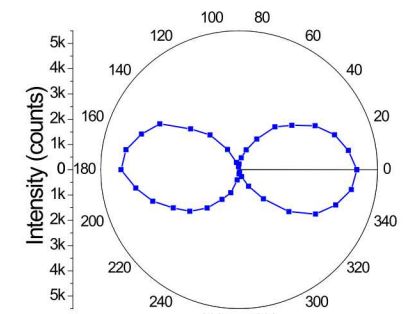
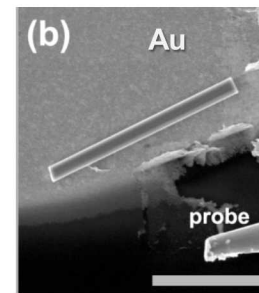
Reversible pressure tuning



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

Polarization Control

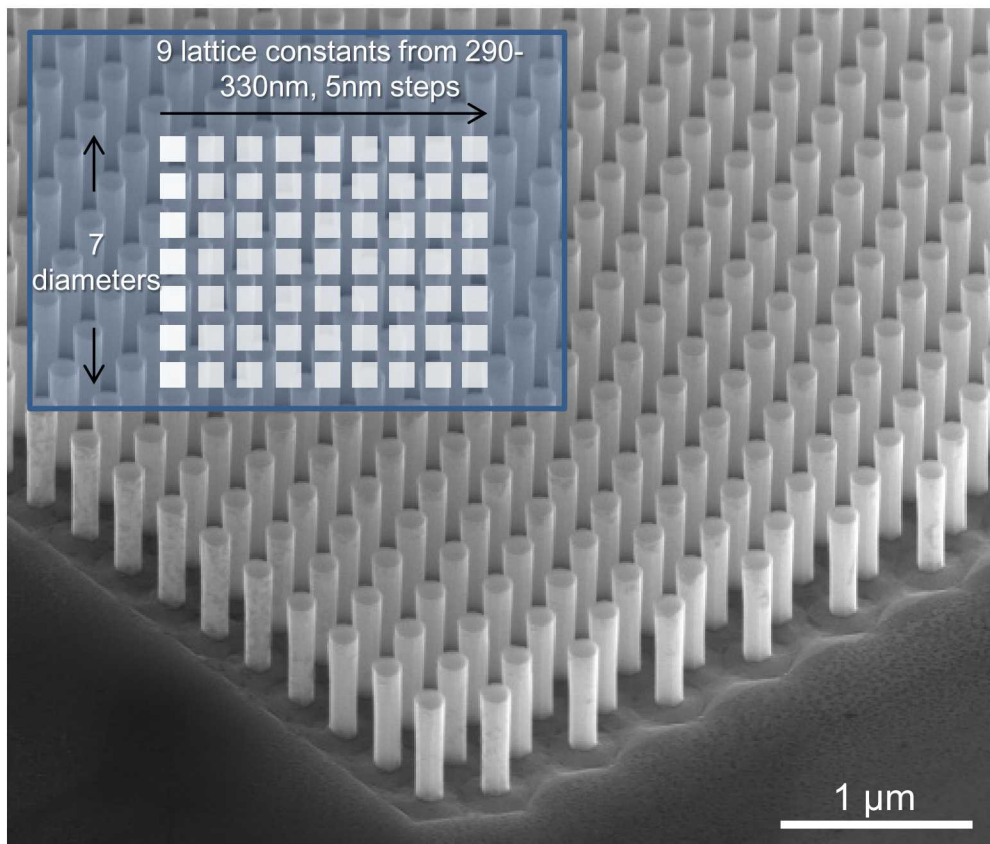
Coupling to metal substrate



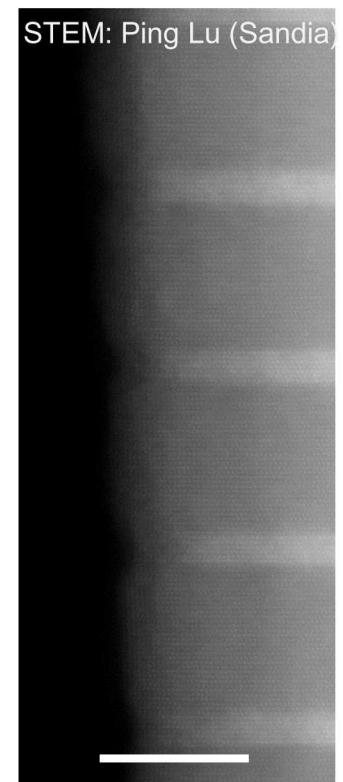
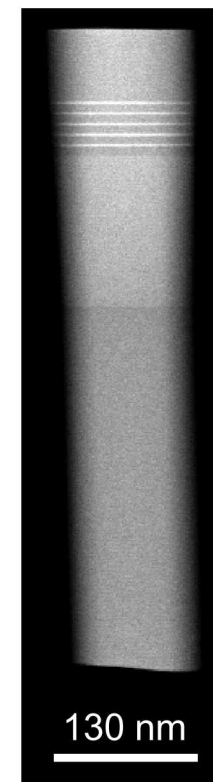
H. Xu et al., *Appl. Phys. Lett.* **101** 221114 (2012); H. Xu et al, *Opt. Exp.* (2014)

Wavelength tuning in III-N Nanowire Photonic Crystal Lasers

Motivation: Achieve single-mode, tunable lasing on same chip. Applications in optical information processing, biology, solid state lighting, displays, etc.



Nanowire PCs fabricated by top-down method using e-beam lithographic mask

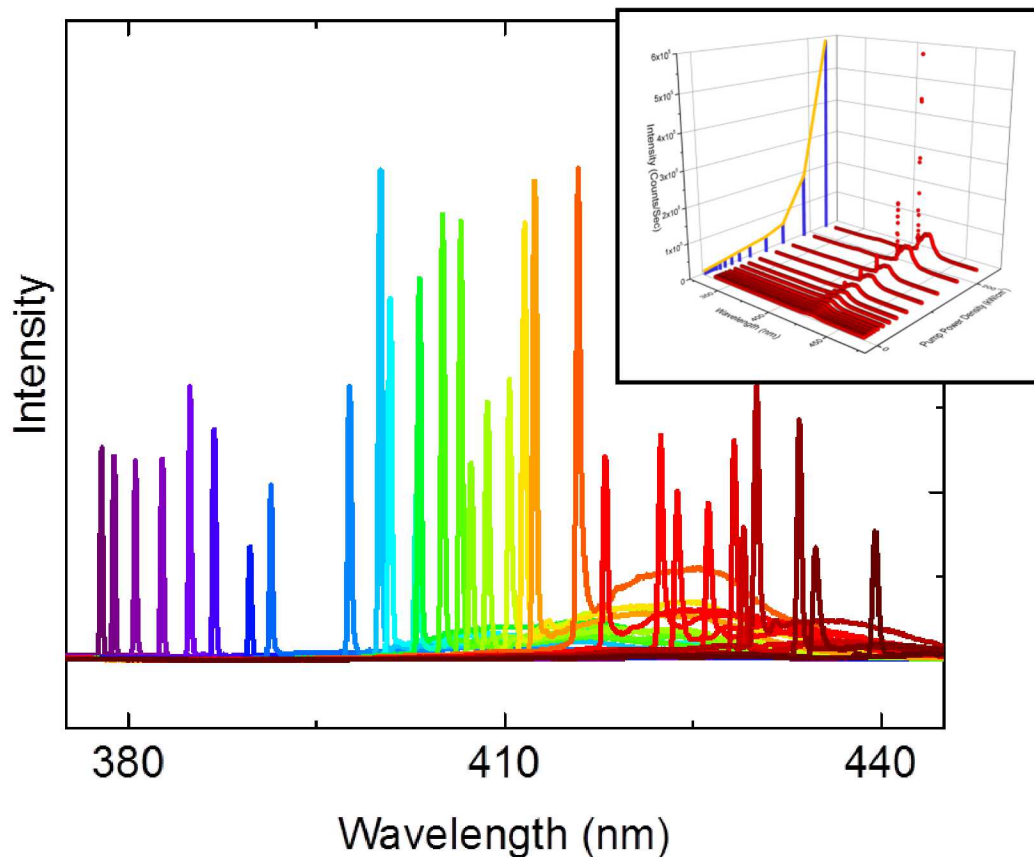


NW STEM images: 5x MQW InGaN emission centered at 420nm, $\text{In}_{0.02}\text{GaN}$ underlayer

Wavelength tuning in III-N Nanowire Photonic Crystal Lasers

Broad gain width of InGaN MQWs with PC design allows for tunable single mode lasing over large range on same chip

61 color nanowire laser array

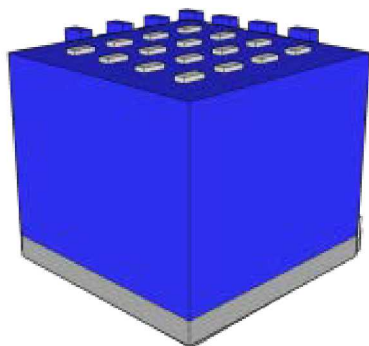


- High-yield >95% (2 of the PCLs were accidentally removed during sample handling.)
- Spectral Coverage from 380-440nm.
- Emission wavelength increases with the diameter and the lattice constant
- Thresholds are reasonable compared to other optically pumped III-N nanowire devices. (<500kW/cm² for all devices)

J.B. Wright et al., "Multi-Colour Nanowire Photonic Crystal Laser Pixels," *Scientific Reports* 3, Article number: 2982 (2013)



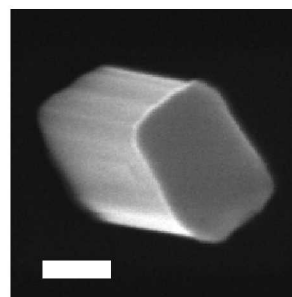
Intrinsic polarization control from rectangular nanowire lasers



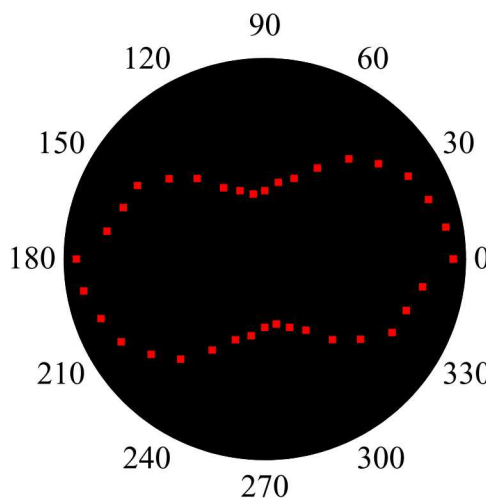
- Top-down approach enables *cross-sectional shape control* of NWs
- Previous work: change from elliptical to linearly polarized emission when nanowire placed on gold substrate H. Xu et al., *Optics Express*, 22, 19193 (2014).
- Rectangular GaN nanowire lasers show *intrinsic linearly polarized emission*, obviating the need for manipulation by external environments

Li, Changyi, et al. "Intrinsic polarization control in rectangular GaN nanowire lasers." *Nanoscale* 8, 5682 (2016).

Less rectangular

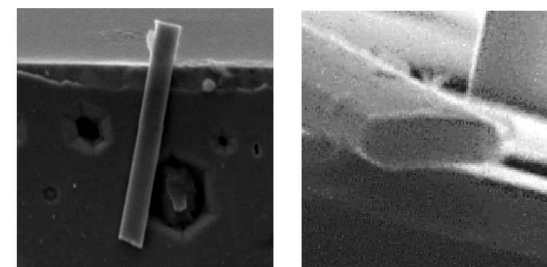


↓ **Y = 300nm**
X = 450nm

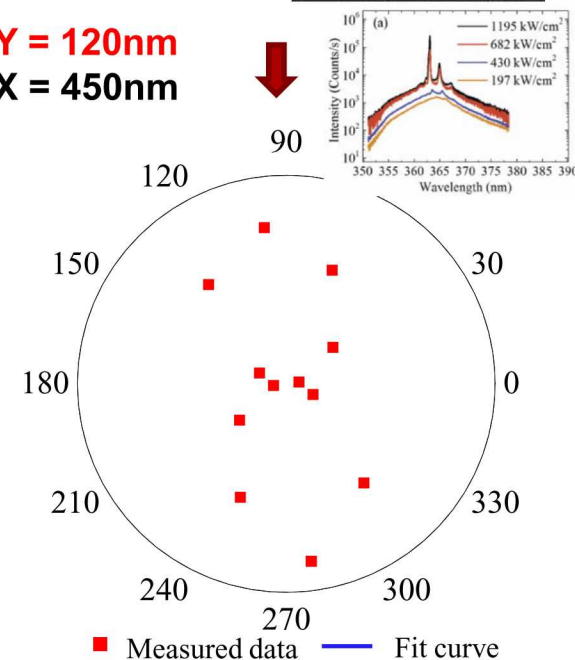


Elliptical polarization

More rectangular



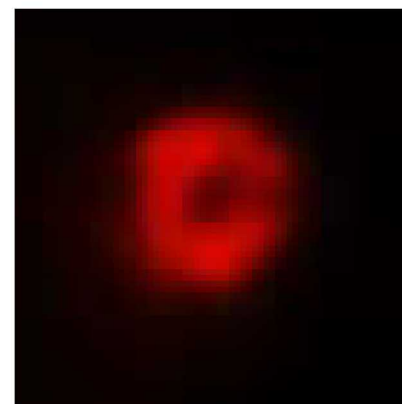
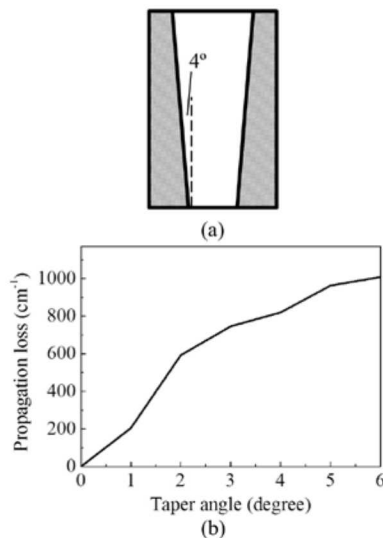
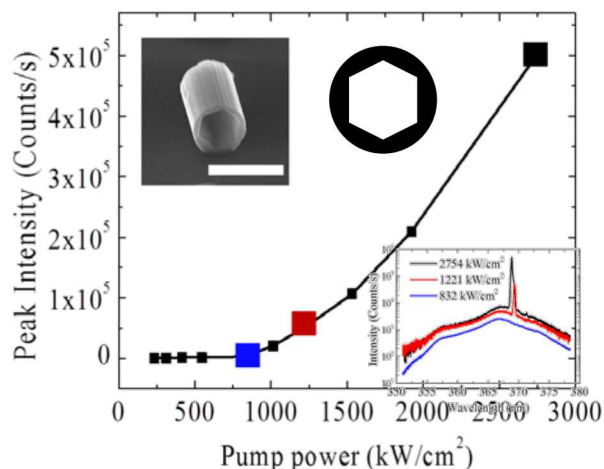
Y = 120nm
X = 450nm



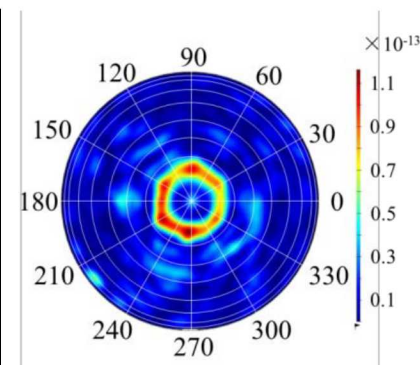
Linear polarization

Annular emission from GaN nanotube lasers

- Length: $4\mu\text{m}$
- Outer Diameter: $1.3\mu\text{m}$
- Thickness: 150nm



CCD image far field lasing emission from nanotube



Simulated far field pattern of nanotube

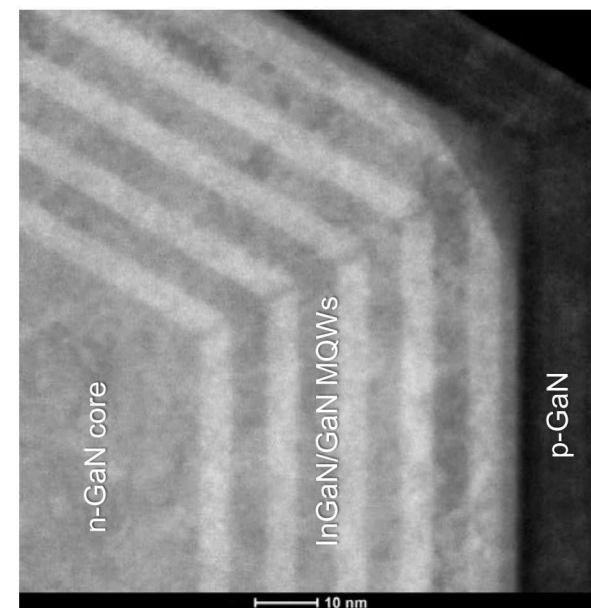
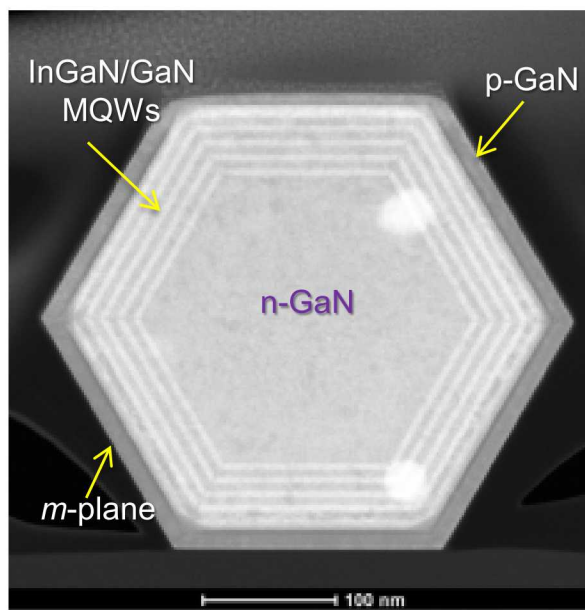
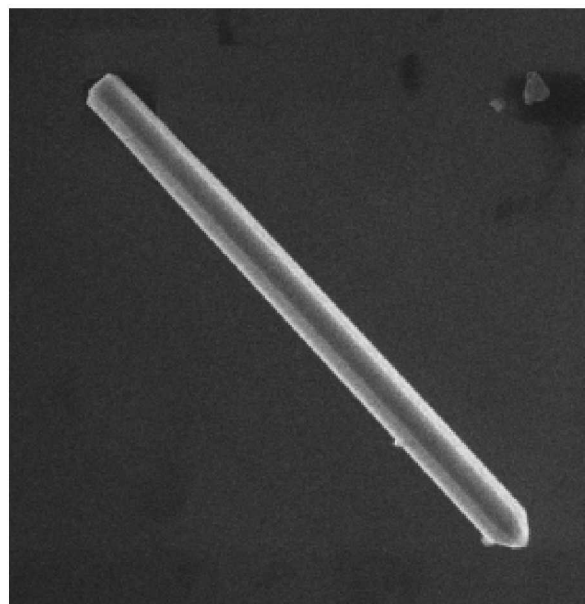
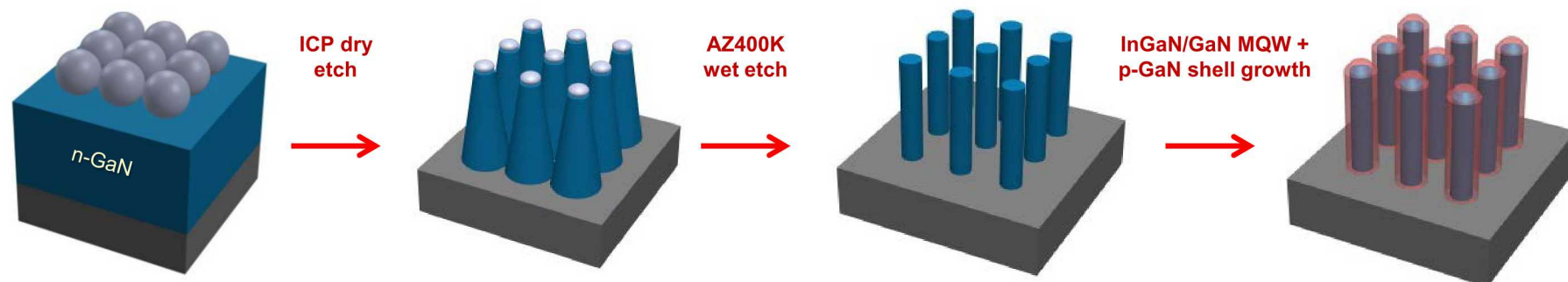
Threshold pump density = 1055 kW/cm^2

- Higher threshold of nanotube vs. nanowire may be due in part to inner taper
- Hollow nanotube geometry potentially useful for optofluidic/biosensing applications (lases in silicone oil but with higher threshold)
- Observed annular shaped emission agrees with predicted emission and shows *use of cross-sectional shape control for beam shaping* in nanowire lasers

C. Li et al., "Annular-Shaped Emission from Gallium Nitride Nanotube Lasers", *ACS Photonics*, **2**, 1025 (2015).

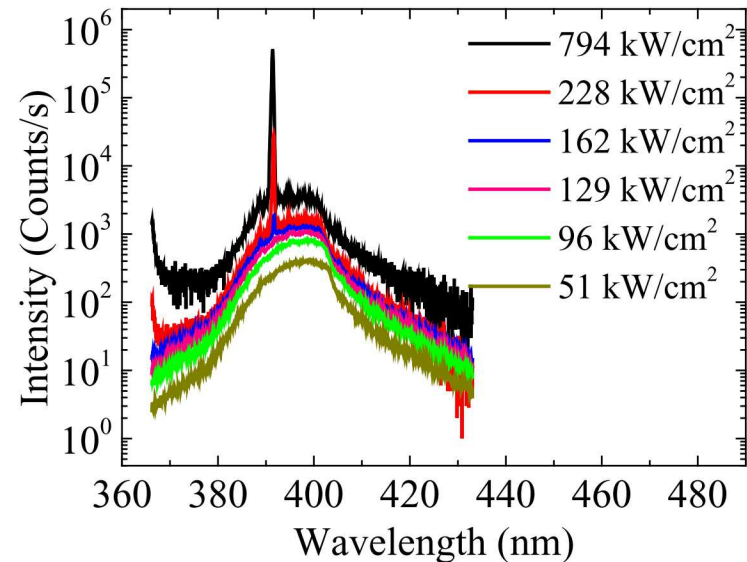
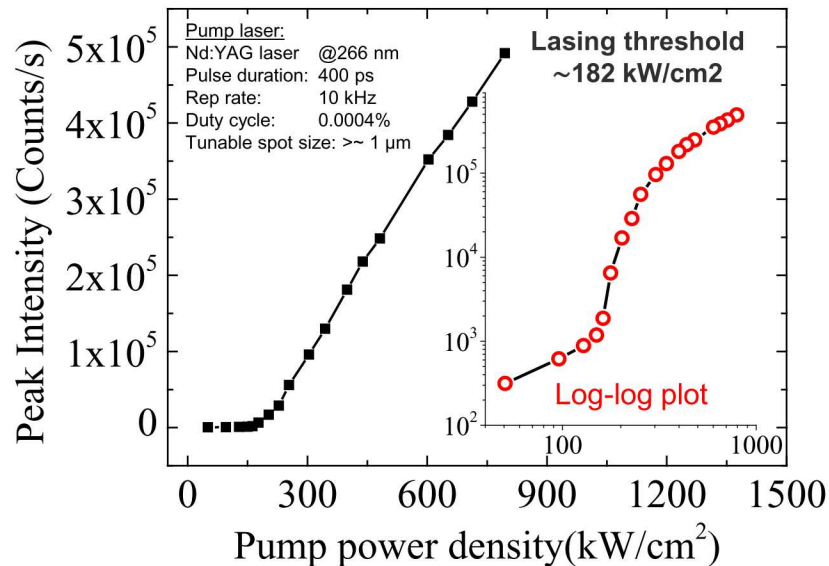


Hybrid top-down + bottom-up regrowth fabrication process for p-i-n InGaN/GaN core-shell nanowires

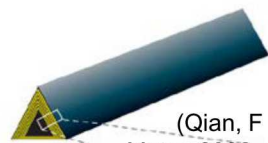


Full radial p-i-n structure needed for electrical injection

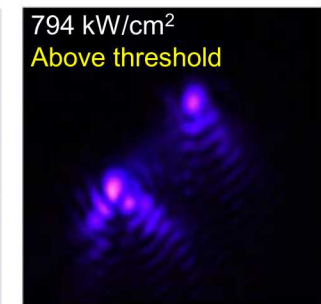
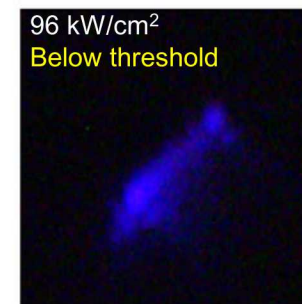
Optically pump lasing from single nonpolar InGaN/GaN MQW core-shell nanowire!



- Threshold pump density range ~75-600 kW/cm²
- **Lower** than thresholds for semipolar InGaN/GaN core-shell nanowires (~700-2000 kW/cm²) despite much shorter lengths

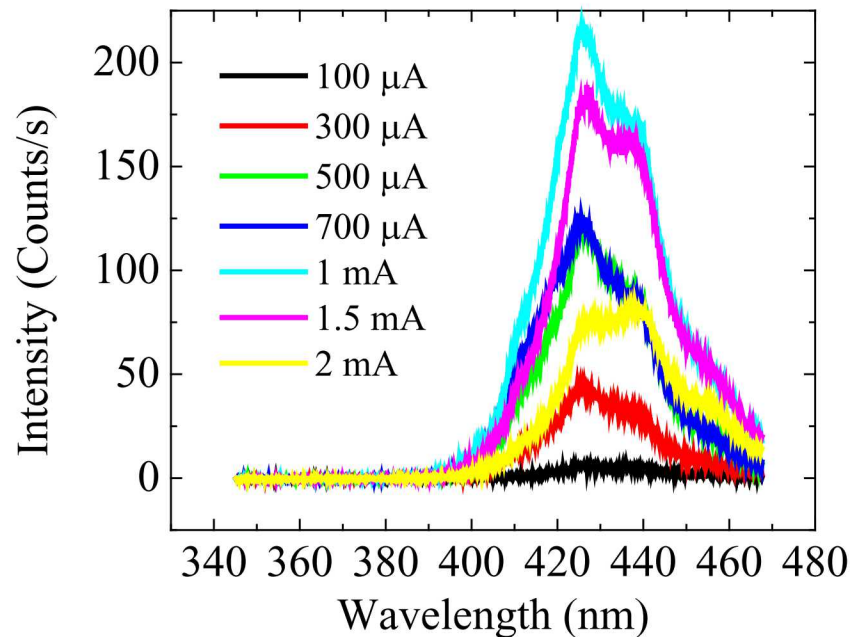


(Qian, F et al. C. M. Nat. Mater. **2008**, 7 (9), 701–706.)



CCD images of emission from single NW

Electrically injected lasing? Electroluminescence of single nonpolar InGaN/GaN core-shell nanowires – pulsed operation

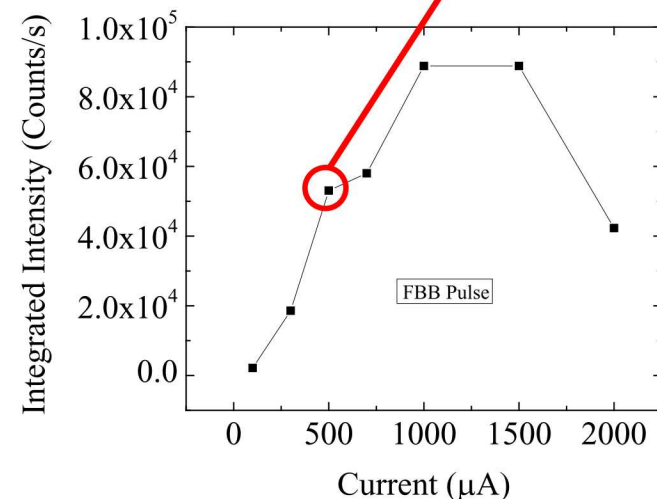
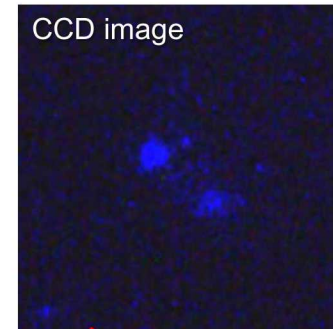
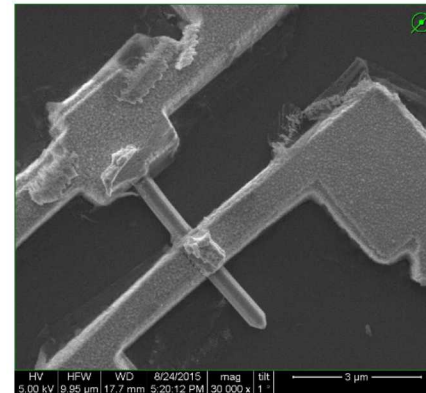


Pulsed operation

Pulse width: 300 μs

Duty cycle: 0.5%

No lasing observed up to 2 mA



Problem: Low injection efficiency due to non-Ohmic, high p-type contact resistance

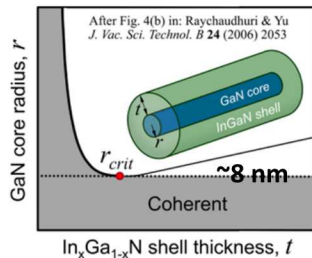
Also: Metal contact deposition shown to increase lasing thresholds significantly.

Subsequent annealing has some benefit but does not recover to bare-wire thresholds

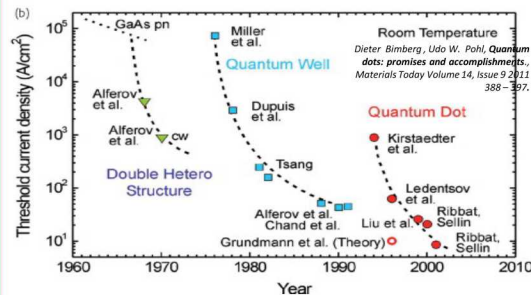
Nanomaterials whose features and bandgaps are precisely controlled at the quantum ($< \sim 10$ nm) scale do not exist

but will be needed for future optoelectronics & microelectronics!

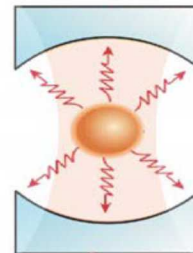
**Holy Grail 1:
Compliant
Nanoepitaxy**



**Holy Grail 2:
Ultra-Low-Threshold
High Efficiency QD
Lasers**



**Holy Grail 3:
Quantum
Nano-
photonics**

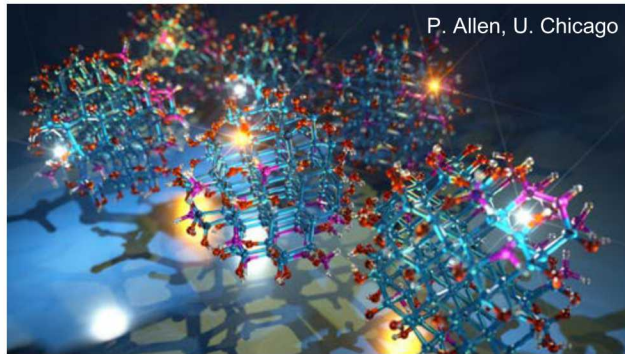


**Holy Grail 4:
The “on Moore’s Law” 5-nm node**

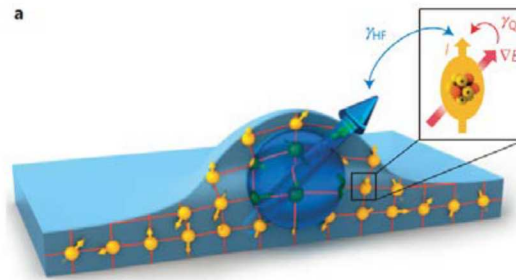


After J. Y. Tsao

Quantum dots

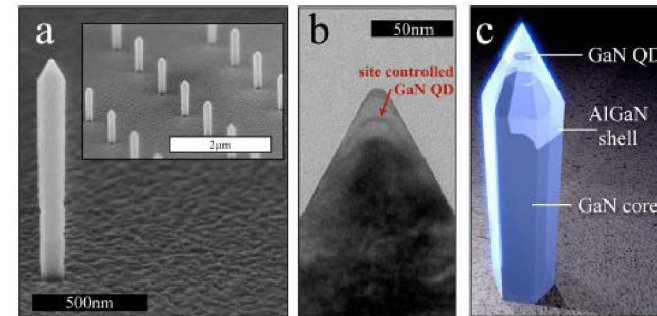


Electron spin qubit -
In(Ga)As /GaAs QD



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 qubits 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

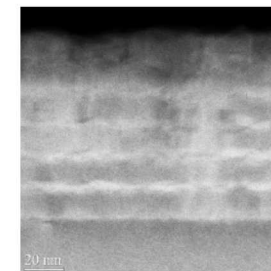


Motivation: InGaN Quantum Dots (QDs) as emitters

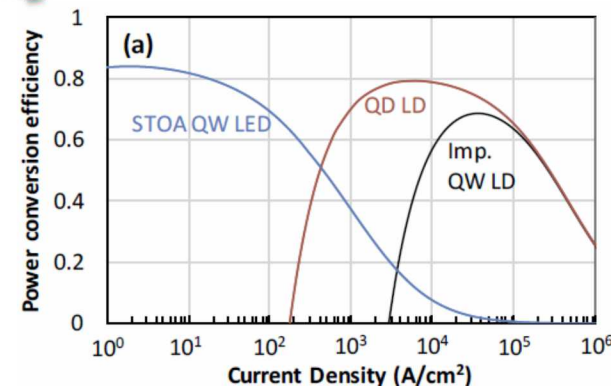
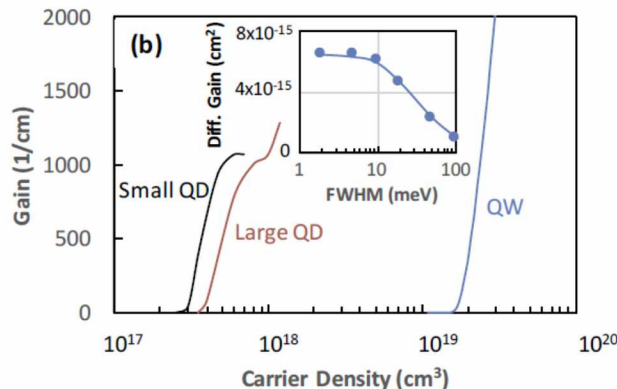
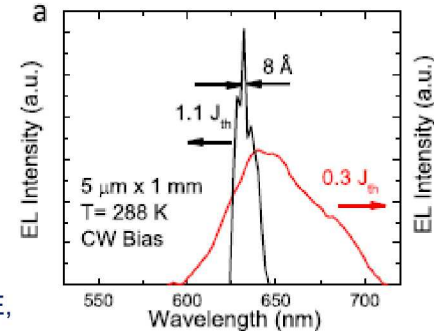
Potential advantages vs quantum wells

- 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).

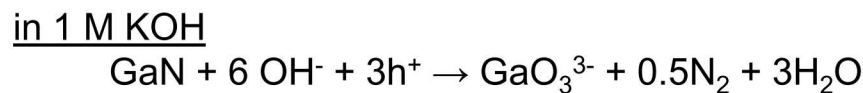
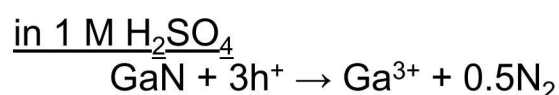


Jonathan J. Wierer, Jr., Nelson Tansu, Arthur J. Fischer, and Jeffrey Tsao, "III-nitride quantum dots for ultra-efficient solid-state lighting," *Laser and Photonics Reviews*, **10**, 612 (2016) / DOI 10.1002/lpor.201500332

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

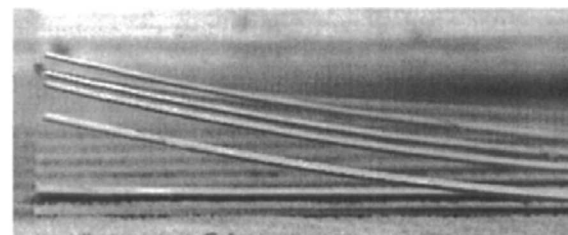
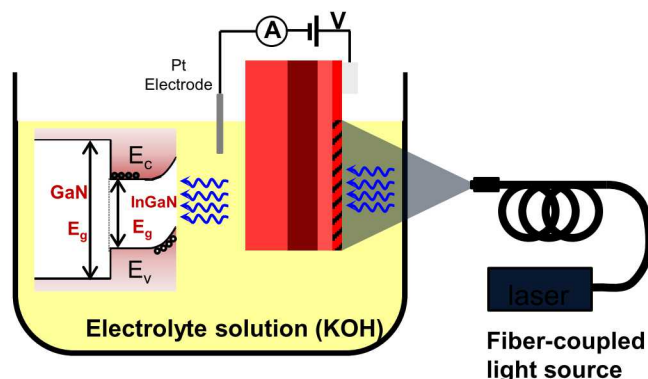
(In)GaN Photoelectrochemical (PEC) Etching

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

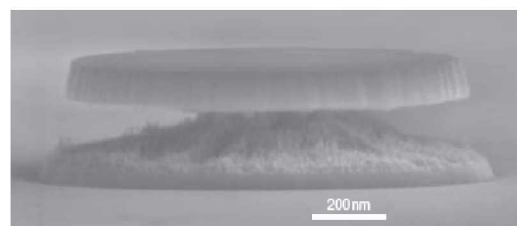


Huygens et al., J. ECS **147**, 1797 (2000)

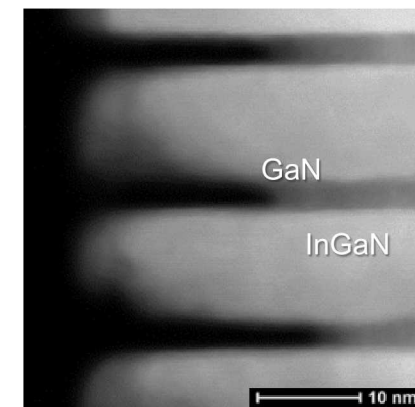
- Laser or lamp excitation (Xe arc lamp, tunable ps Ti:S)
- KOH (~0.1M) typically used as electrolyte for GaN
- Band gap selective (etch InGaN over GaN) based on wavelength used



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



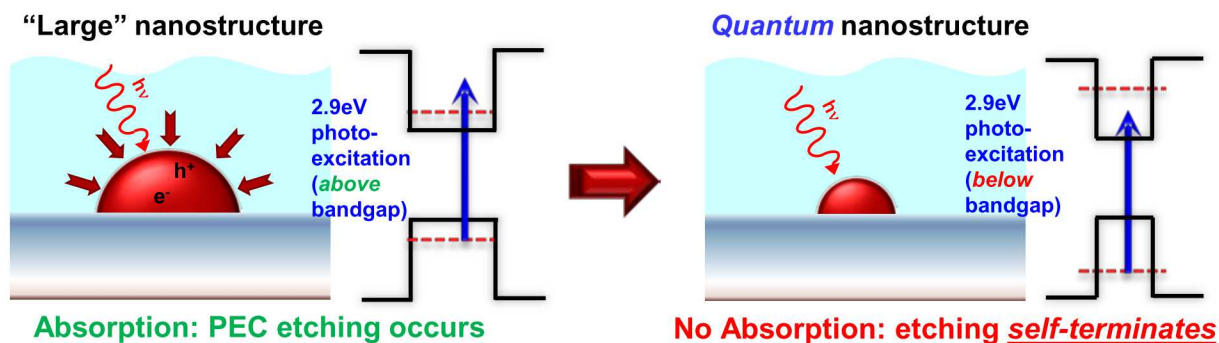
Tamboli et al., Nat. Phot. **1**, 61 (2007)



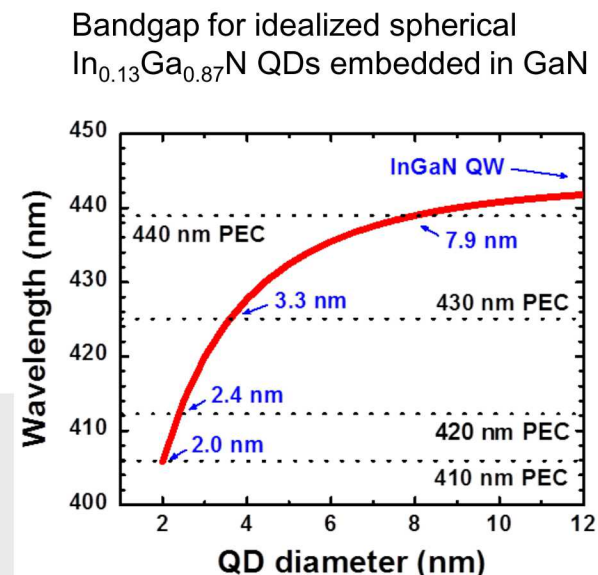
Xiao et al, Elec. Acta 162, 163 (2015)

Controlled fabrication of QDs via PEC etching

Quantum Size Control: Use size quantization to control QD size



- For QDs, band gap depends on size
- As PEC etch proceeds,
 - QD size gets smaller, band gap goes up
 - Etch should terminate for $E_g > E_{\text{photon}}$ 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}

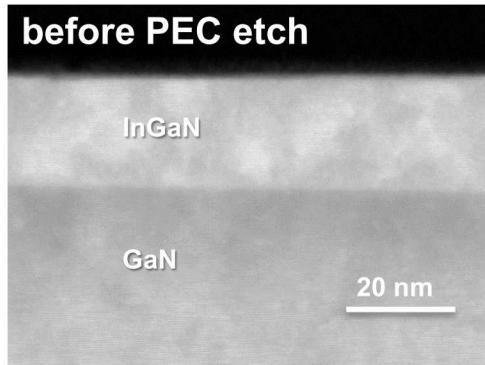


¹Matsumoto et al., J. Phys. Chem. **100**, 13781 (1996)

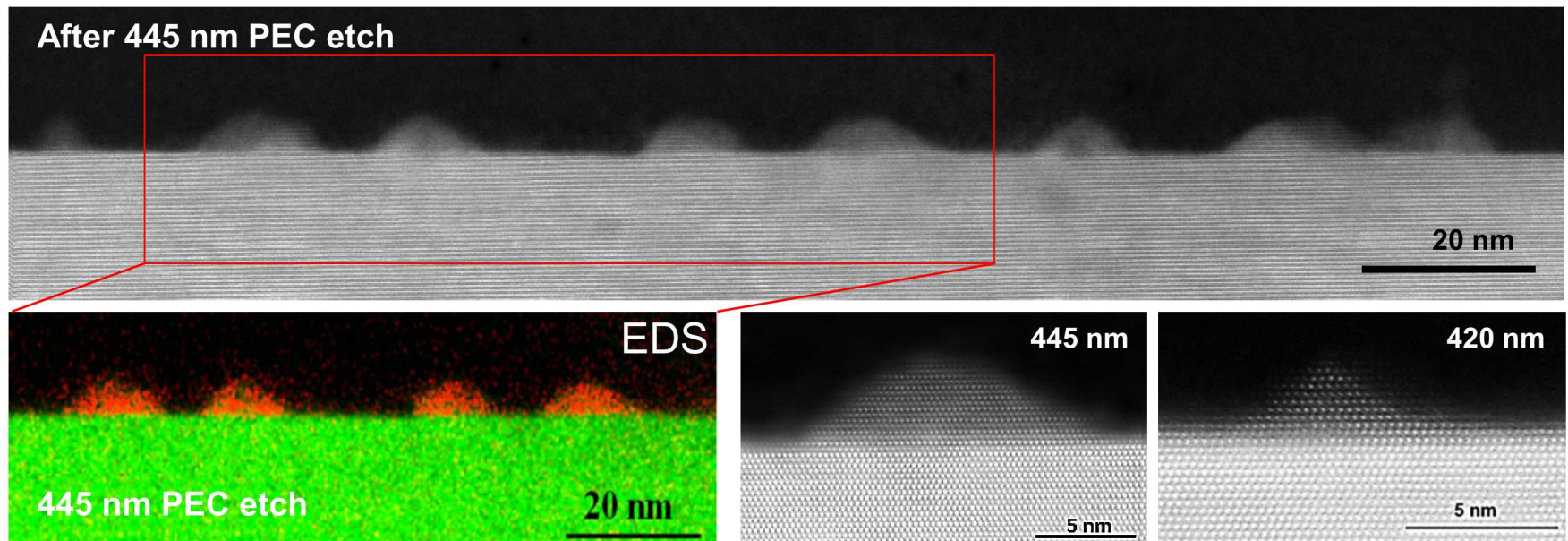
²Torimoto et al., J. ECS **145**, 1964 (1998)

QSC-PEC etched uncapped InGaN layer – Scanning TEM measurements

Uncapped InGaN QW

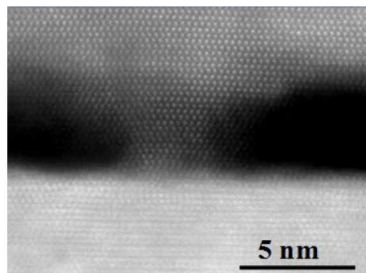


- Cross-sectional high-angle annular dark-field (HAADF) scanning TEM images
- Samples etched at 420 nm and 445 nm
- Energy dispersive (EDS) x-ray mapping
 - QDs on surface are InGaN (Red = In, Green = Ga)
- InGaN QDs are epitaxial to the underlying GaN
- No underlayer, no cap → PL is not very bright



LT Photoluminescence from QSC-PEC etched InGaN QDs

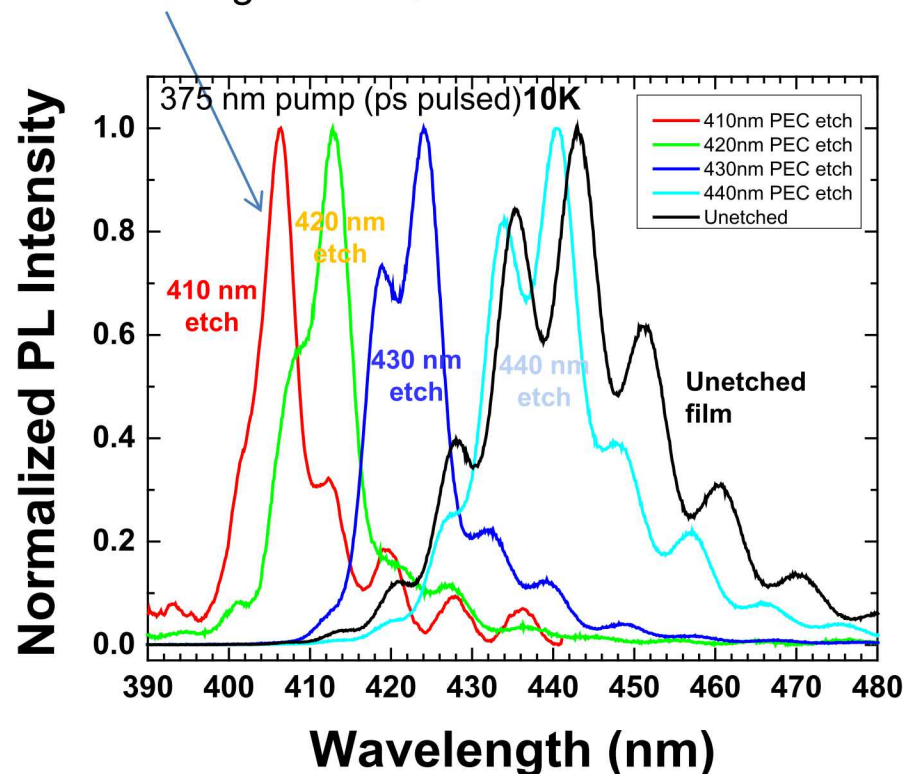
Capped InGaN QDs



Photoluminescence (PL) data:

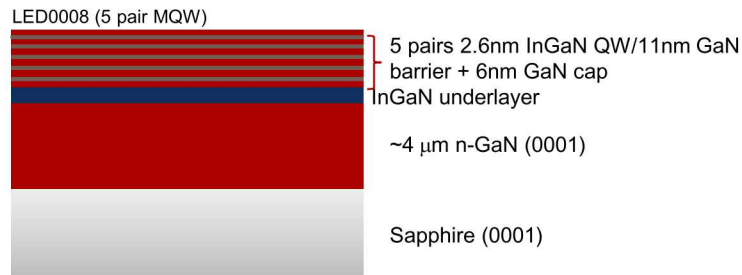
- Etched QD PL **wavelength correlates** (but doesn't exactly coincide) **with PEC etch wavelength**
- PL linewidth **decreases with decreasing etch wavelength**: 24 nm (film) $\rightarrow$ 6 nm (QDs etched at 410 nm)
- Strong evidence for quantum-size controlled etch!**

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

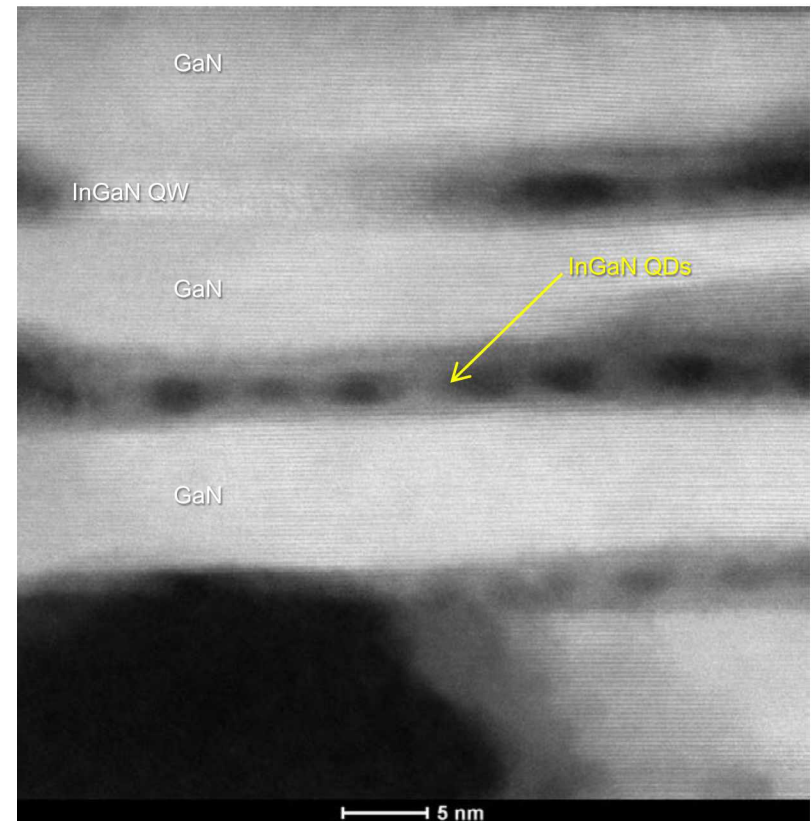
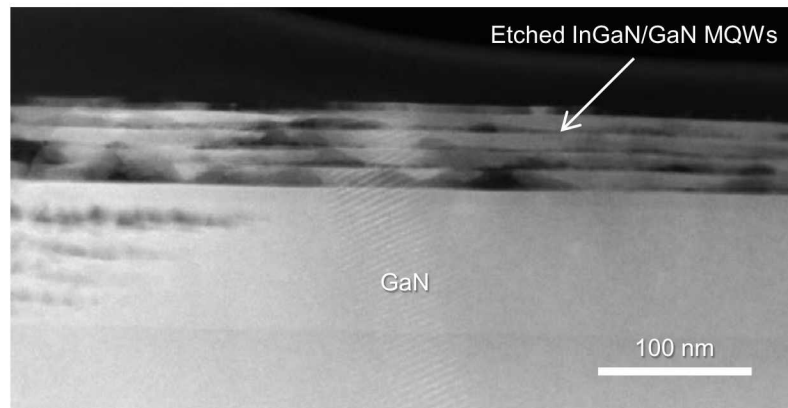


QSC-PEC Etching of InGaN/GaN Multiple Quantum Wells

- 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

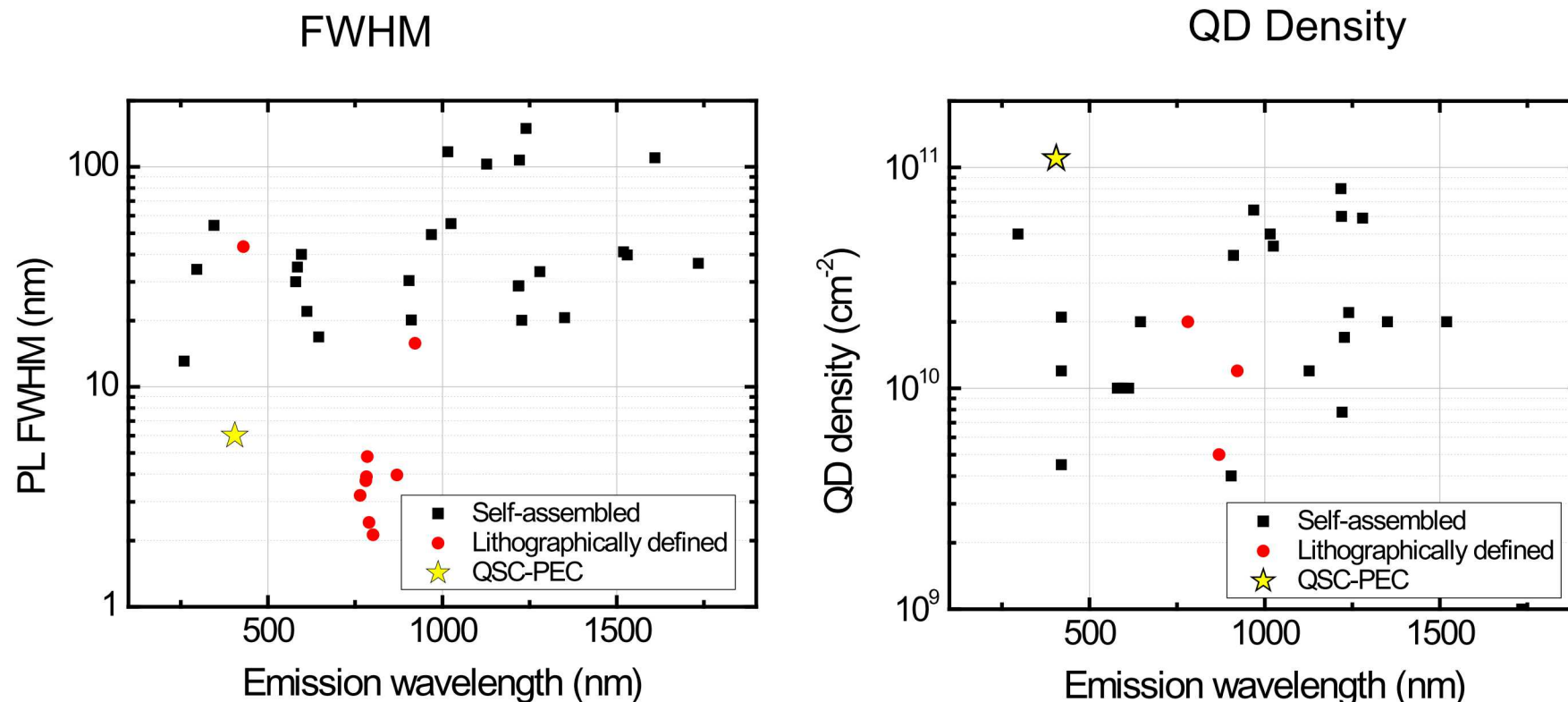


PEC etch: 420 nm, 20mW, 1.4V, 0.2M H₂SO₄, 45min



STEM by Ping Lu

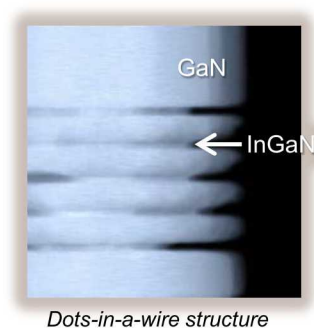
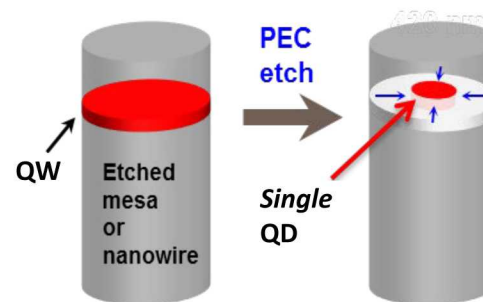
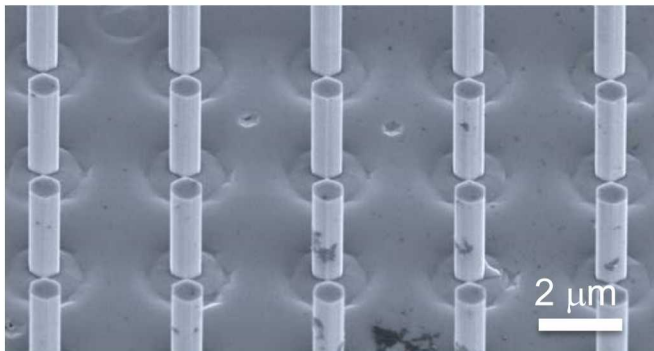
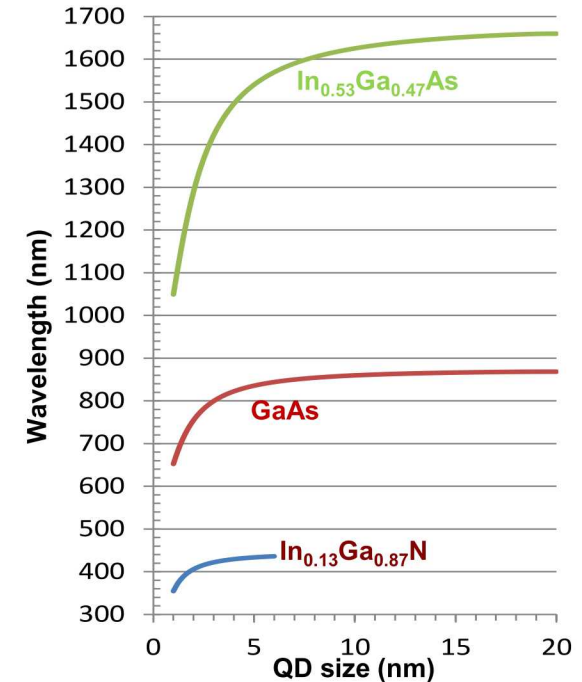
(Partial) Survey of III-V/N QD literature



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

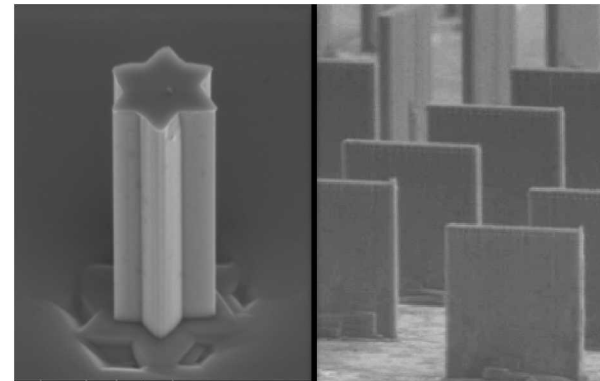
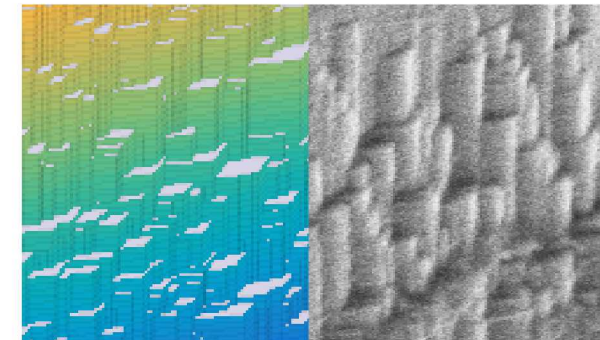
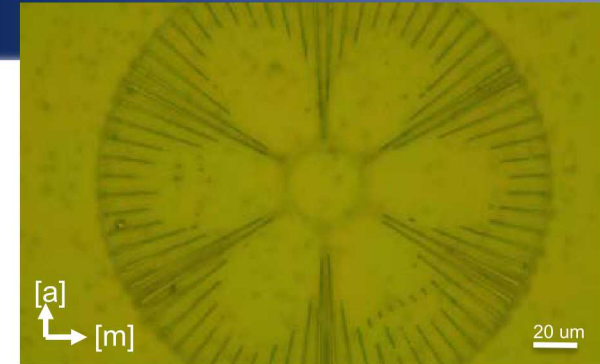
Quantum size controlled etching: The Future

- Extend to a range of available bandgaps/wavelengths across multiple materials systems (e.g. InGaAs/GaAs)?
- Lattice matched QDs possible! – any material on any substrate theoretically possible, not limited by need for compressively strained self-assembled QDs! Realize QDs of specific composition/energy never demonstrated before.
- Combine with lithographic techniques to deterministically place quantum emitters at defined locations



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 based on concave and convex configurations & slow & fast wet etch facets
- Demonstrated **complex cross-sectional geometries** for vertical nanostructures with possible atomic-scale sidewall smoothness, enabling **III-nitride based nano-optoelectronics (lasers, LEDs, etc.)**
- **Quantum size controlled** fabrication of quantum dots demonstrated



Acknowledgments

Qiming Li - nanowire growth, nano-CL, TEM/EDXS, nanofabrication, strain-modeling

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

Jianyu Huang, Ping Lu – In-situ TEM and scanning TEM

Mary Crawford – PL, IQE measurements

Jonathan Wierer (Lehigh U.) – Device fabrication and testing

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

Benjamin Leung, Miao-Chan Tsai (Glo) - GaN etching, PEC Etching, SnTe nanostructures

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

Keshab Sapkota – PEC etching, SnTe, ZrTe, Te nanostructure growth

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

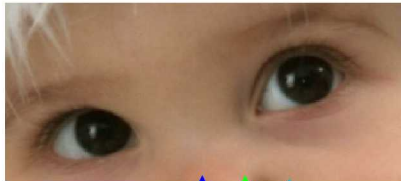
BACKUP SLIDES



Why Only 30% Efficient?

Four SSL Technology Grand Challenges

85%



<http://labbymercerbook.com>

4 Functional Light

(control of light in intensity, chromaticity, time, and space)

1 Efficiency Droop
(near-100% efficiency
at all currents)

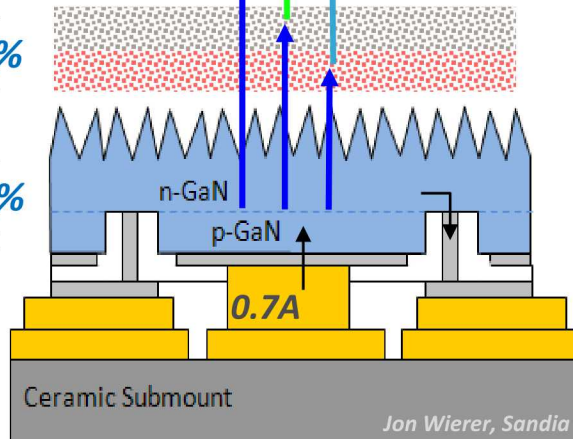
2 Green-Yellow Gap
(near-100% efficiency
at all wavelengths)

3 Narrow-linewidth
 λ downconversion
(esp. red)

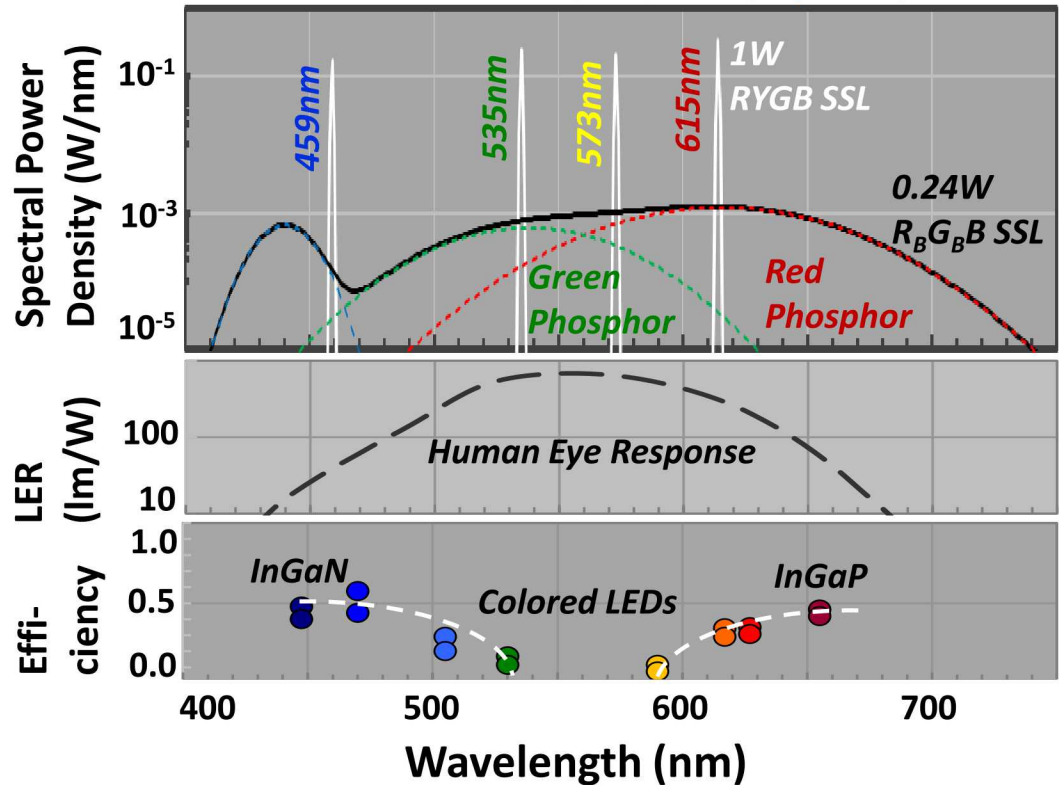
Efficiencies

56%

43%



1 mm

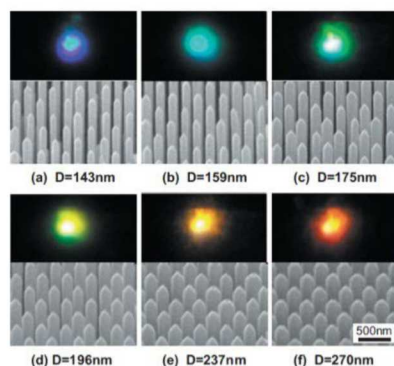
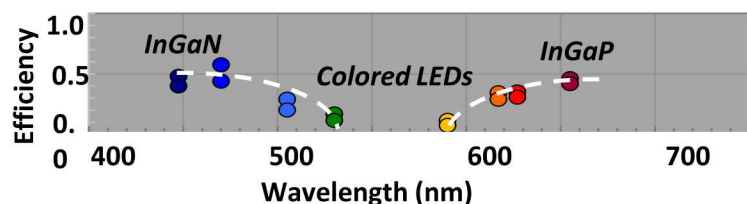


Why III-nitride nanowires for SSL?

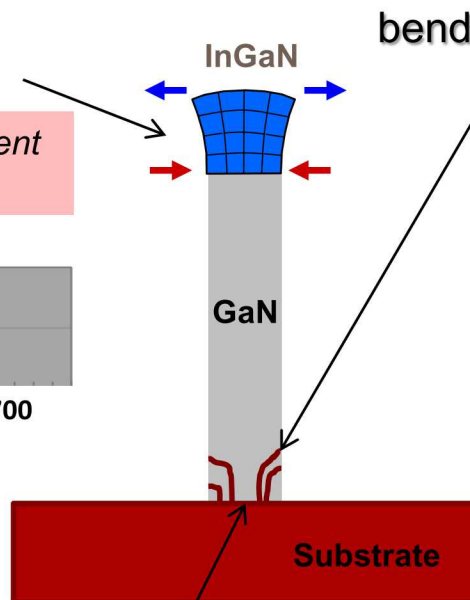
Advantages due to enhanced strain accommodation in nanowires

elastic strain relaxation at surface

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



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

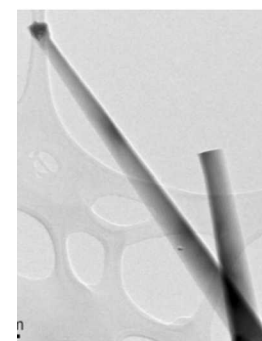


small interfacial area

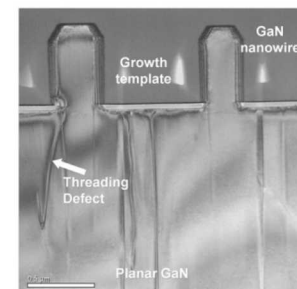
benefit: can grow on cheaper, lattice mismatched substrates; integration with Si devices

bending of dislocations (TDs) toward surface

benefit: reduced TDs, higher IQE

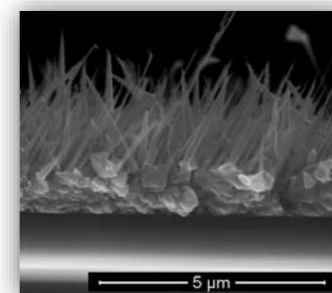


VLS-grown TD-free GaN NWs - Sandia

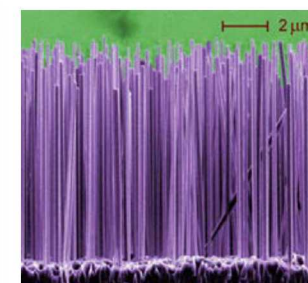


Hersee et al., J. Mat. Res. **17**, 2293 (2011) - UNM

Bending & termination of TDs at nanowire base



GaN NWs on tungsten foil - Sandia

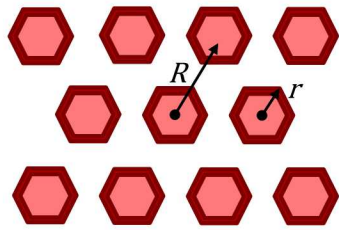


GaN NWs on Si - NIST

Why III-nitride nanowires for optoelectronics?

vertical device integration

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

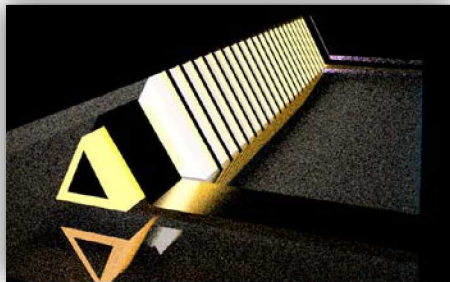


$$\frac{A_{\text{sidewall}}}{A_{\text{substrate}}} = \frac{6rh}{2.6R^2} \cong 4.6F \cdot AR$$

example: $4.6 \cdot 0.5 \cdot 3 = 6.9 \times$ increase!

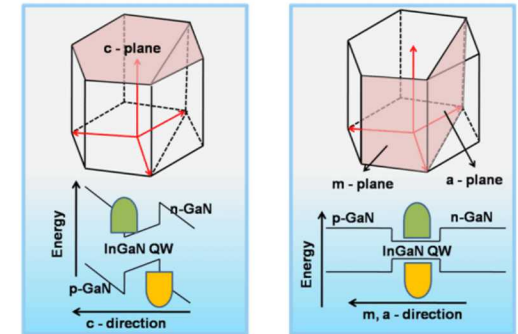
nanolasers

benefit: ultracompact, low power coherent light source



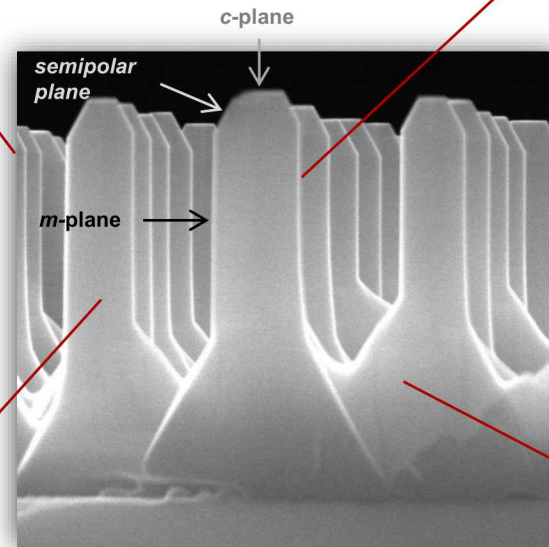
access to nonpolar & semipolar planes

benefit: higher IQE, reduced wavelength shift



Non-polar direction GaN thin film growth → higher quantum efficiency

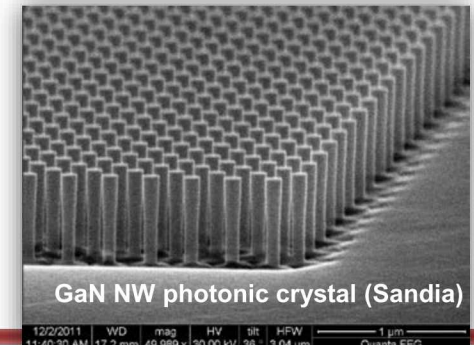
<http://csl.snu.ac.kr/research/LED.php>



Radial GaN/InGaN MQW NW (Sandia)

2D arrangements (photonic crystals)

benefit: higher light extraction, IQE, wavelength tuning



GaN NW photonic crystal (Sandia)

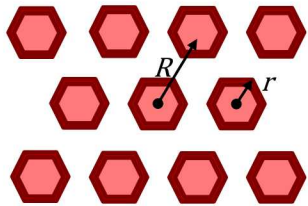
12/2/2011 WD mag HV tilt HFW 11:40:30 AM 17.2 mm 49 989 x 30.00 kV 36 3.04 μm Quanta FEG

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

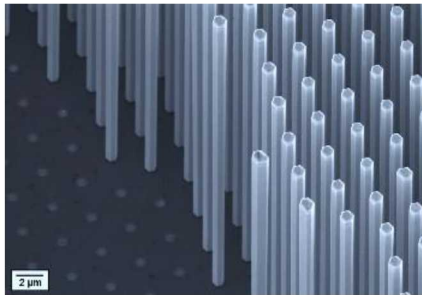


AR = aspect ratio
FF = fill factor

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

ex: AR=3, FF=0.5 → **6.9× increase!**

Microrod LEDs (Osram Opto)

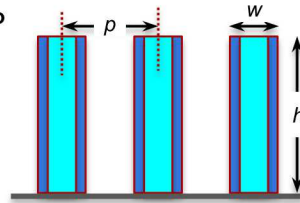


Microwire LED Blue IQE~65%

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

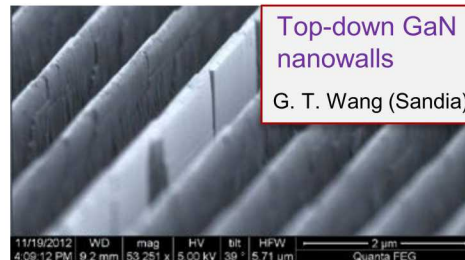
Complex 3D growth and injection

Nonpolar sidewall nanowalls



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

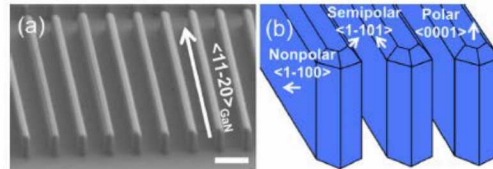
ex: p=0.5 μm, h=3 μm → **12× increase!**



Top-down GaN nanowalls

G. T. Wang (Sandia)

InGaN/GaN MQWs on m-plane nanosheets

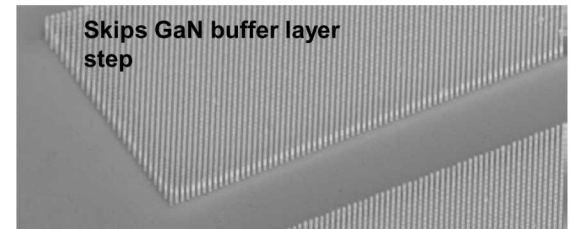


Dapkus (USC), APL 100 033119 (2012)

Use of alternative substrates

benefit: lower cost, new form factors

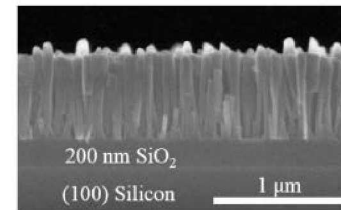
Core-shell nanowire LEDs grown on 8" Si



Skips GaN buffer layer step

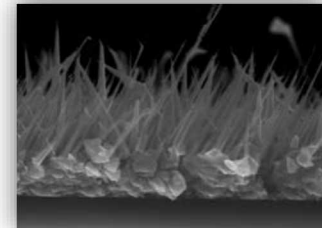
Aledia, Inc.

Nanowire LEDs grown on SiO₂



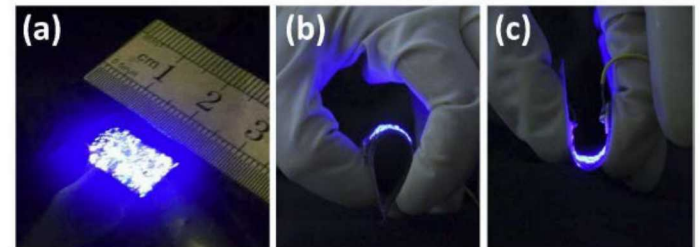
Bhattacharya (Michigan) Opt. Exp. 23 A650 (2015)

GaN NWs on tungsten foil



G. T. Wang (Sandia)

Flexible core-shell NW LEDs by MOCVD



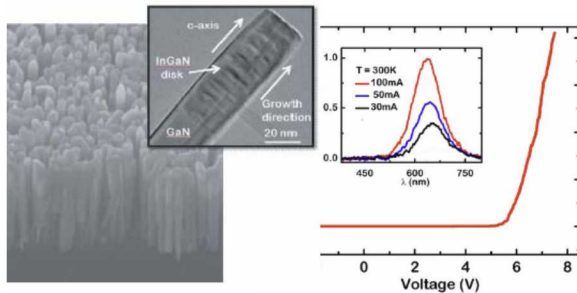
CNRS (Grenoble), NL, just accepted 8/31/15

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

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

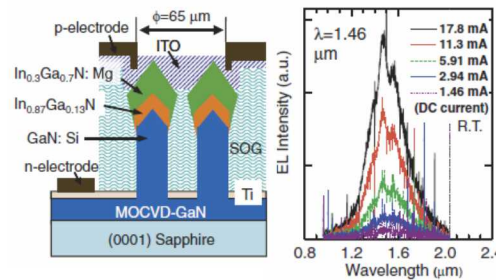
Axial c-plane InGaN disc/dot-in-a-wire grown by MBE: long wavelength emission demonstrated

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



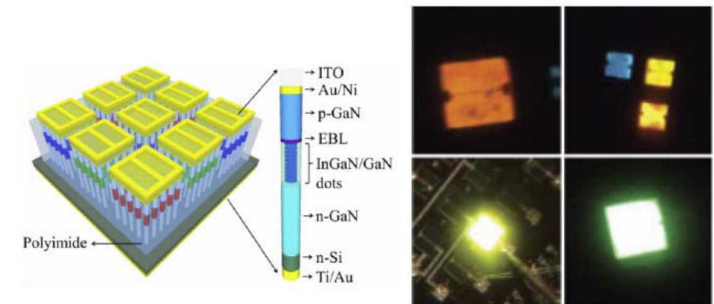
Bhattacharya (U. Michigan) *APL* **102** 071101 (2013)

Near IR InGaN LEDs at 1.46 μm



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

Phosphor-free RGB nanowire arrays on Si



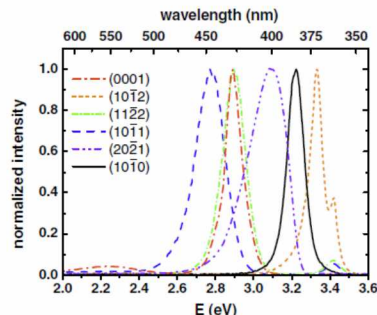
Z. Mi (McGill U.), *Opt. Exp.* **22** A1768 (2014)

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

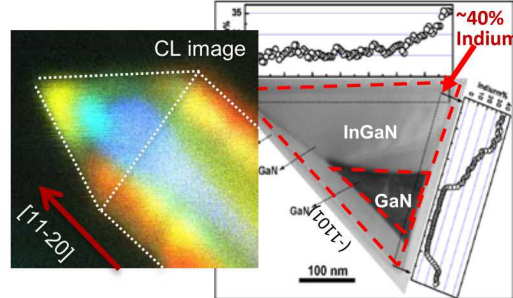
InGaN MQW emission by facet orientation



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

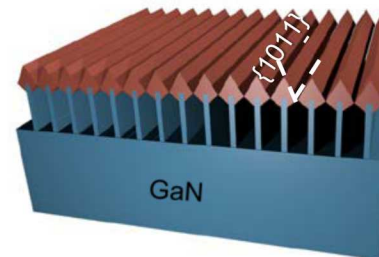
Wernicke (TU Berlin), *SST* **27** 024014 (2012)

High In incorporation on {10-11} NW sidewalls



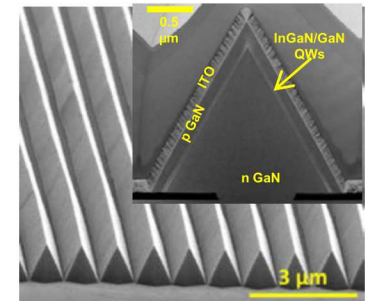
G. T. Wang (Sandia), *APL* **97** 181107 (2010)

InGaN pseudo-templates based on semipolar nanostructures?



G. T. Wang (Sandia)

{10-11} semipolar nanowall LEDs



Feezell (U. New Mexico)

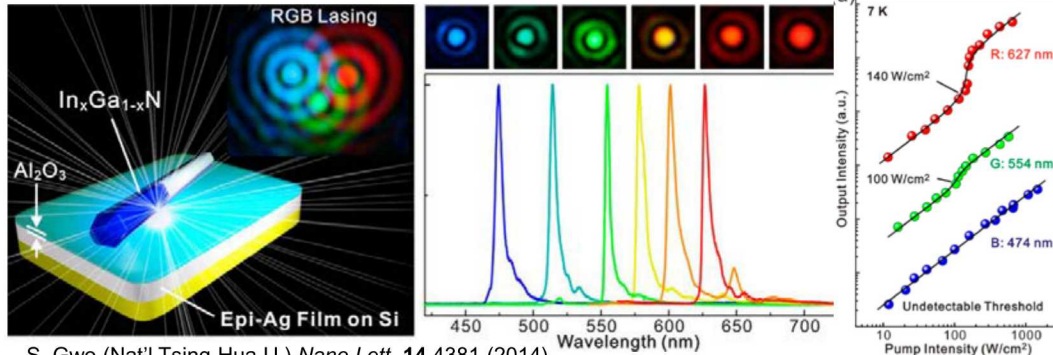
See also work by Wunderer (U. Ulm)

Corner effects (nonuniform In incorporation), material quality?

III-N Nanowire and Quantum Dot Lasers

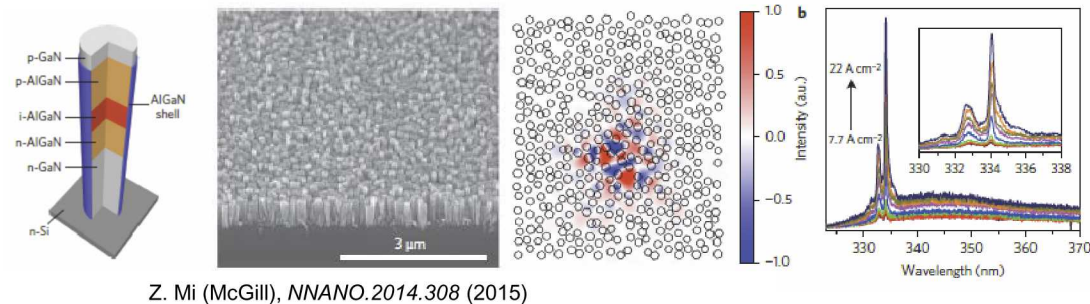
Potential benefits: long wavelengths, low thresholds, higher efficiencies, wavelength tuning, nanophotonics

Ultralow threshold full-color plasmonic lasers (Gwo)



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

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

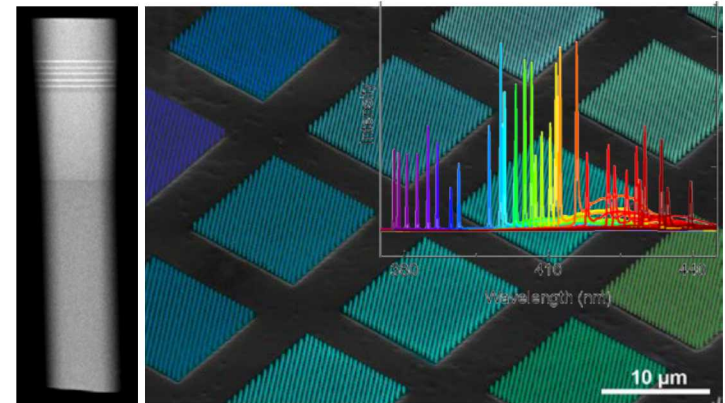


Electrically injected lasing at 263 nm @ 0.6 kA/cm² threshold, deepest UV reported to date

Absolute EQEs and Output Powers?

Electrical Injection for single NWs?

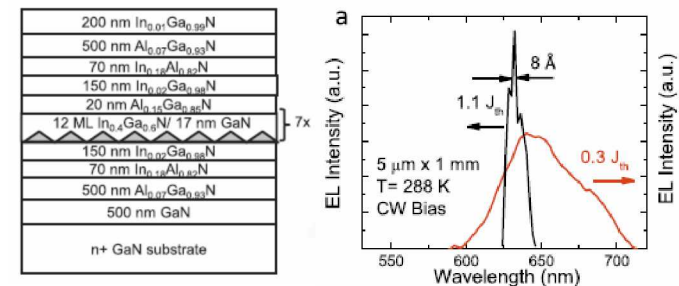
Top-down nanowire photonic crystal laser pixels



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

60 nm λ tuning demonstrated purely by PC geometry

Red Edge-Emitting QD Lasers by MBE



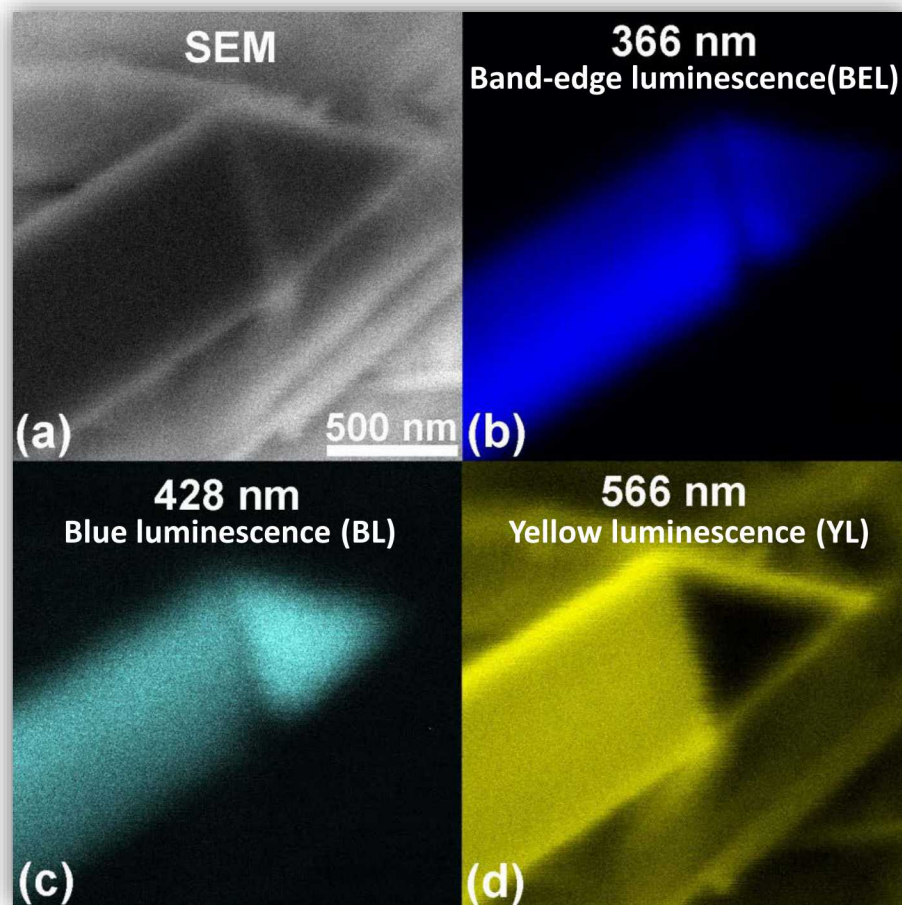
Bhattacharya (U. Michigan) *IEEE J. Quant. Electr.* **49** 923 (2013)

~36% IQE at 630 nm, 2.5 kA/cm² threshold

MOCVD Compatible Processes?

Spatial distribution of luminescence in GaN NWs

Nanoscale cathodoluminescence



- Band-edge luminescence (BEL) at ~ 366 nm and defect-related blue luminescence (BL) at ~ 428 nm observed in NW core/bulk
- **Defect-related yellow luminescence (YL) exhibits strong surface component** -- associated with surface states or concentrated near surface region
- YL in GaN attributed to many possible sources (C, O impurities, Ga vacancies, etc.)
- Isolated Ga vacancies have low diffusion barrier (~ 1.5 eV) & may migrate toward surface during growth
- BL linked to $V_{\text{Ga}}\text{-O}_{\text{N}}$ ($D \sim 2.2$ eV), less mobile

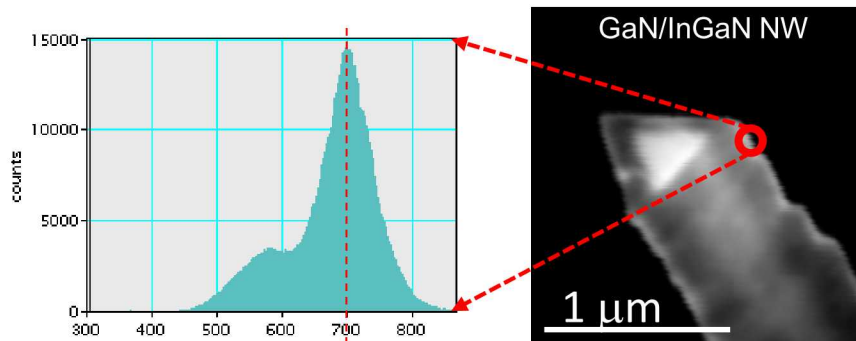
**Nanoscale Cathodoluminescence (CL)
imaging: Cross-section GaN NW**

Q. Li, G. T. Wang, *Nano Lett.*, 2010, **10** (5), 1554

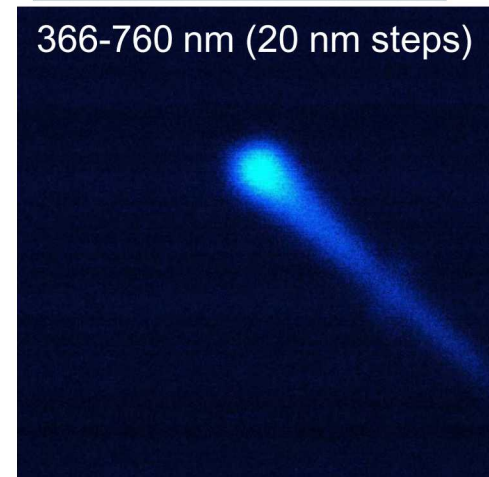
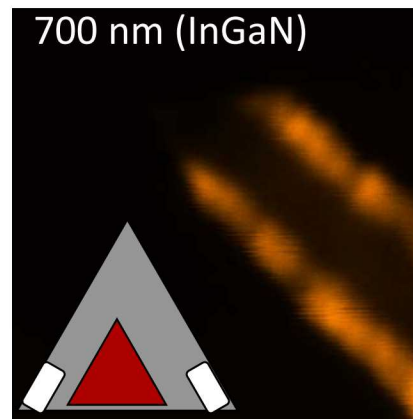
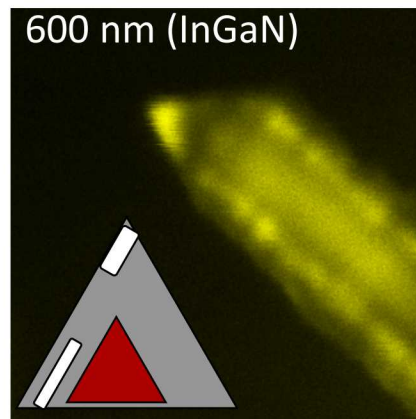
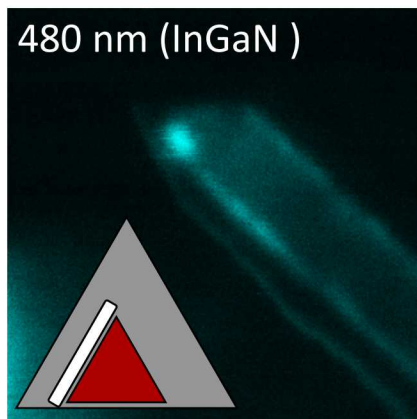
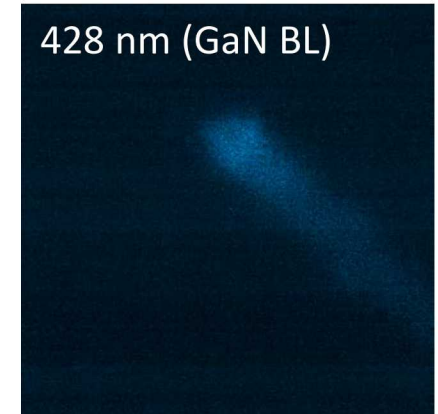
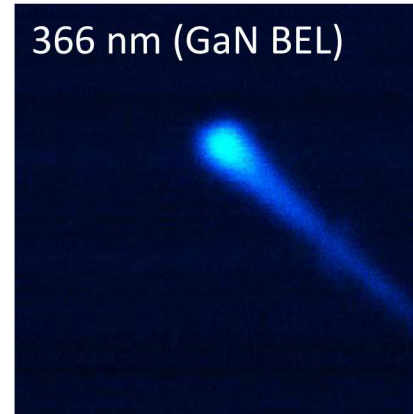
Spatially dependent indium Incorporation in GaN/InGaN core-shell NWs

Nanoscale cathodoluminescence

- InGaN: visible wavelengths for solid-state lighting, PV, etc.
- Strain limits practical In incorporation in InGaN thin films (e.g., green-yellow-red gap)



Growth conditions: GaN core – 900 °C, 10 min.
InGaN shell – 760 °C, 60 min.



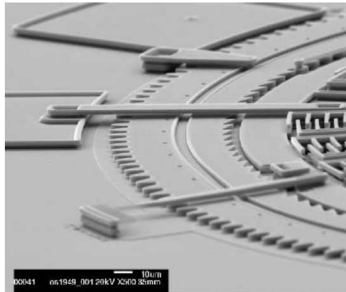


Problem: Lack of 3D nano-microfabrication processes for III-nitrides and III-V compound semiconductors

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

3D Silicon structures

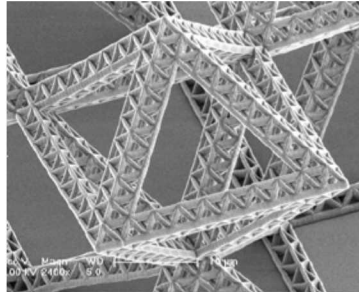
N/MEMS



Torsional Ratcheting Actuator

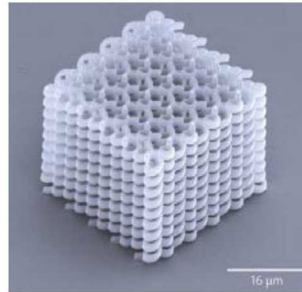
SNL

Nanolattice/truss



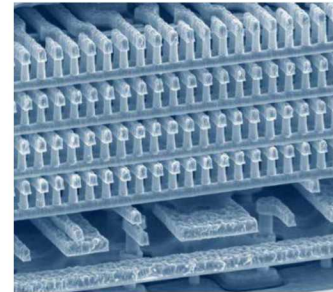
J. Greer, Caltech (2014)

3D Photonic Crystals and Metamaterials



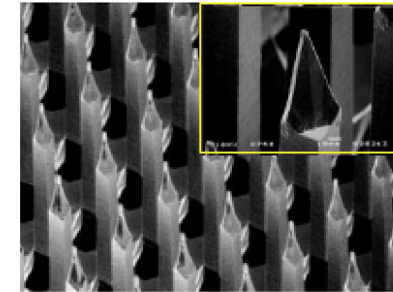
Farsari et al. *Nat. Phot.* (2009)

3D FinFET/NAND



Matrix Semiconductor (2012)

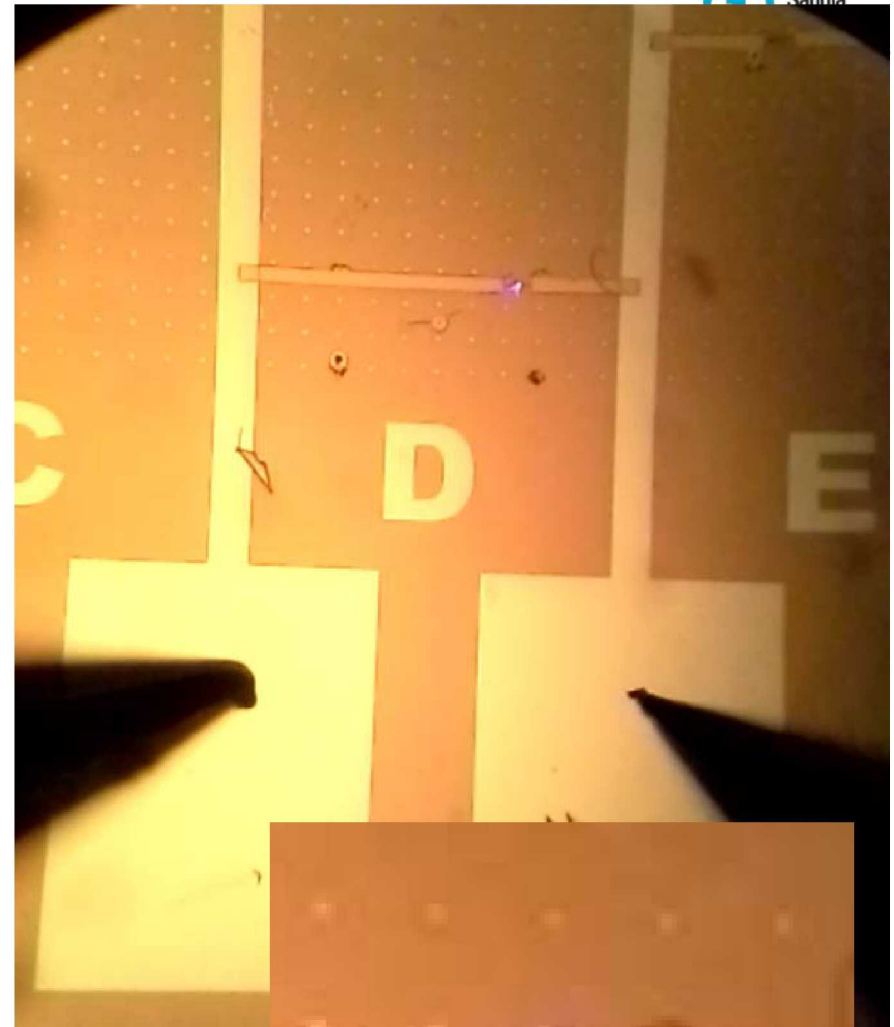
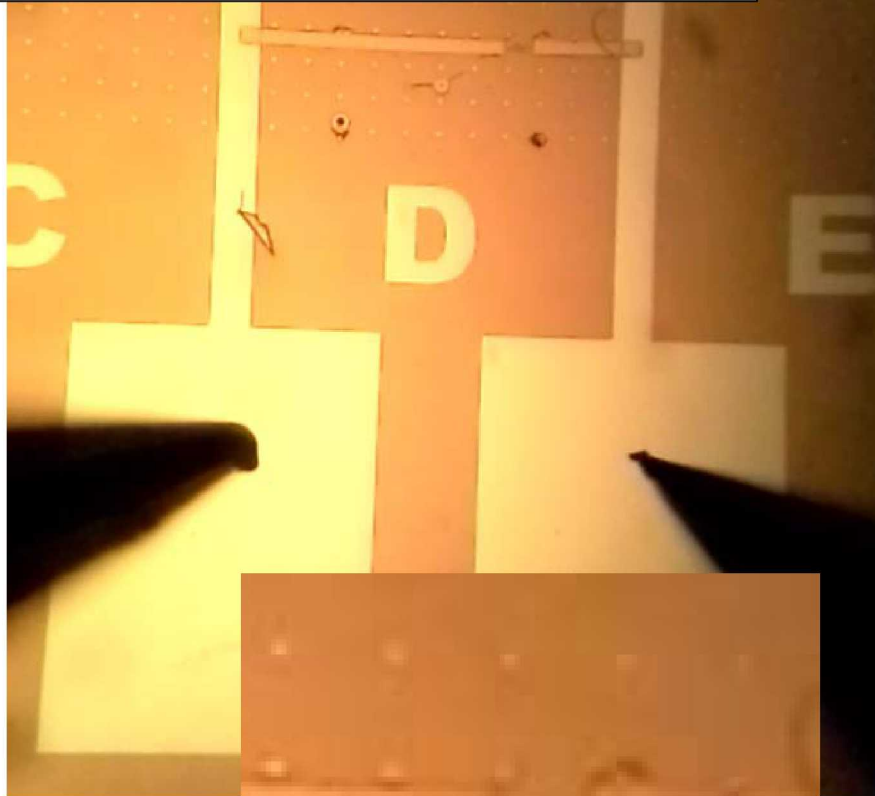
3D Nanoneedles



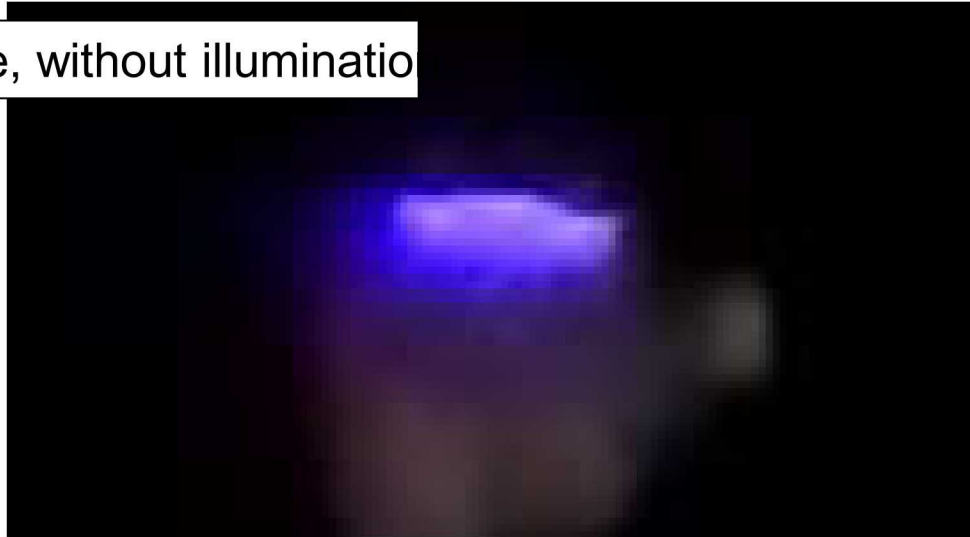
Shikida et al. (2004)

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.

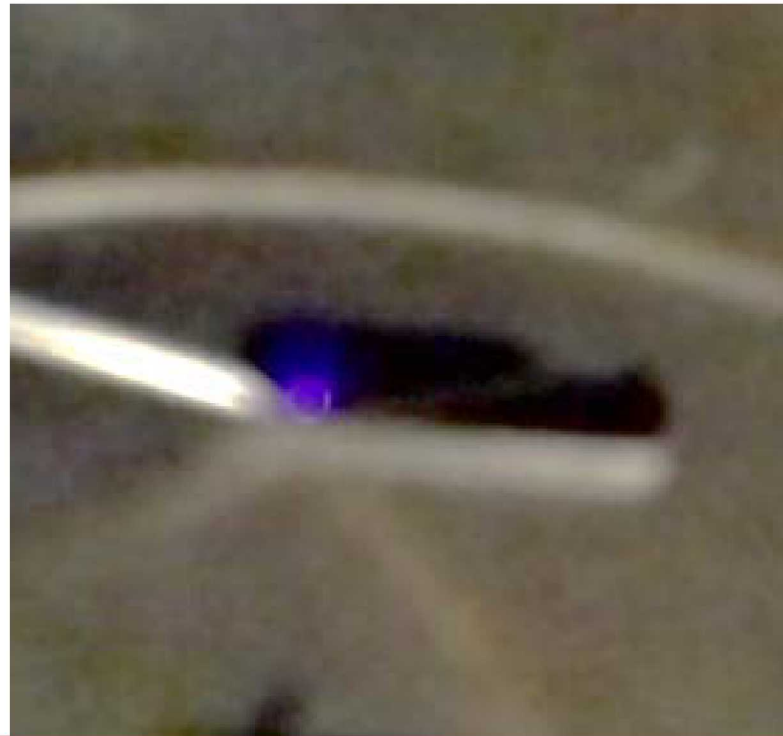
Axial nanowire LED (from LED0051, 1 μ m p-GaN)
200 nm diameter, 3 μ m length
400 nm Ni/200 nm Au, both sides
500 C anneal, air, 2 min
After ebeam exposure, 30 kV, spot size 6.0 (~nA)
~25V, 5 μ A



Through microscope, without illuminatio

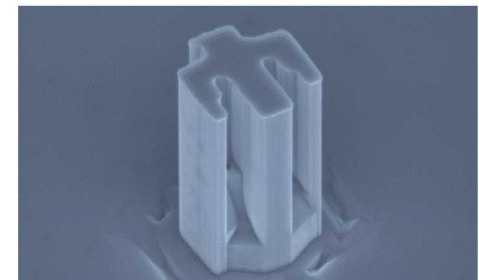
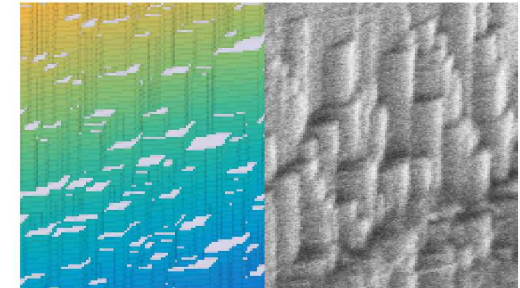
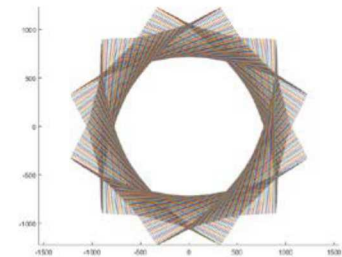
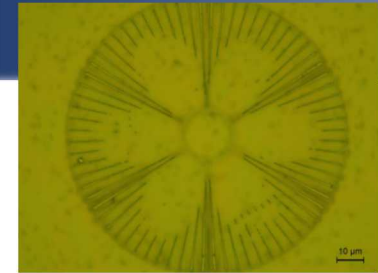


Room illumination



Outline

- Atomic understanding of GaN etch anisotropy
- Direct measurement of orientation resolved etch rates for GaN
- Prediction of etched geometries
- Elucidate facet evolution during wet etching
- Measurement of facet smoothness
- Application of chemical wet etching for vertical and smooth nano structures with cross-sectional shape control
- Nanowire optoelectronics fabricated with top-down etch approach



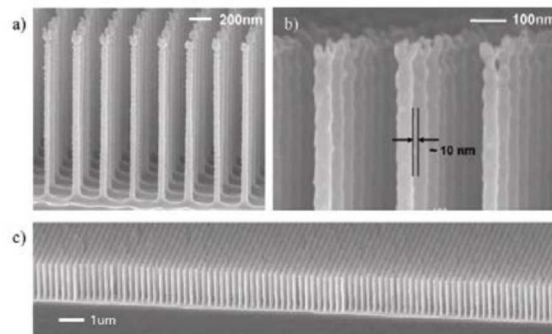
Top-down fabrication of semiconductor nanowires

Main technique to produce anisotropic structures are plasma-based dry etches

Advantages:

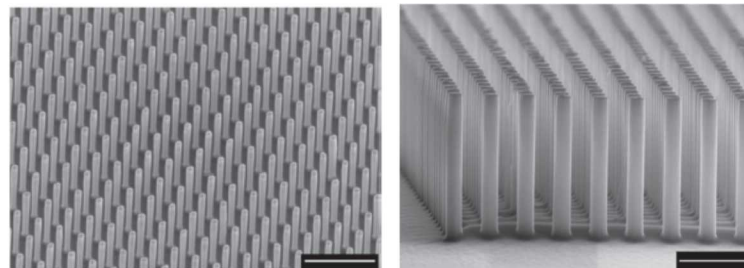
- Wide range of growth conditions to tune material properties
 - Not limited to nanowire growth window
- Lower point defect densities
 - Growth temperature
- Ordered/periodic arrays
 - Difficult with catalyst/VLS based methods
- Axial III-nitride nanowire heterostructures possible by MOCVD
- Geometry control
 - Independent control over height, width & pitch
- Easier vertical device integration
 - Height uniformity, base GaN layer

Silicon



K. J. Morton et al., Nanotechnology, 19, 345301 (2008)

GaAs



GaN

N. Dhindsa et al., Nanotechnology, 25, 305303 (2014)

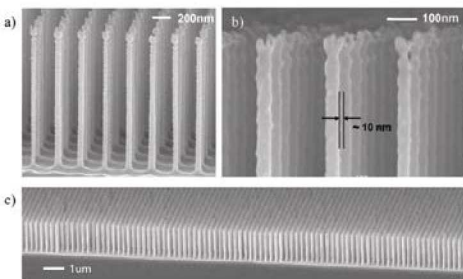
Plasma etching of GaN is not sufficient to produce high aspect ratio III-nitride nanowires



Nanowires by plasma-based dry etches

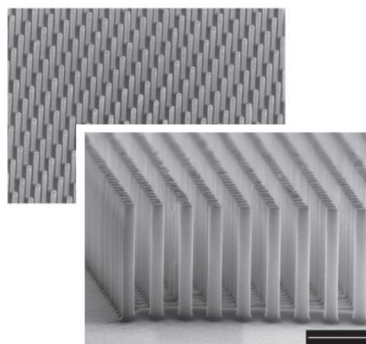
The main technique to produce anisotropic structures are plasma-based dry etches:

Silicon



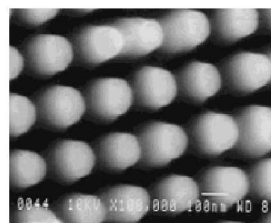
K. J. Morton et al., Nanotechnology, 19, 345301 (2008)

GaAs

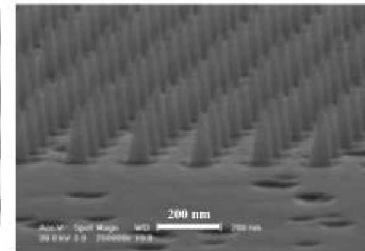


N. Dhindsa et al., Nanotechnology, 25, 305303 (2014)

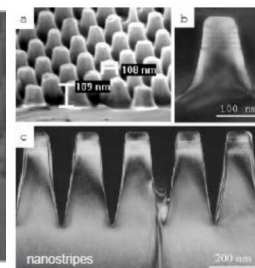
GaN



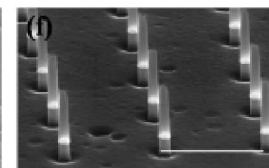
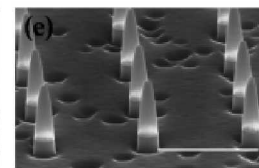
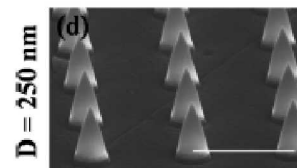
L. Chen et al., PSSa 188 135 (2001)



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



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

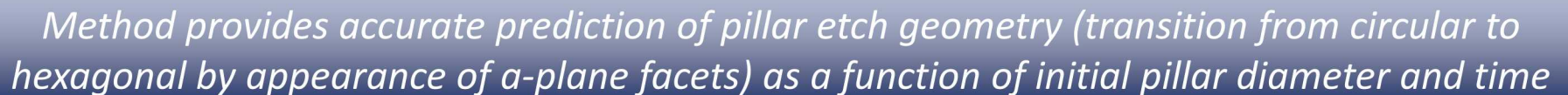


Debnath et al., J. Vac. Sci. Technol. B, 32, 021204 (2014)

- Dry etch on Silicon and GaAs have yielded high aspect ratio and vertical nanowires
- Surface roughness and damage are still an issue.

- Mainly nanoposts with tapered sidewalls

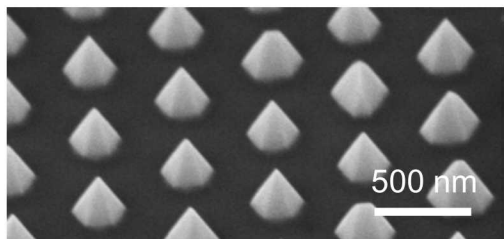
Plasma etching alone is not sufficient to produce high quality, high aspect ratio III-nitride nanowires



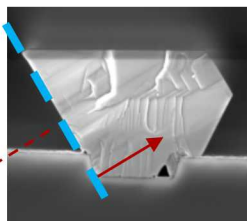
Scientific Motivation

Growth

SAG on *Ga-polar* GaN, bounded by (10 $\bar{1}1$)



SAG of *N-polar* facet, growth rate ~ 0



Ga-polar facet

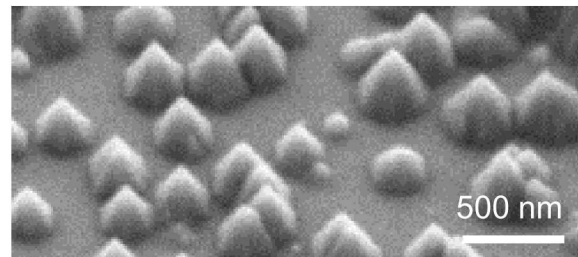
N-polar facet

Growth rate anisotropy –
GaN $> 50:1$

Wet etching

Etch of *Ga-polar* substrates, etch rate ~ 0

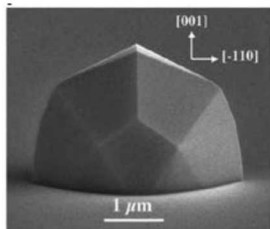
Etch of *N-polar* substrates, bounded by (10 $\bar{1}1$)



Etch rate anisotropy –
 $> 2000:1$

For other materials:

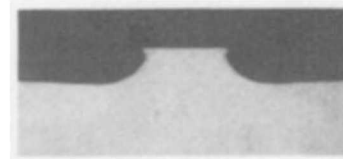
GaAs
SAG



GaAs $\sim 3:1$

Renard et al., J. Cryst.
Growth 401, 554 (2014)

GaAs
etch
profiles



Si $\sim 160:1$, GaAs $\sim 4:1$

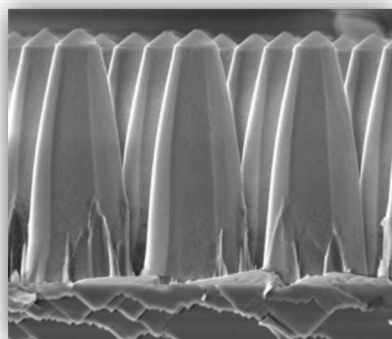


Adach et al., J. Electrochem.
Soc. 130, 2427 (1983)

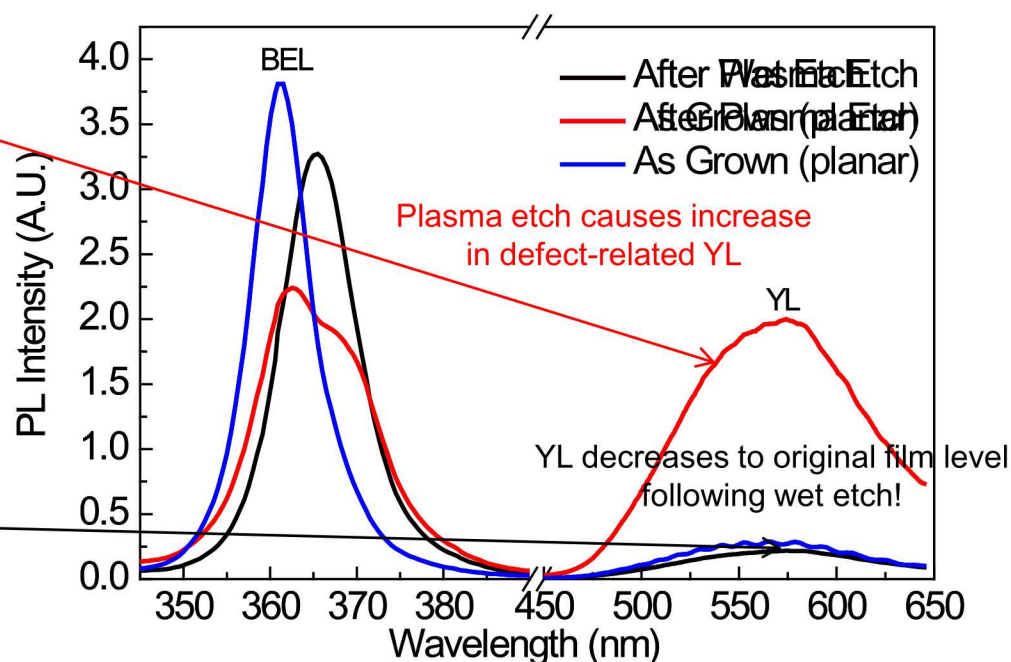
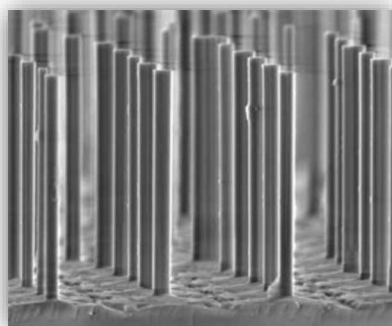
Why is GaN so crystallographically anisotropic?

Wet etch step removes plasma etch damage

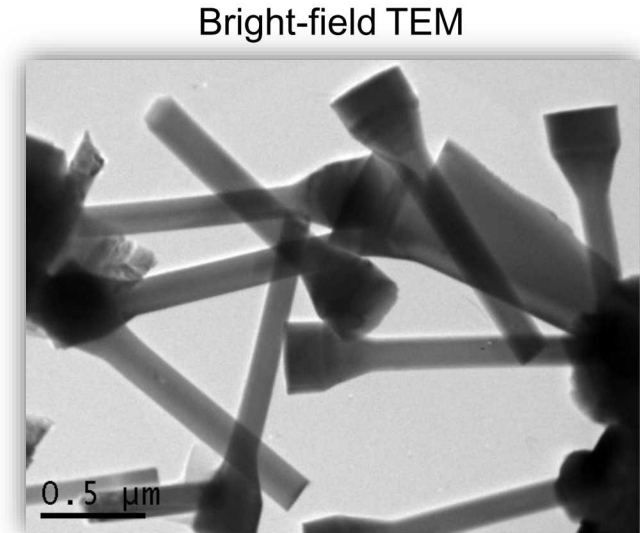
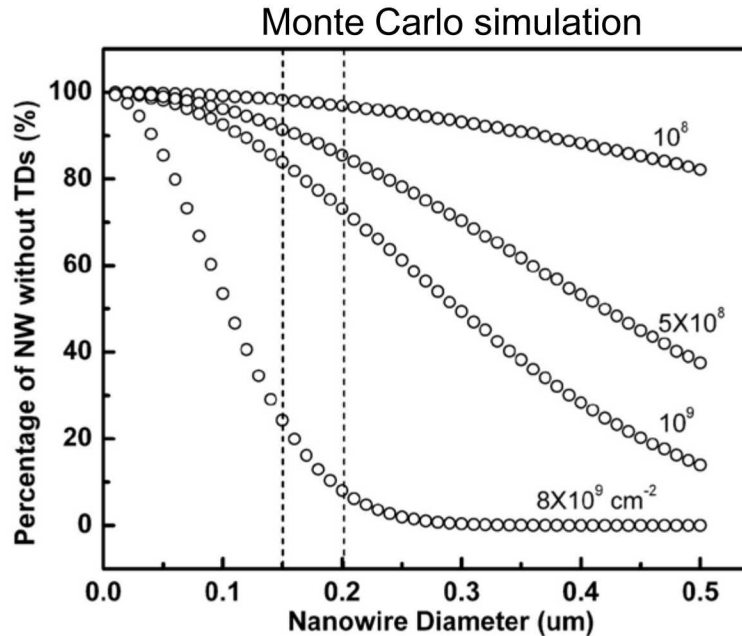
Plasma etch only



After wet etch



Top-down nanowire threading dislocations

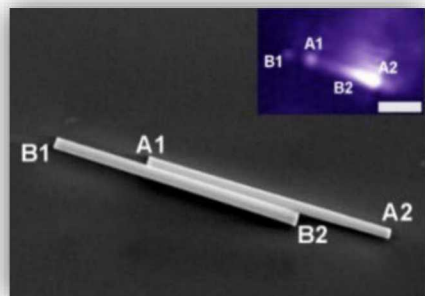


Nanowires etched from $\sim 5 \times 10^8 \text{ cm}^{-2}$ planar LED

- Etched nanowires inherit the dislocation density of the parent film
- However, as the diameter approaches zero, the *fraction* of nanowires with one or more dislocations also approaches zero! [$\# \text{ TDs per rod} \sim (\text{TDD}) \times (A_{\text{cross-section}})$]
- $\sim 94\%$ of nanowires $\sim 150 \text{ nm}$ in diameter from $\text{TDD} \sim 5 \times 10^8 \text{ cm}^{-2}$ film dislocation free!
- *Thus, nanowire LEDs can function as arrays of largely dislocation-free individual lighting elements*

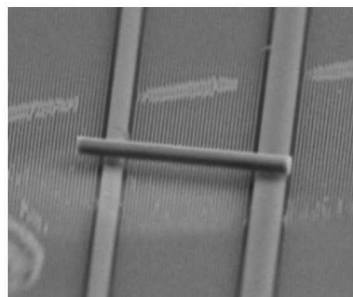
Summary – top down nanowire lasers

Mode & polarization control in GaN nanowire lasers

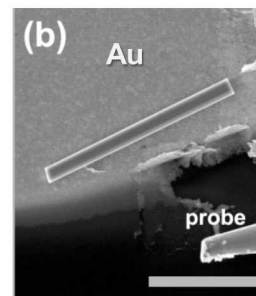


Q. Li et al., *Optics Express* **20** 17874 (2012)

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

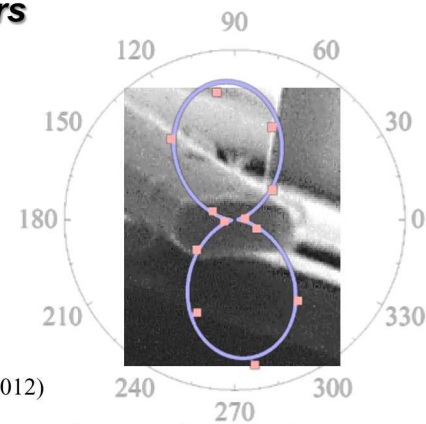


J.B. Wright et al., *Appl. Phys. Lett.*, 104, 041107 (2014)



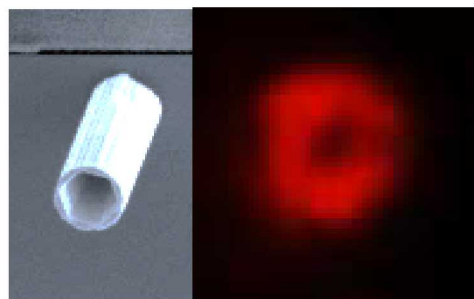
H. Xu et al., *Appl. Phys. Lett.* **101** 221114 (2012)

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



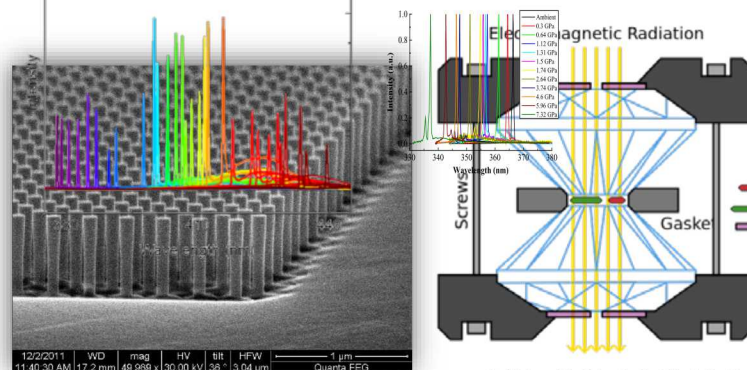
Li, Changyi, et al. *Nanoscale* **8**, 5682 (2016).

Beam shape control nanotube lasers



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

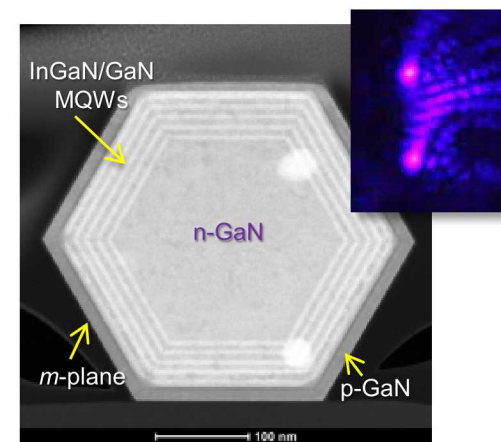
Tunable wavelength nanowire lasers



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).

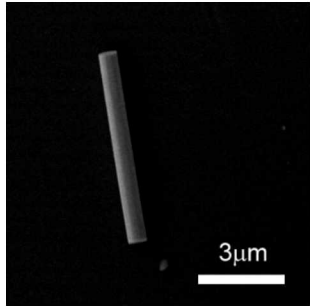
Nonpolar core-shell nanowire lasers



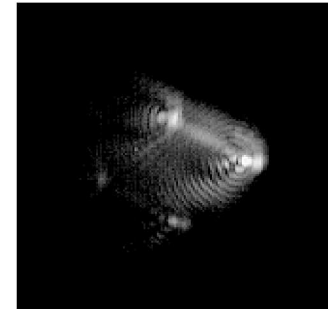
C. Li et al., *Nano Lett*, **17**, 1049 (2017)



Typical GaN Nanowire Lasing: Multimode Operation



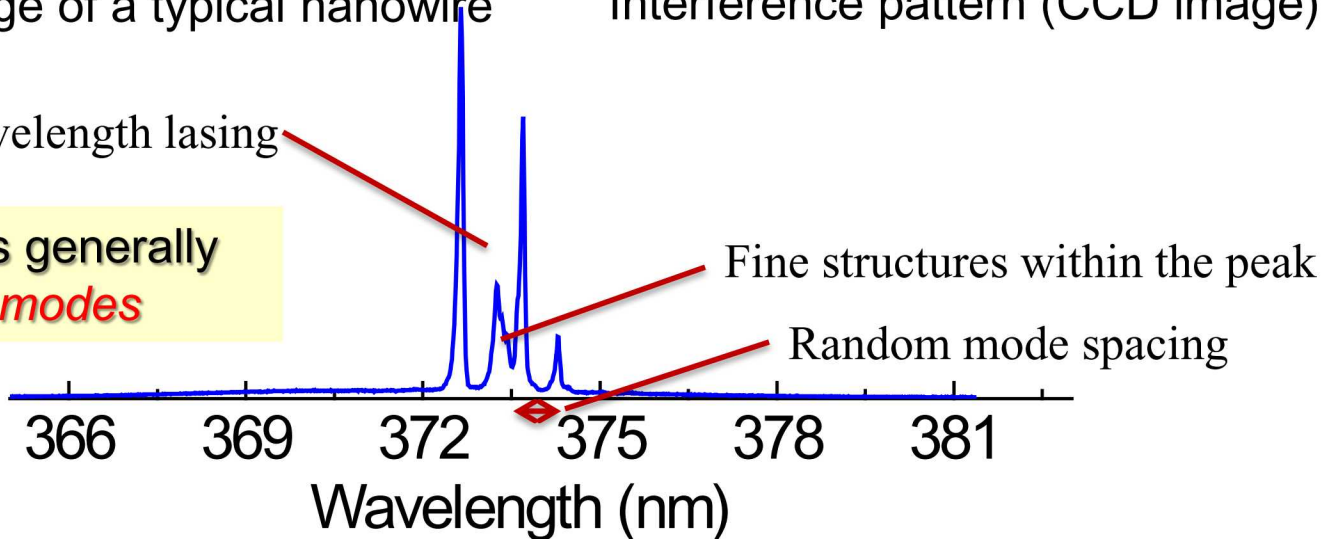
SEM image of a typical nanowire



Interference pattern (CCD image)

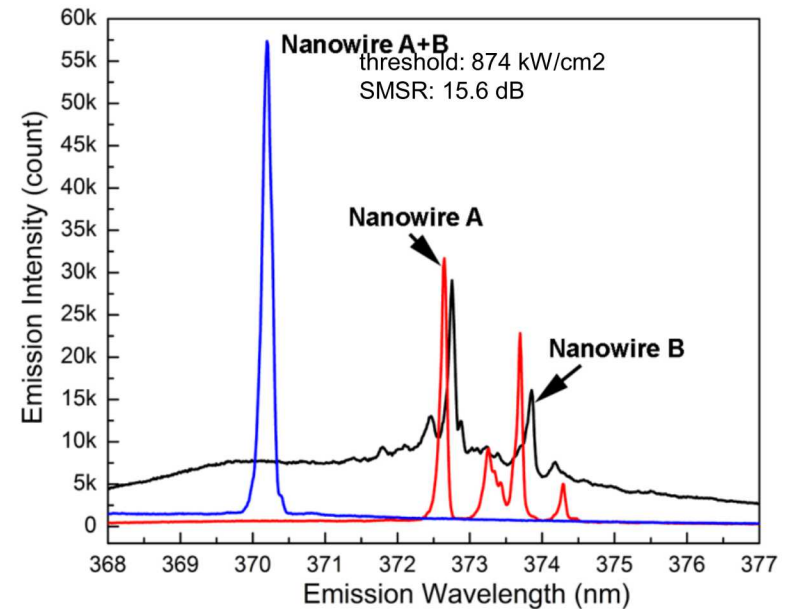
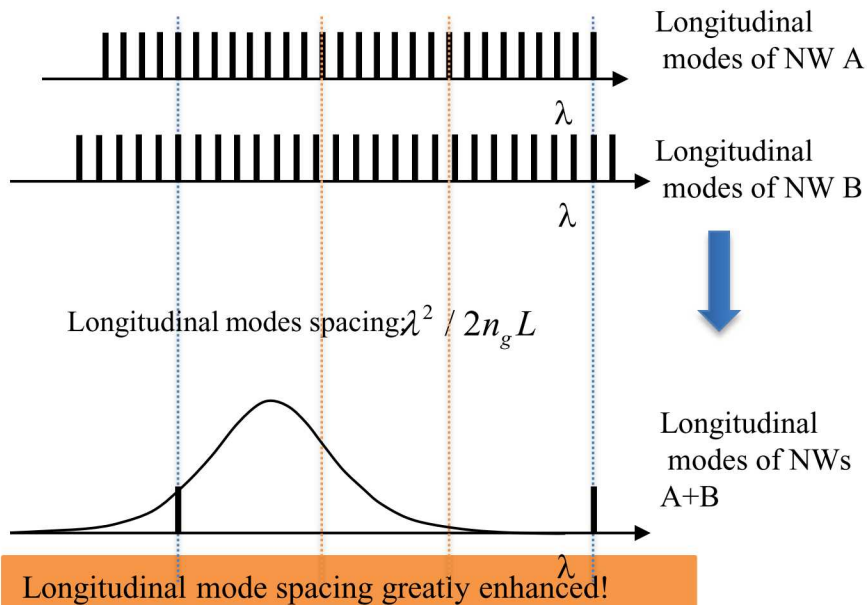
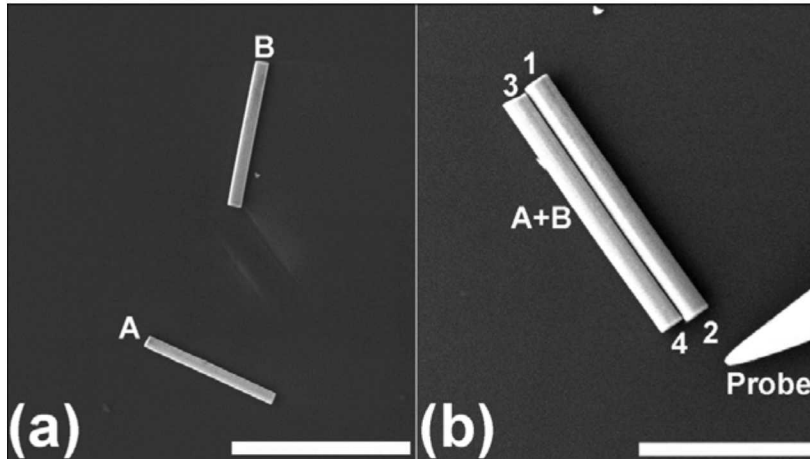
Multi-wavelength lasing

Nanowire lasers generally exhibit *multiple modes*



- *Single mode* behavior desired for highest resolution and beam quality; may also reduce lasing threshold due to reduced mode competition

Method 2: Single-mode lasing via coupled nanowire cavities



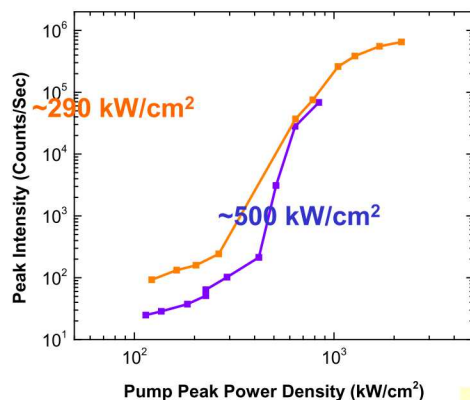
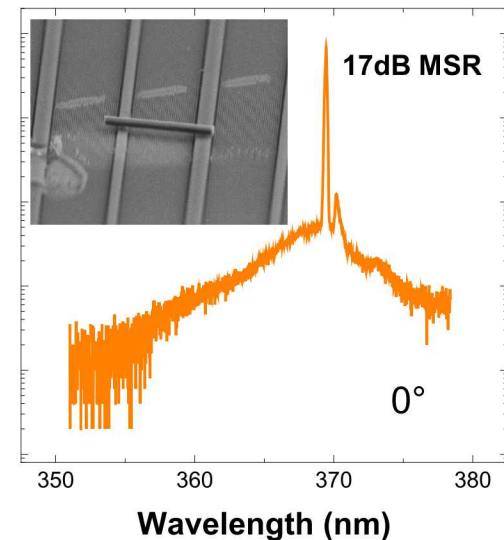
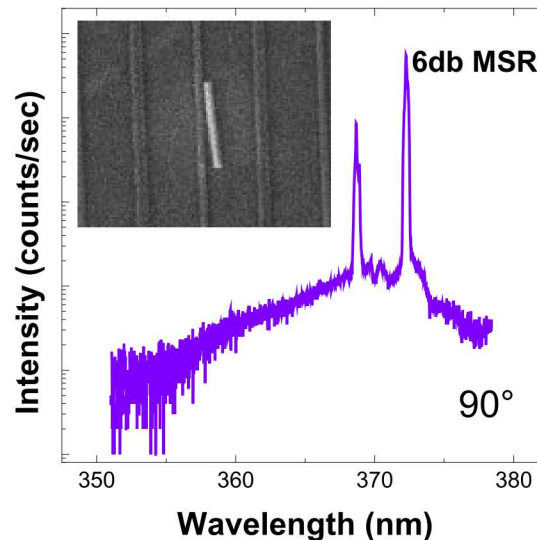
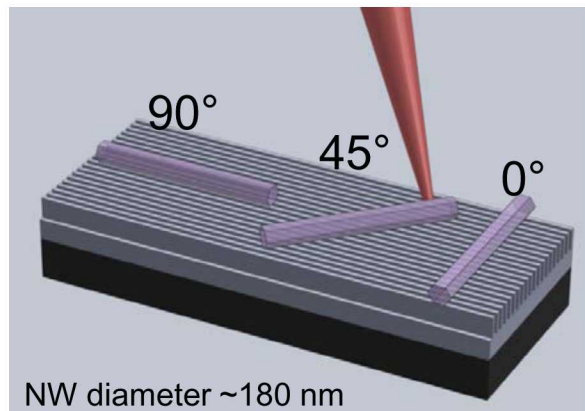
- Individual large NWs shows multiple modes.
- Coupled nanowires show single mode!
- Vernier effect – only resonant modes survive

H. Xu et al., "Single-mode lasing of GaN nanowire-pairs," *Appl. Phys. Lett.* **101** 113106 (2012)



Method 3: Distributed Feedback (DFB) Nanowire Laser

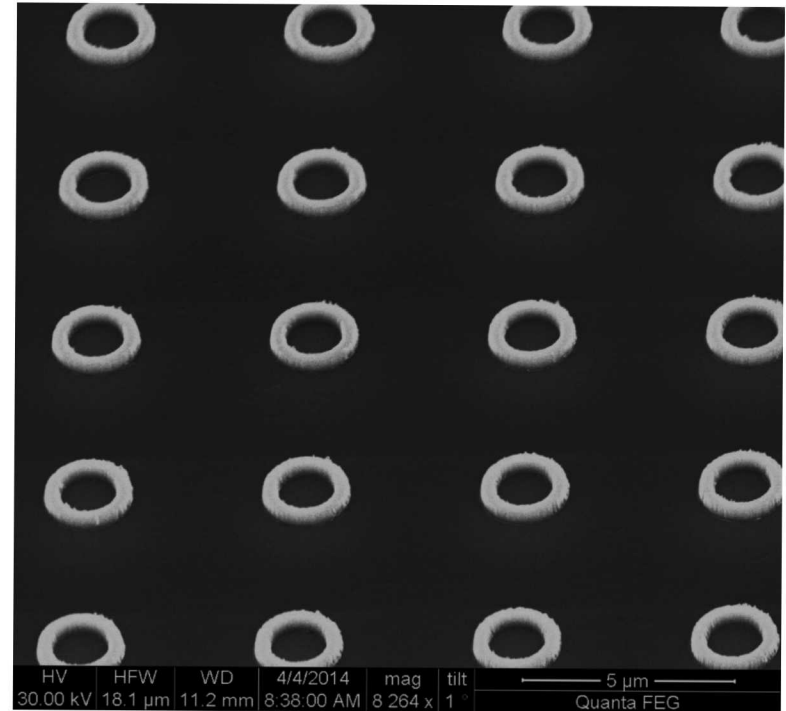
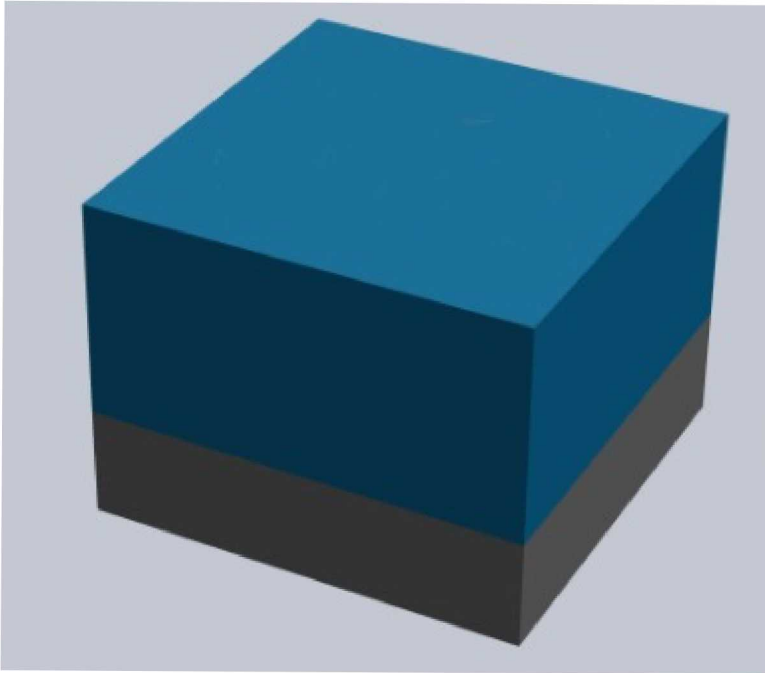
- Standard method for mode control in semiconductor lasers
- Here, single nanowires are coupled to grating substrate to achieve DFB
- Stop-band position and width tuning via nanomanipulation of the angular alignment



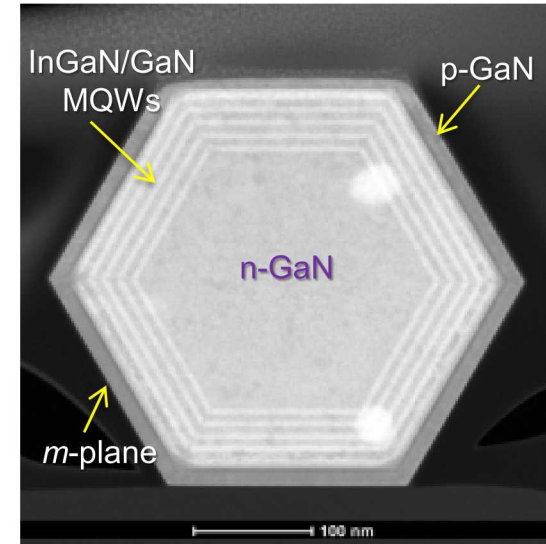
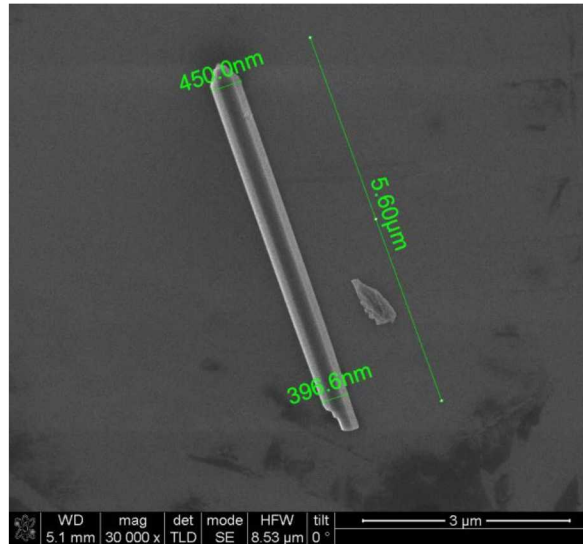
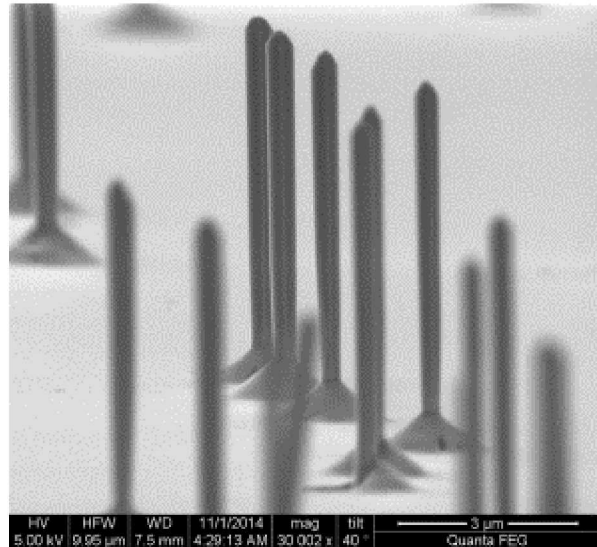
- At the designed alignment single-mode lasing was achieved with a 17dB mode suppression ratio.
- Observed reduction in the lasing threshold

Cross-sectional shape control - GaN nanotubes

EBL Patterning
AZ4062 Photoresist
GaN Growth
MMA Lift-off

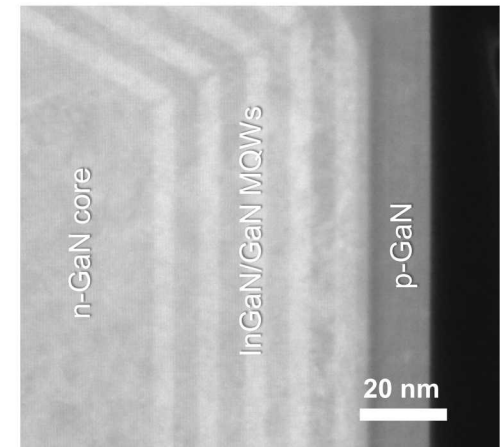


Hybrid top-down bottom-up fabrication of core-shell p-i-n InGaN/GaN core-shell NWs



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

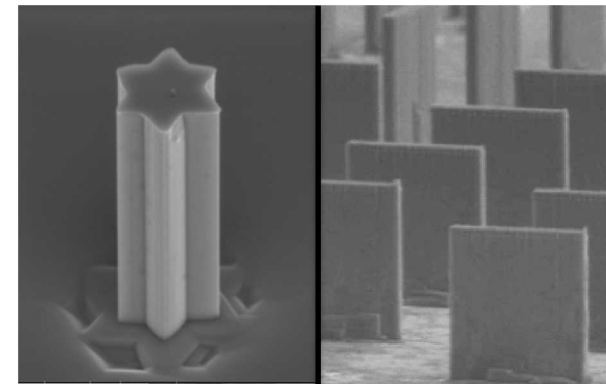
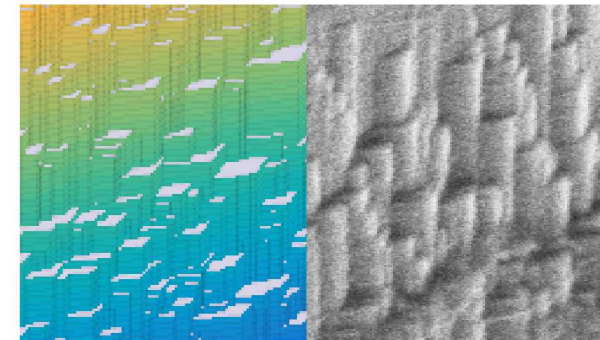
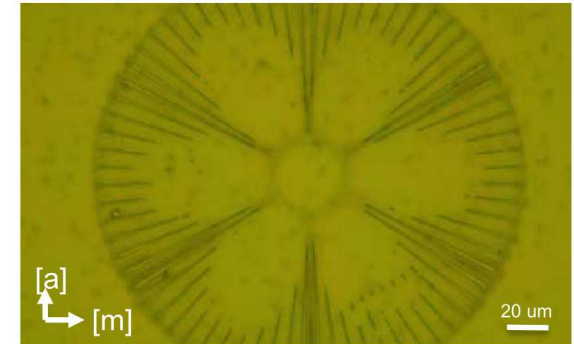
- Regrowth on top-down n-GaN nanowire results in taper. Growth of semipolar planes also results in non-flat tip, which may lower mirror reflectivity
- Growth conditions, layer thicknesses, varied over several runs, then nanowires tested by optical pumping for lasing



STEM by Ping Lu

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

- **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**

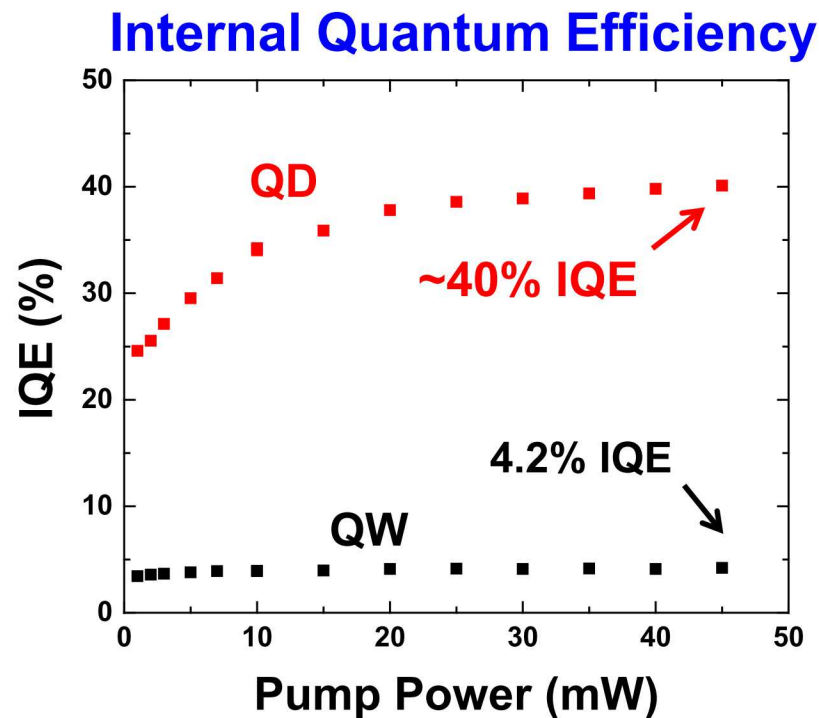
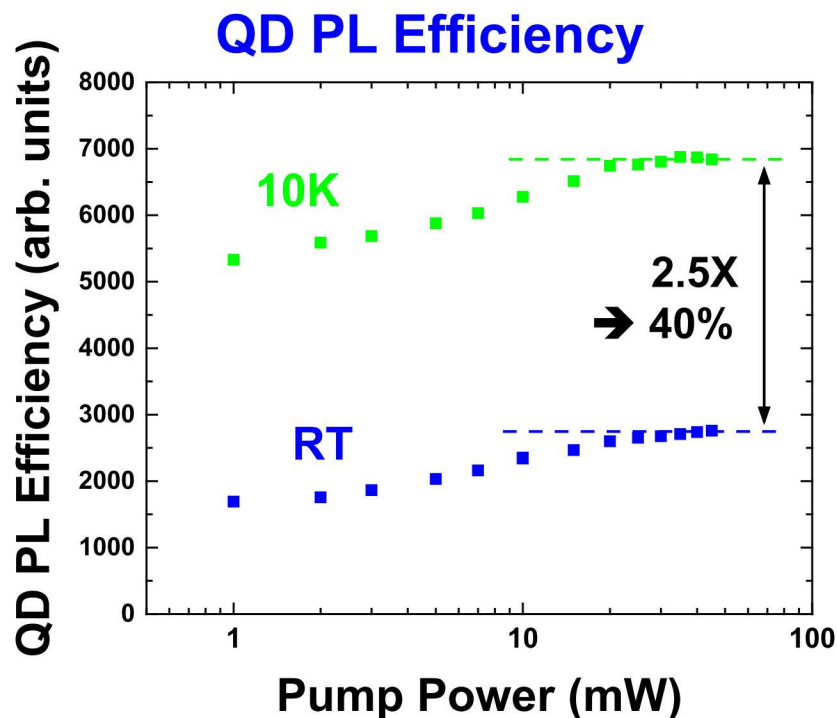


InGaN QD internal quantum efficiency

Capped InGaN QW



- Compare 10K and RT PL efficiency
- Assumes 10K PL is 100% efficient
- PL Intensity drops by >100X after QD etching
- IQE goes up by almost 10X after QD etching



Summary

20 nm

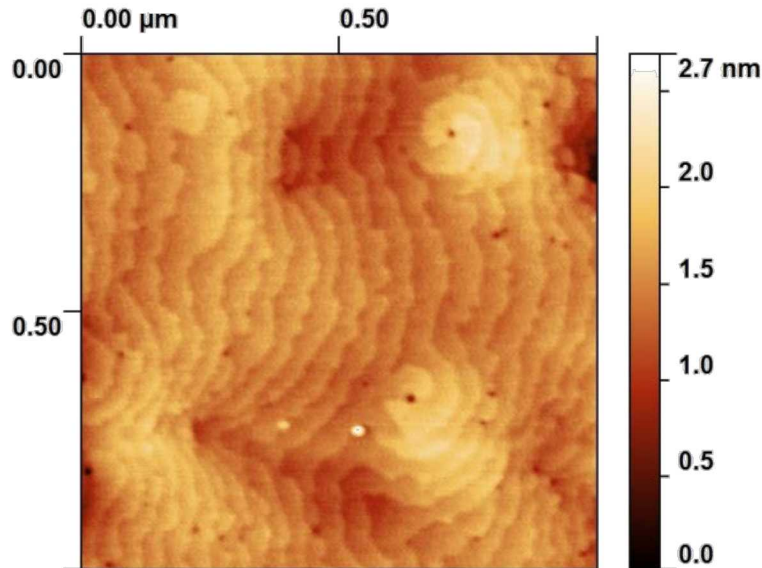
- Demonstrated controlled fabrication of InGaN QDs from epitaxial layer using quantum-size controlled PEC etching
 - AFM data indicates extremely high QD density ($\sim 10^{11}$ per cm^2)
 - PL linewidth reduced from 24 nm to less than ~ 6 nm, indicating improved QD size distribution vs. Stranski-Krastanov grown InGaN QDs (~ 30 -40 nm)
 - PL measurements show significant enhancement of IQE for etched QDs vs initial QW
 - QD size and PL emission determined by PEC etch wavelength used
 - Multiple layers of QDs demonstrated, but with lower per-layer density
 - Challenges remain in passivating the etched QDs and demonstrating for other materials systems



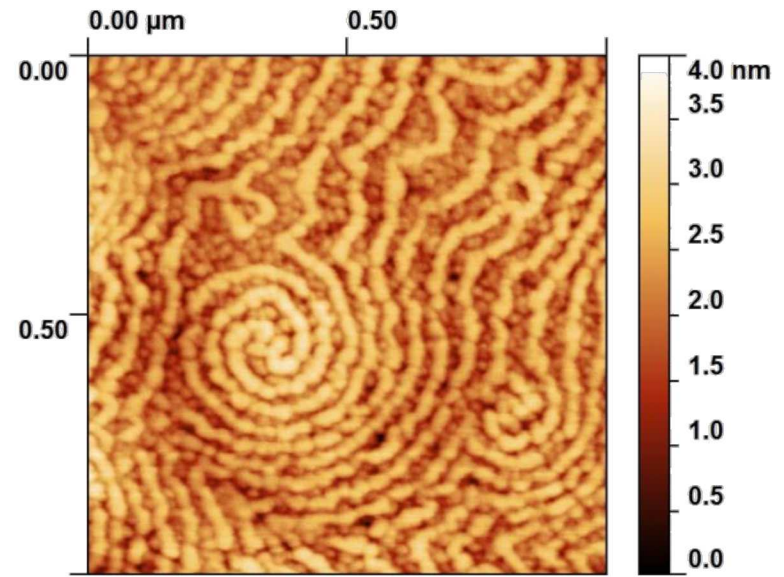
QSC-PEC Etch Evolution of InGaN QDs

Goal: Identify and investigate mechanism of film transition to dots

- Analysis of AFM images indicates initial dot distribution is not random, as originally assumed
- Dot/island “nucleation” along step edges?
- QD distribution and density may be controllable by initial surface morphology



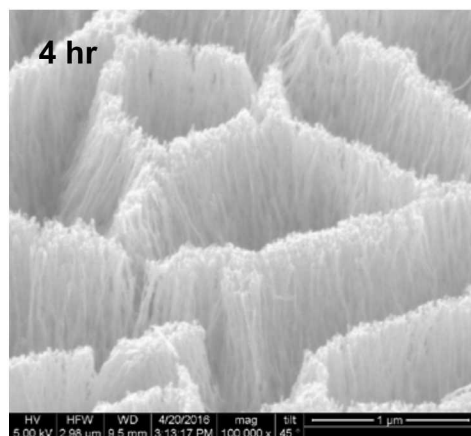
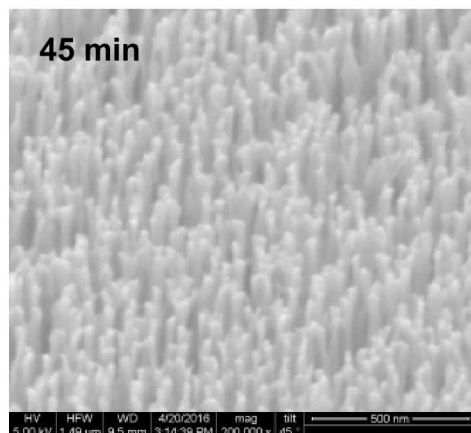
unetched



PEC etched 0.5 V

PEC etched GaN nanowires with very high aspect-ratios

PEC etch: 370 nm, 4 mW,
1V, 2M H₂SO₄



- 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

