SAND2012-4500P

III-Nitride Nanowires: Novel Materials for Lighting and Photovoltaics

Solid-State Lighting Science Energy Frontier Research Center
Sandia National Laboratories, Albuquerque, NM

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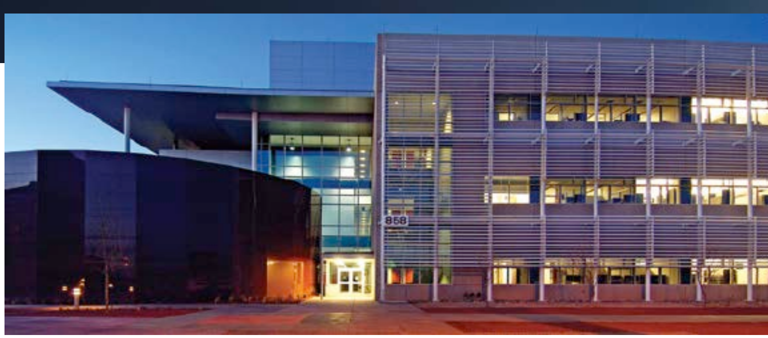

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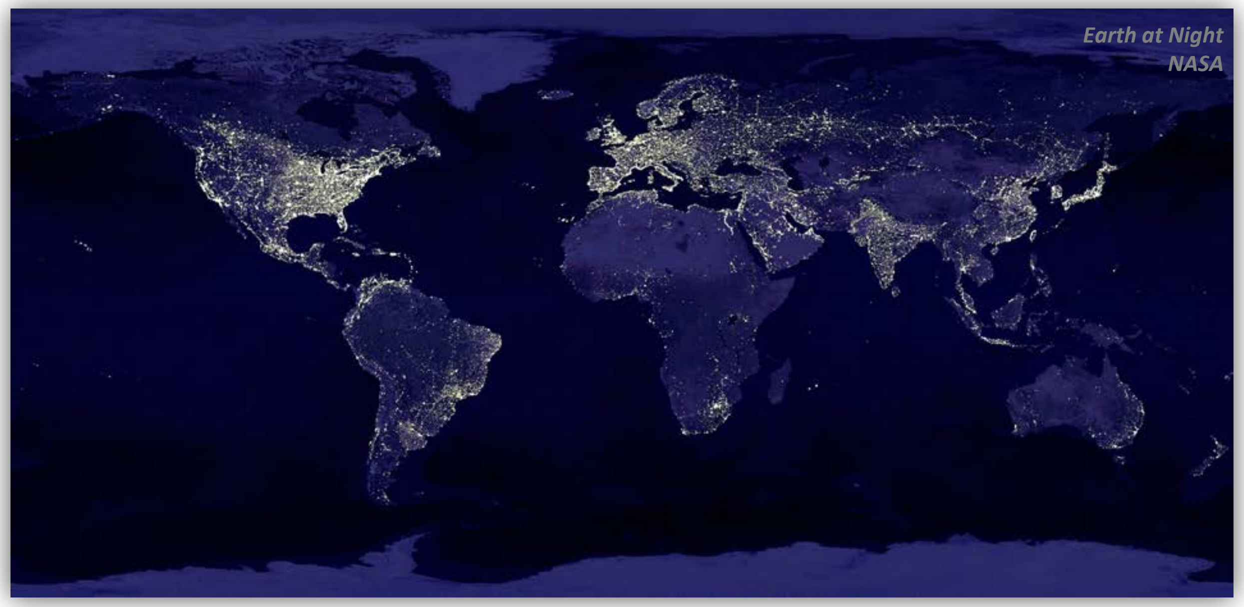
Outline

- Solid-state lighting (SSL) overview
- Why nanowires for SSL?
- Bottom-up nanowires
    - Growth, characterization, nanowire-templated film growth
- Top-down nanowires
    - Fabrication, axial and radial LEDs, solar cell, lasers
- Summary

Lighting is a large fraction of energy consumption and is low efficiency



Efficiencies of energy technologies in buildings:

Heating:	70 - 80%
Elect. motors:	85 - 95%
Fluorescent:	**~17%**
Incandescent:	**~4%**

Lighting is one of the most *inefficient buliding* energy technologies → opportunity!

*~**22%** of US electricity use is for general illumination (~1/15 world's energy, $330B in 2005)*

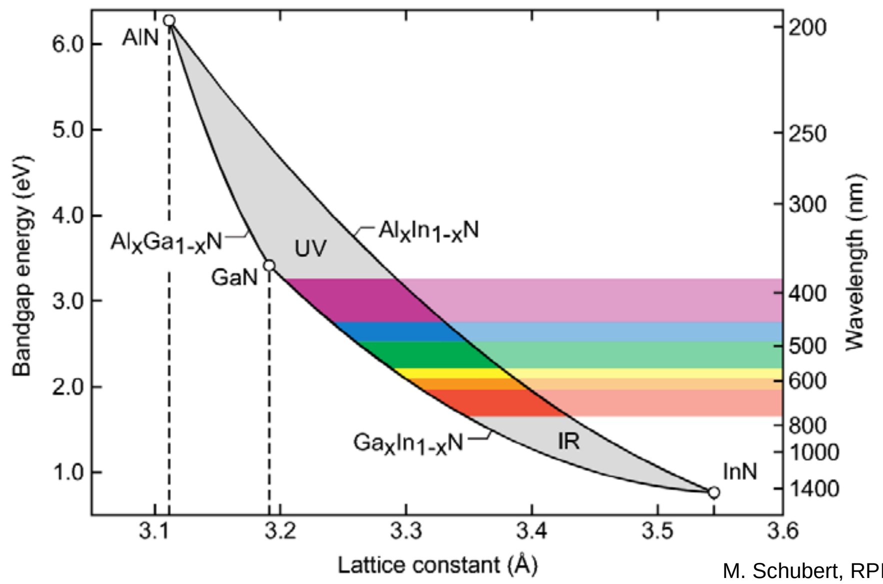
Current SSL efficiency: ~20%
US DOE target: 50%
"Ultra-efficient" SSL*: ≥ 70%

2011 Philips L-prize 60W equivalent (940 lumens) 10W LED light bulb replacement http://www.lightingprize.org/philips-winner.stm $49 (as of May 2012)

Achieving 50% or greater efficient lighting would have tremendous global impact!

Foundation of SSL: III-Nitride (AlGaInN) Semiconductors

- **Direct RT bandgaps: ~0.7-6.2 ev**
- Solid alloy system (tuneable bandgaps)
- High breakdown field, mobility, thermal conductivity, melting temperature
- Radiation resistant and chemically inert
- InGaN covers entire visible & bulk of solar spectrum (PV material?)



M. Schubert, RPI

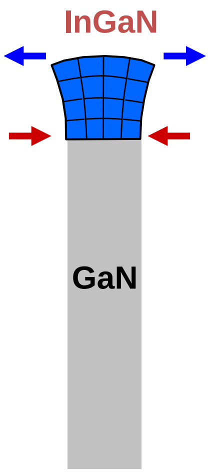
- *Used in LEDs, blue laser diodes, high power transistors, HEMTs*

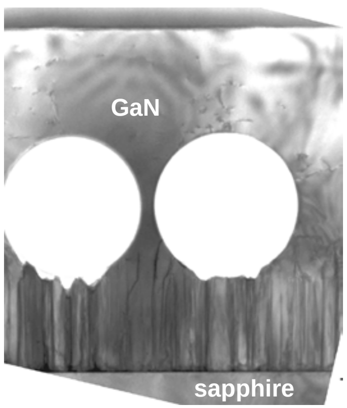
Nitronex GaN power transistor

Why III-nitride (AlGaInN) nanowires for SSL, PV, etc.?

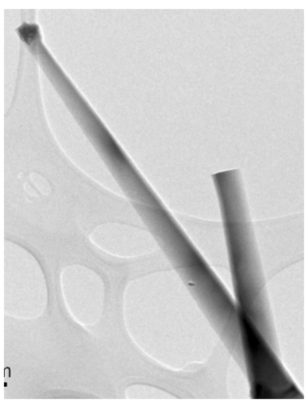
Strain accommodation

Nanowire attribute	SSL Benefit
Few or no threading dislocations	IQE, device lifetimes
Growth on variety of substrates	Cost, flexibility
Reduced piezoelectric strain	IQE (less QCSE)
Wider range of alloy compositions possible	Wider color space (green-yellow-red)

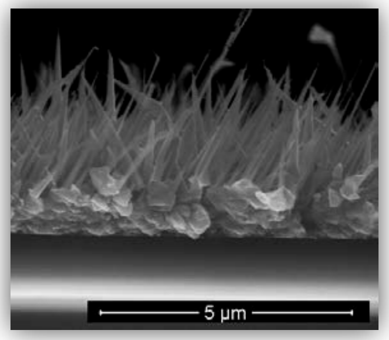




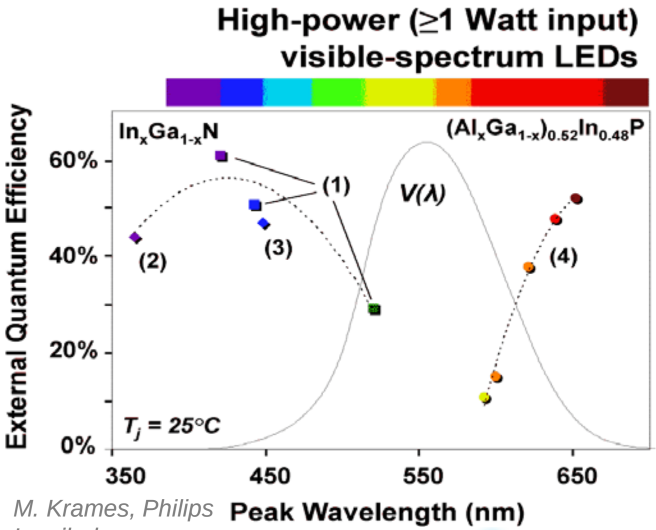
GaN on sapphire
(SiO_2 spheres for dislocation blocking**)**



Dislocation-free GaN NWs



GaN NWs on tungsten foil

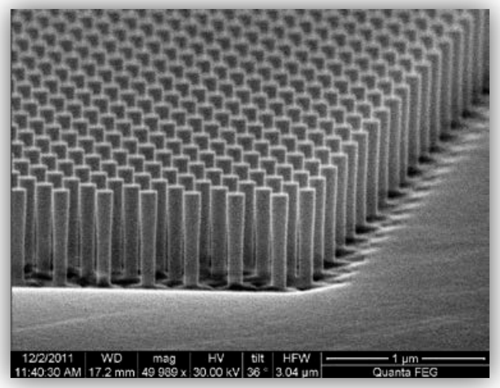


M. Krames, Philips Lumileds

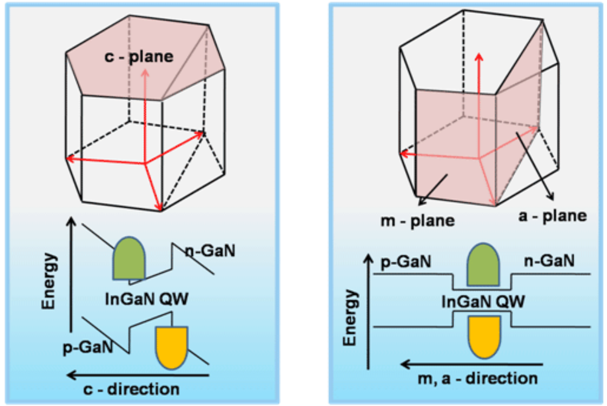
Why III-nitride (AlGaInN) nanowires for SSL, PV, etc.?

Size, geometry

Nanowire attribute	SSL Benefit
2D arrangements, e.g. photonic crystals	Enhanced/controlled light extraction, enhanced radiative recombination (IQE)
Vertical 3D device integration	High surface/device area = lower cost;
Non-polar, semi-polar facets	Reduced polarization effects (IQE)
Lasers	Lower threshold lasers; reduced eff. droop
Discrete; all of the above	Scientific test system

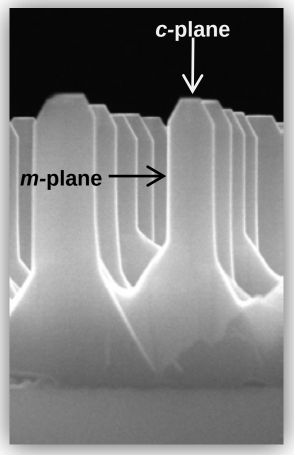


GaN NW photonic crystal



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

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



GaN/InGaN MQW NW

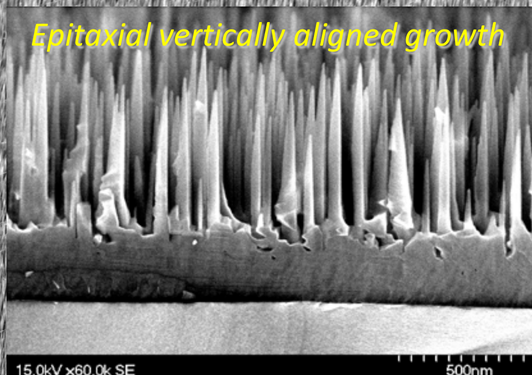
NW lasing (lying down)

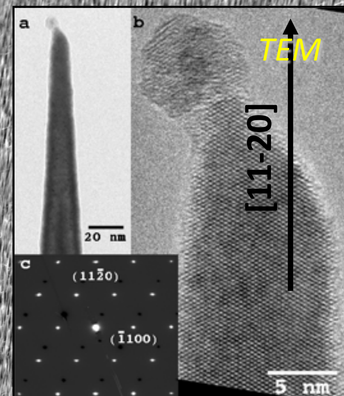
SSLS EFRC

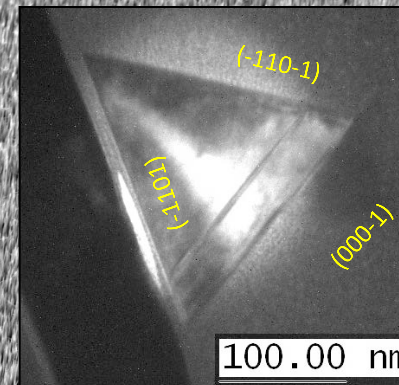
Bottom-up III-Nitride Nanowires

Research Highlights

"Bottom Up" aligned GaN nanowire growth



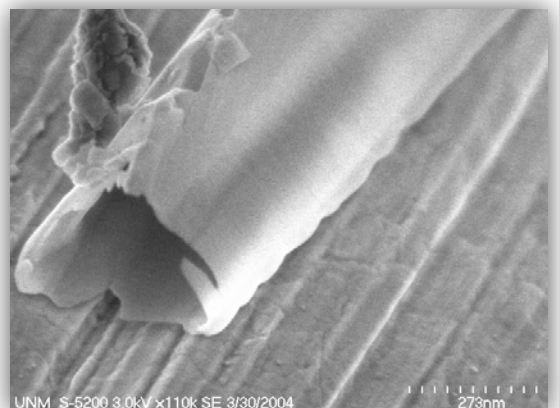




- Nanowires grown by Ni-catalyzed MOVPE/MOCVD (VLS)
- Highly-aligned vertical growth over large areas (2" r-sapphire wafer)
- Controllable densities as high as ~150 nanowires μm^{-2}
  - **Q. Li, G. T. Wang, *Appl. Phys. Lett. 93, 043119* (2008)**
  - **Q. Li, J. R. Creighton, G.T. Wang. *J. Crys. Growth 310 3706-3709* (2008)**
- Primary [11-20] growth orientation (⊥ to (11-20) *a*-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)**

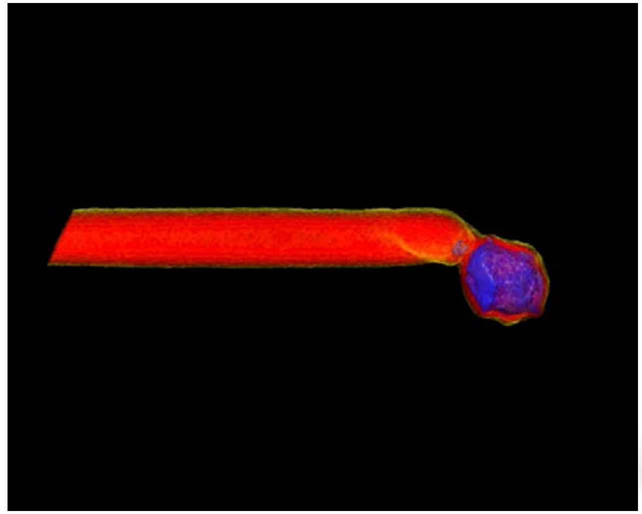
100 µm

Radial heterostructure nanowire growth

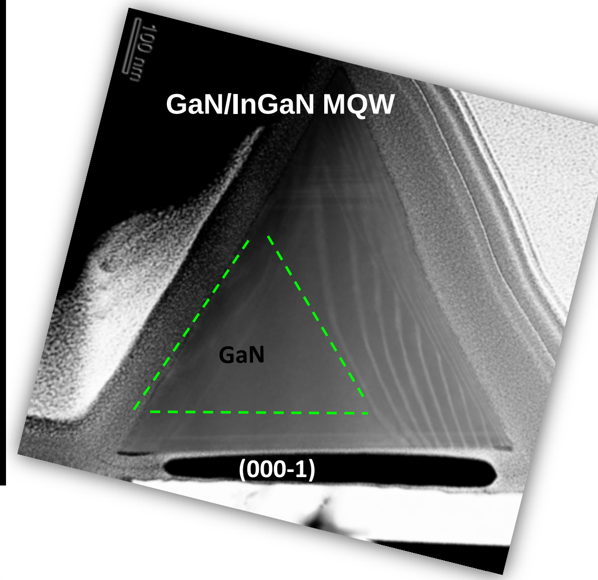


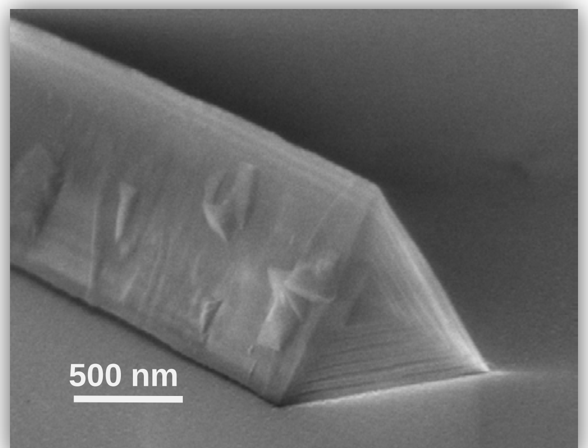
G. Stan et al. , *Nanotechnology*, ***20***, **2009**

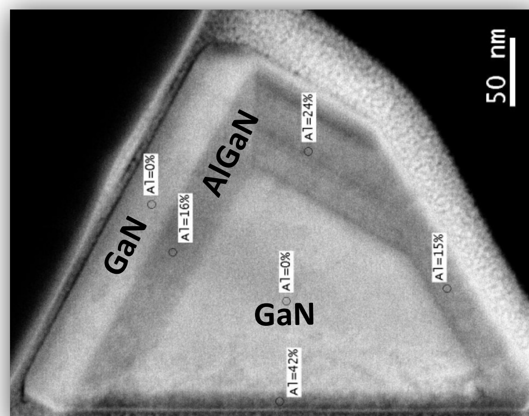
AlN Nanotubes



GaN/AlN NW

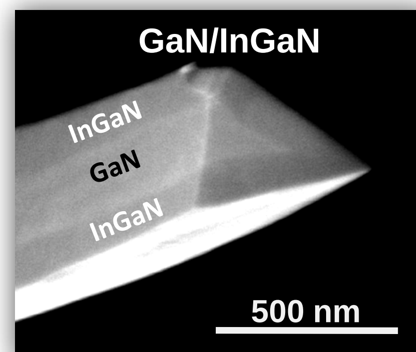




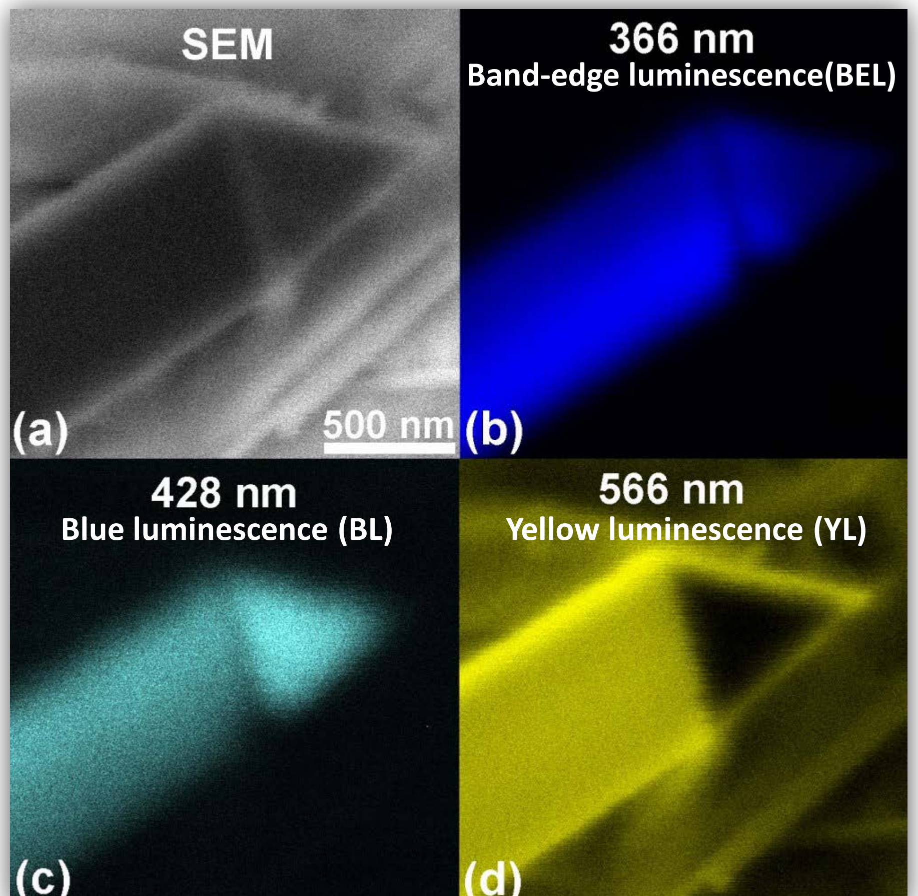


GaN/AlGaN/GaN

Double heterostructure



Spatial distribution of luminescence in GaN NWs



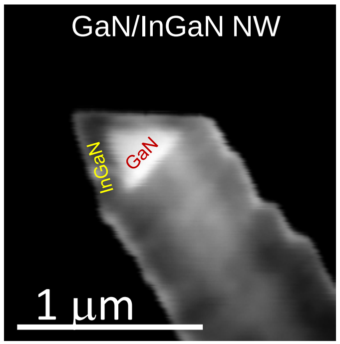
***Nanoscale Cathodoluminescence (CL) imaging:* Cross-section GaN NW**

- 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_{Ga}-O_N (D ~2.2 eV), less mobile

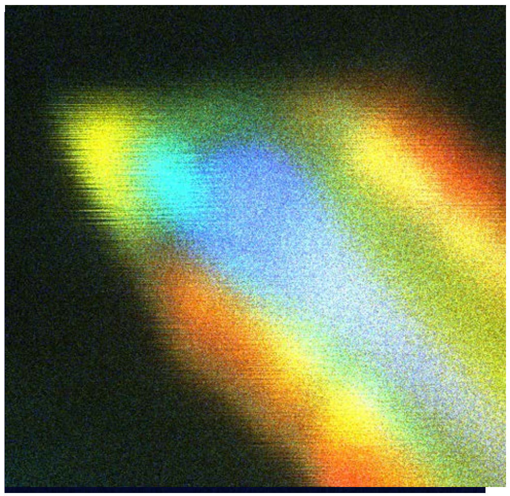
Q. Li, G. T. Wang, *Nano Lett.*, 2010, 10 (5), 1554

Highlight: Core-shell NWs – A good platform for high In InGaN?

- ***Issue: Strain limits In incorporation in InGaN thin films (green-yellow-red gap)***
- Radial core-shell NWs: much higher active region area than axial NW or planar heterostructures

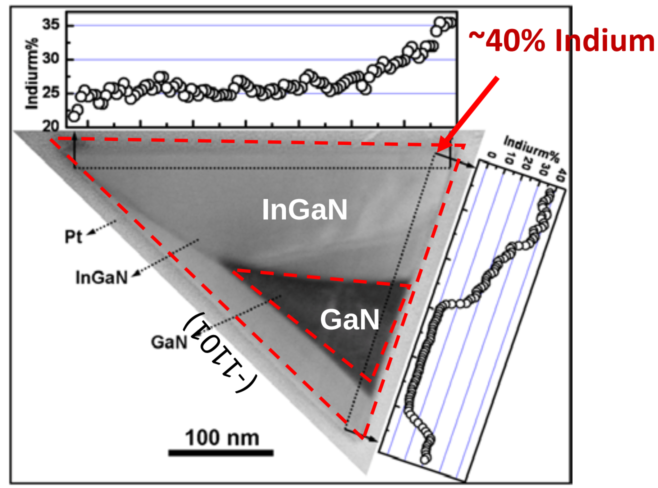


GaN core – 900 ˚C, 10 min.
InGaN shell – 760 ˚C, 60 min.



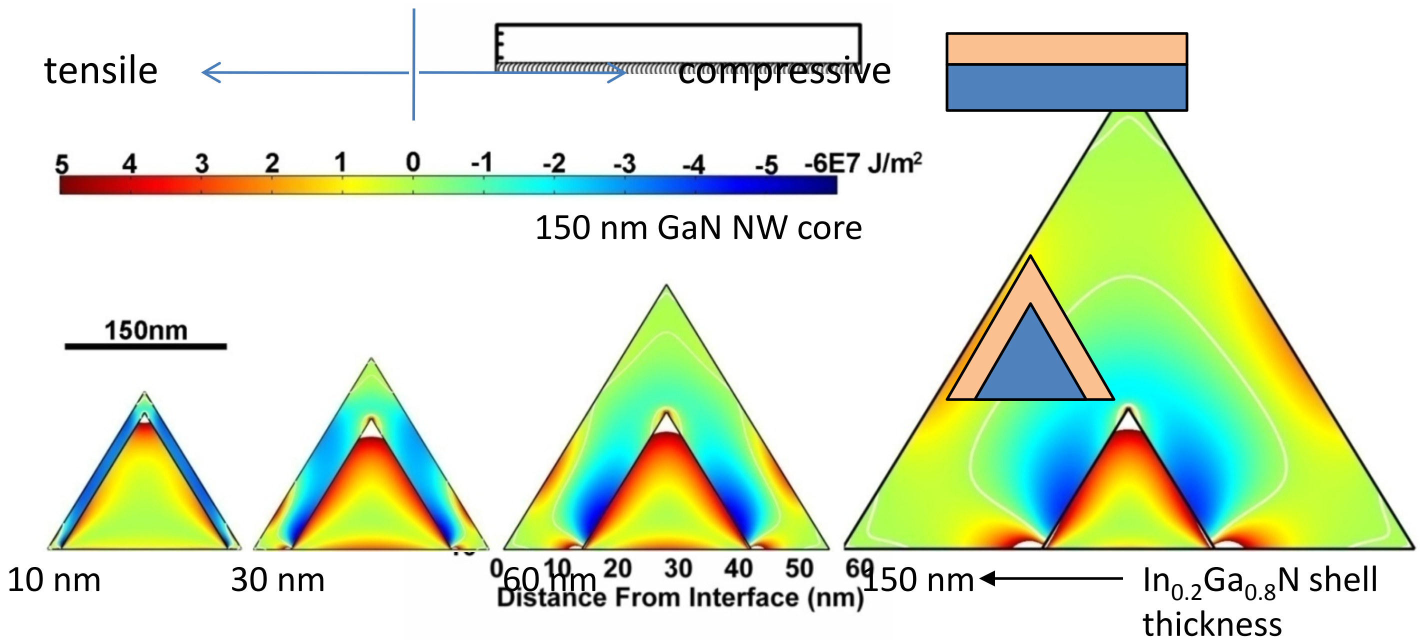
CL shows strong multicolor emission up into the IR!

- **high In incorporation with high material quality**
- nonuniform In composition?



STEM/EDS shows In distribution, **highest at surface/corners**

Reduced strain in nanowires allows higher In incorporation

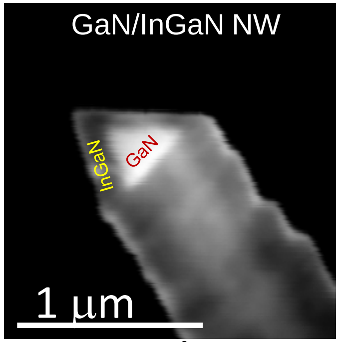


- Strain lower for GaN/InGaN nanowire than for GaN/InGaN thin film
- Compressive strain decreases away from GaN/InGaN interface, lowest in corners

Q. M. Li, G. T. Wang, "*Appl. Phys. Lett.*, ***97***, 181107 **2010**.

Highlight: High In incorporation in GaN/InGaN core-shell NWs

- ***Issue: Strain limits In incorporation in InGaN thin films (green-yellow-red gap)***
- Radial core-shell NWs: much higher active region area than axial NW or planar heterostructures



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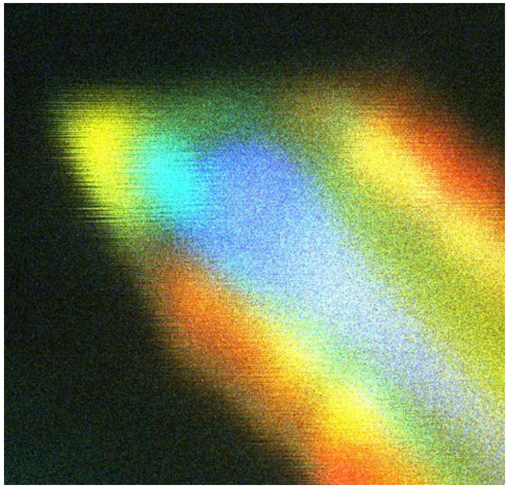
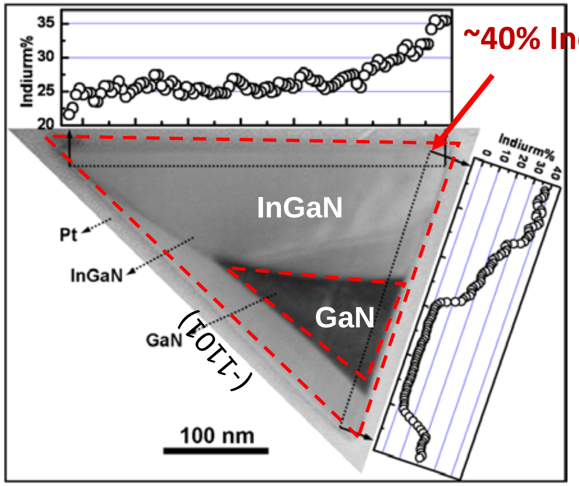
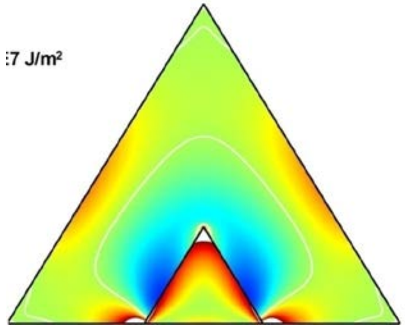






CL shows strong multicolor emission up into the IR!

- **high In incorporation with high material quality**
- nonuniform In composition?

STEM/EDS shows In distribution, **highest at surface/corners**

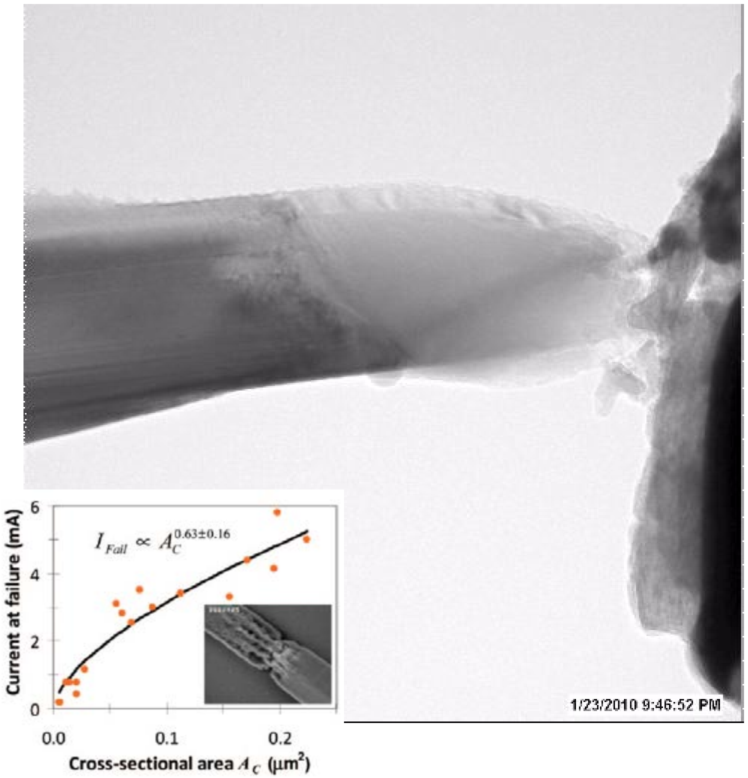
2D FEA: highest In regions correlated w/lowest compressive strain regions

Q. M. Li, G. T. Wang, "*Appl. Phys. Lett.*, ***97***, 181107 **2010**.

Radial InGaN/GaN nanowires promising for addressing green-yellow-red gap

In-situ TEM studies

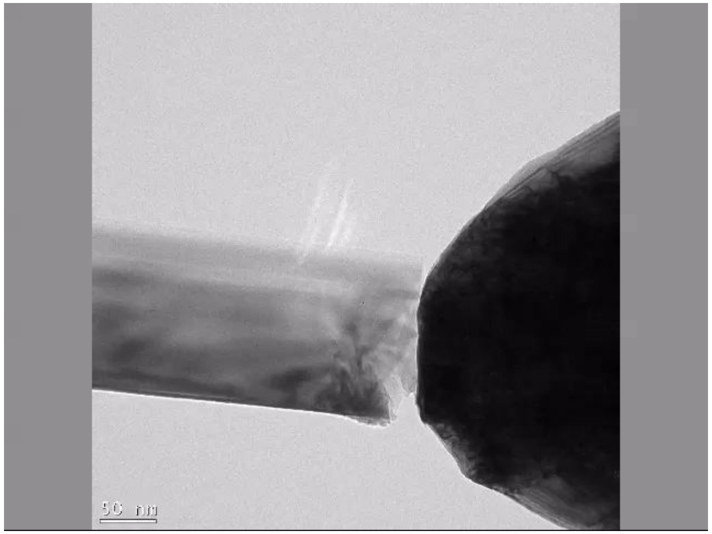
GaN NW decomposition via Joule heating
(relevant for NW devices)



NW breakdown at 60V, 20 μA
(avg. breakdown I ~3000 kW/cm²)

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

Local plastic deformation of GaN NW
(relevant for NW devices)

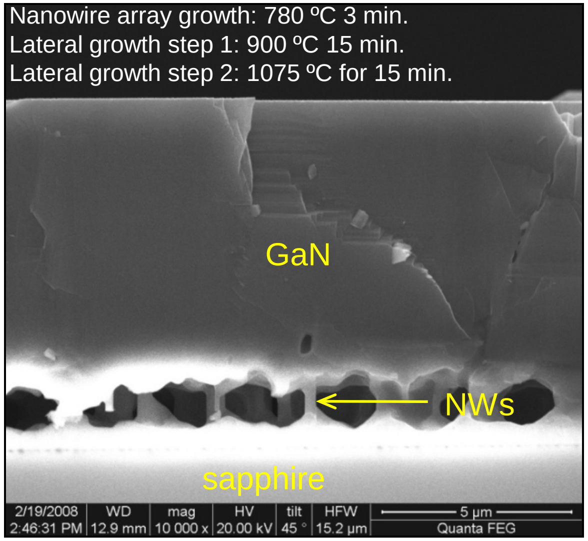


- Dislocation-free NW shows significant surface plastic deformation
- Mediated by dislocation nucleation & pile up, grain boundary sliding

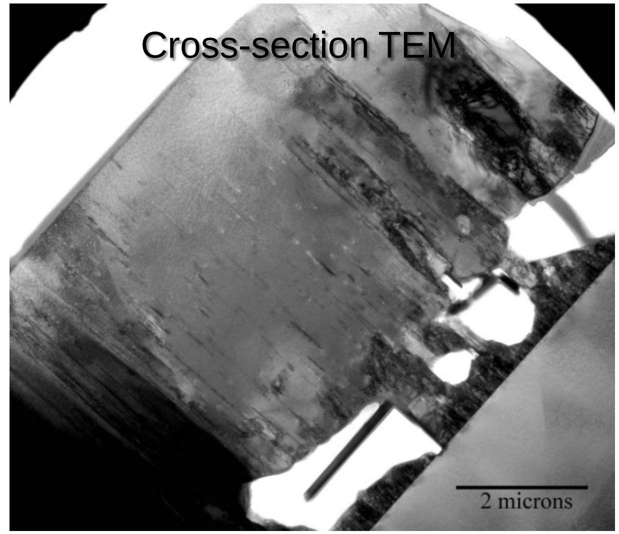
J. Y. Huang, H. Zheng, S. X. Mao, Q. Li, and G. T. Wang, *Nano Lett*, **11 (4),** 1618 (2011).

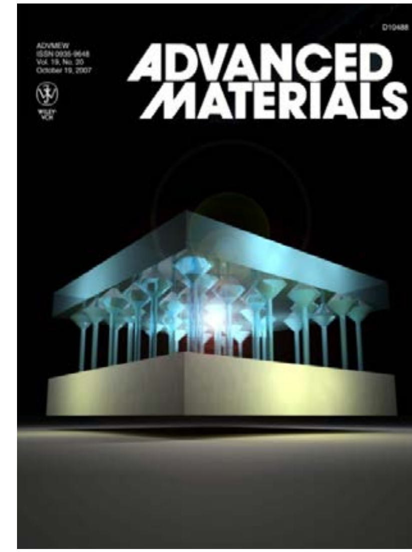
Nanowire-templated lateral epitaxial growth (NTLEG) of GaN

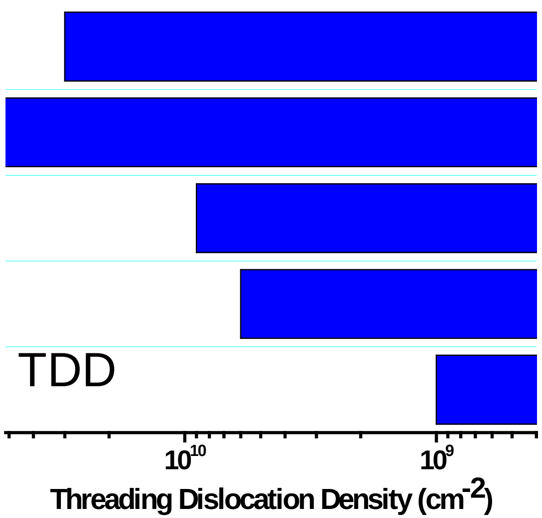
Inexpensive method to reduce dislocation density in GaN films growth on lattice mismatched substrates



Cross-section SEM







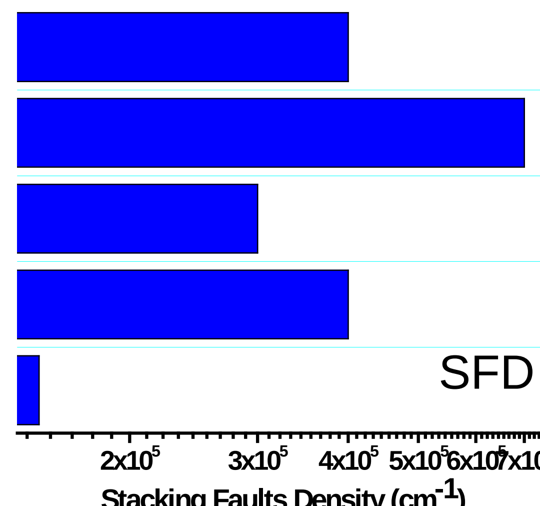
Craven et al., *APL* 81(2002), 469 (LT nucl. Layer)

Chakraborty et al. *APL* 89(2006), 041903 (LT nucl. Layer)

Chakraborty et al. *APL* 89(2006), 041903 (SiNx Nanomask)

Qian et al, *JAP* 106(2009), 123519 (HT AlN nucl. Layer and 3-step growth)

Li et al. *Adv. Mat.*, 21(2009), 2416 (NTLEG) THIS WORK



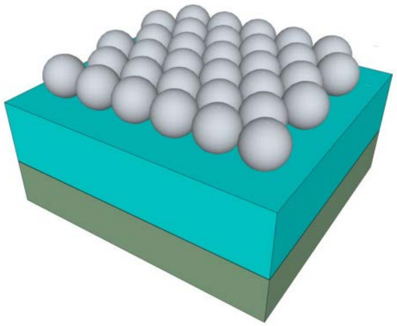
Q. Li, Y. Lin, J. R. Creighton, J. J. Figiel, and G. T. Wang, *Adv. Mat.*, **21**, 2416–2420 (2009)

SSLS EFRC

Top-down III-Nitride Nanowires

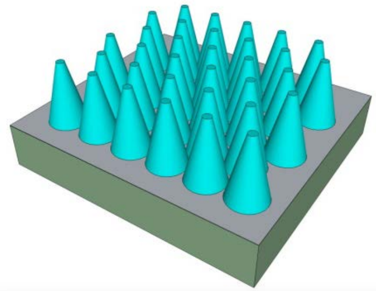
Research Highlights

New dry + wet top-down ordered nanowire fabrication process

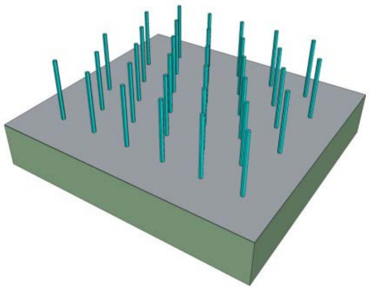


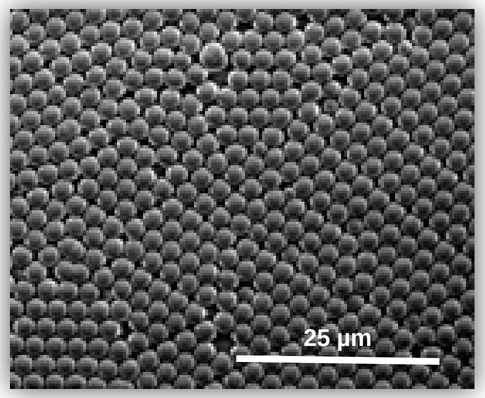
(0001) GaN on sapphire

ICP etch

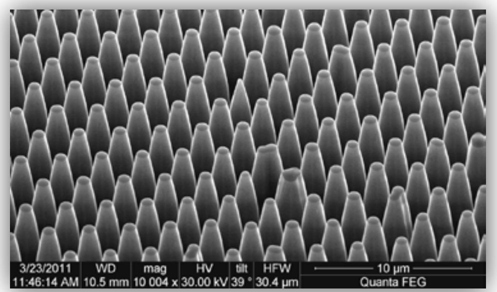


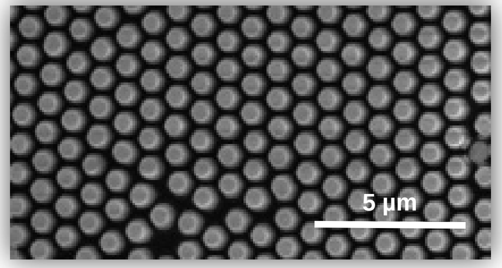
Selective wet etch
(AZ-400K developer)





Q. Li, J. J. Figiel, G. T. Wang, Appl. Phys. Lett., **94**, 231105 (2009).

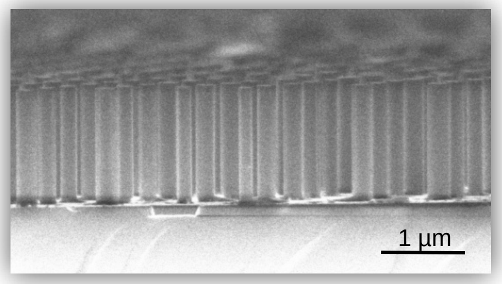


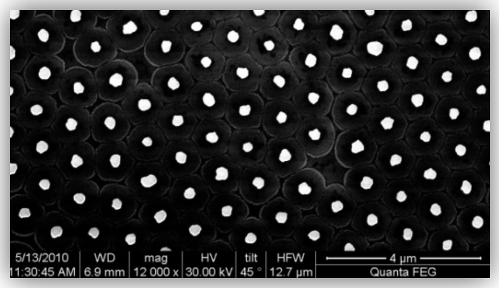


Plasma etch causes sidewall damage

C. Y. Wang et al., Opt. Expr. *16,* 10549–10556, 2008.

Tapered; no well-defined facets



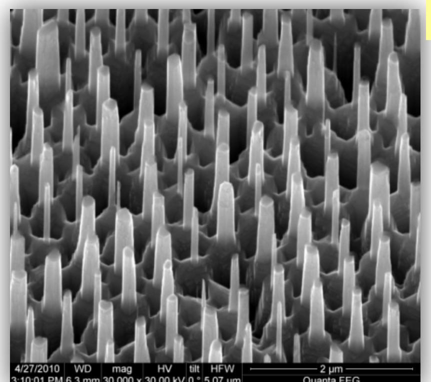


Wet etch: straight sidewalls, removes sidewall damage

Straight GaN nanowires with controllable geometries

Wet etch rate negligible for top *c*-face & fast for {10-10} *m*-facets, leads to hexagonal NWs with **straight & smooth** *m*-facets

0.5 µm sphere size

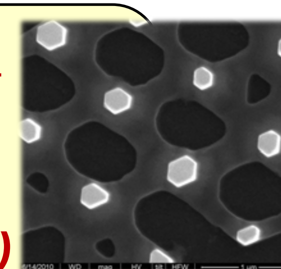


<u>*New fabrication method allows for superior control of:*</u>

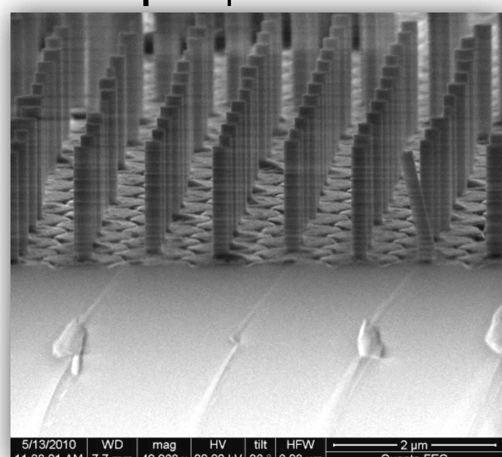
Height (dry etch depth)

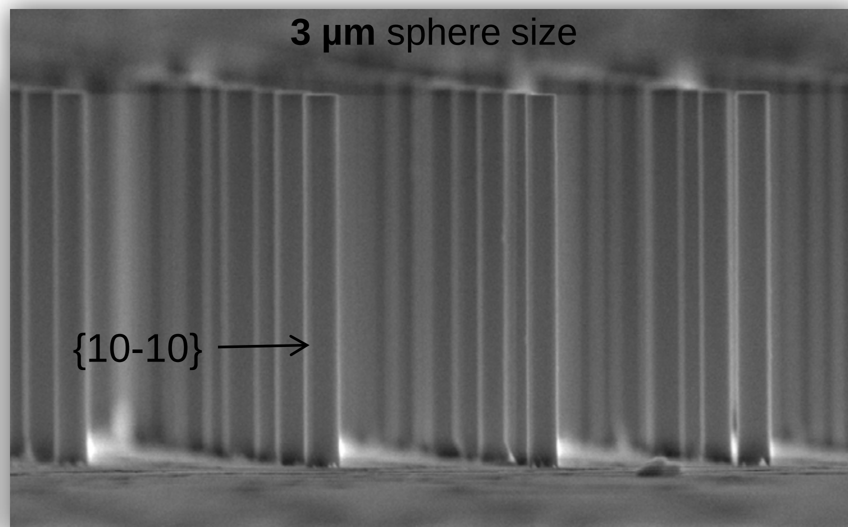
Diameter (wet etch time)

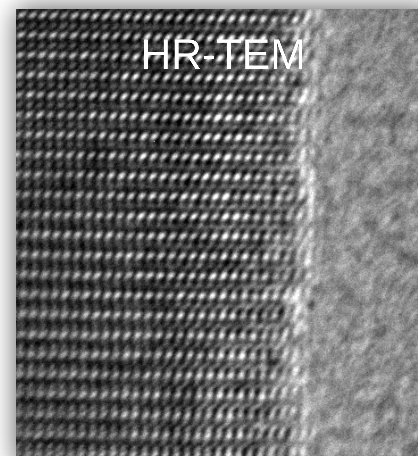
Pitch/arrangement (defined by masking template)



1 µm sphere size

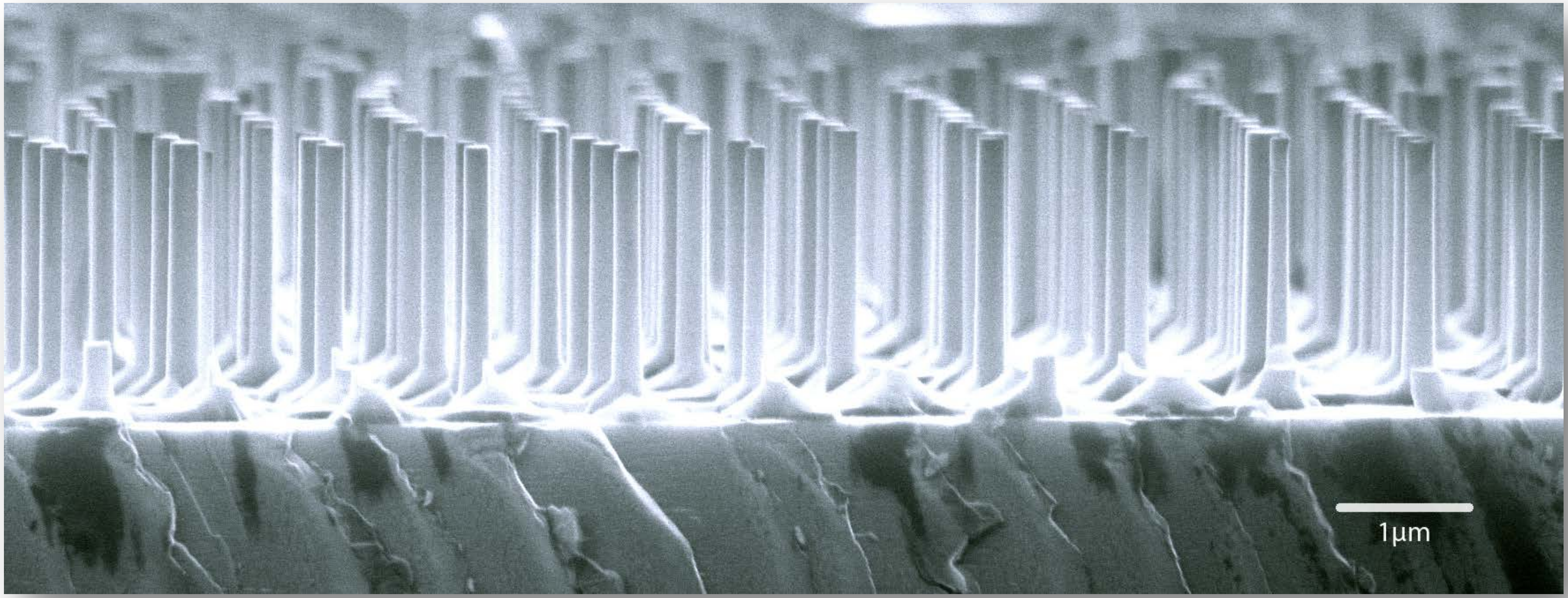






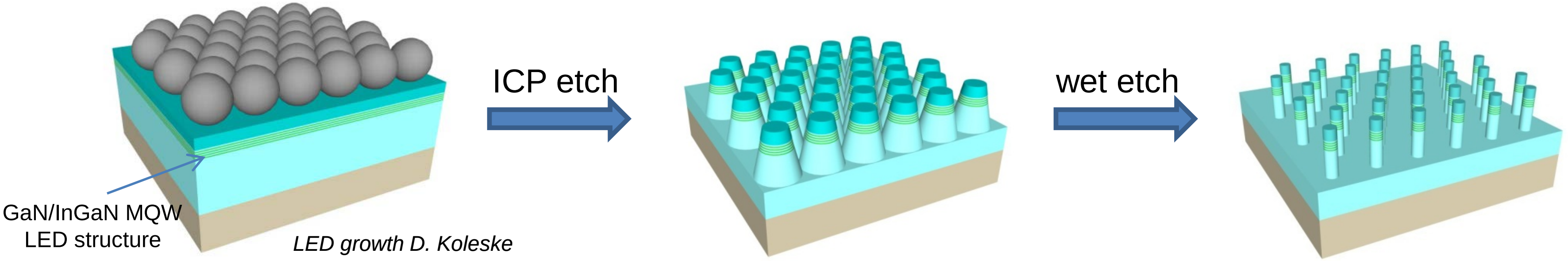
Smooth sidewall created by wet etch

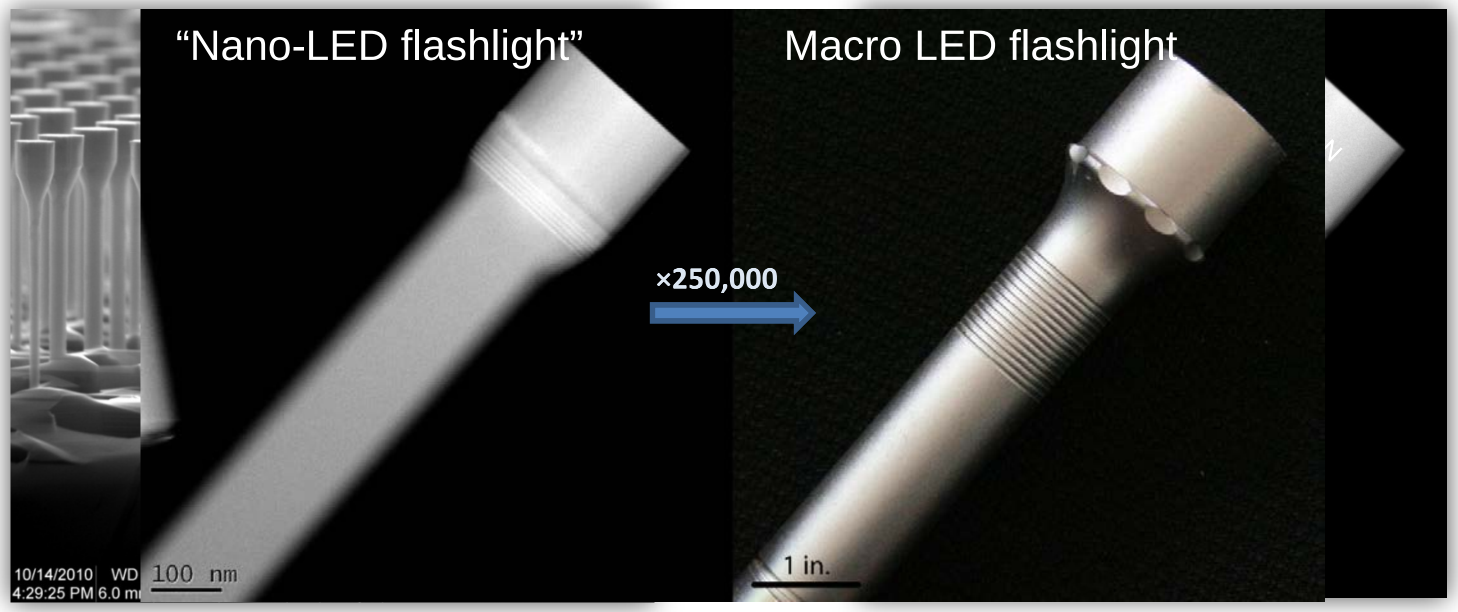
Advantages of new top-down nanowire fabrication method



- Wider range of growth conditions, material tunability (1D growth cndns not needed)
- Lower point defect densities (higher growth temperature)
- Ordered/periodic arrays (difficult with catalyst/VLS-based methods)
- Axial III-nitride nanowire heterostructures possible by MOCVD
- Better control of geometry (independent control over height, width, & pitch)
- Improved uniformity
- Easier vertical device integration (height uniformity, base GaN-layer)

Highlight: Axial GaN/InGaN nanowire LEDs

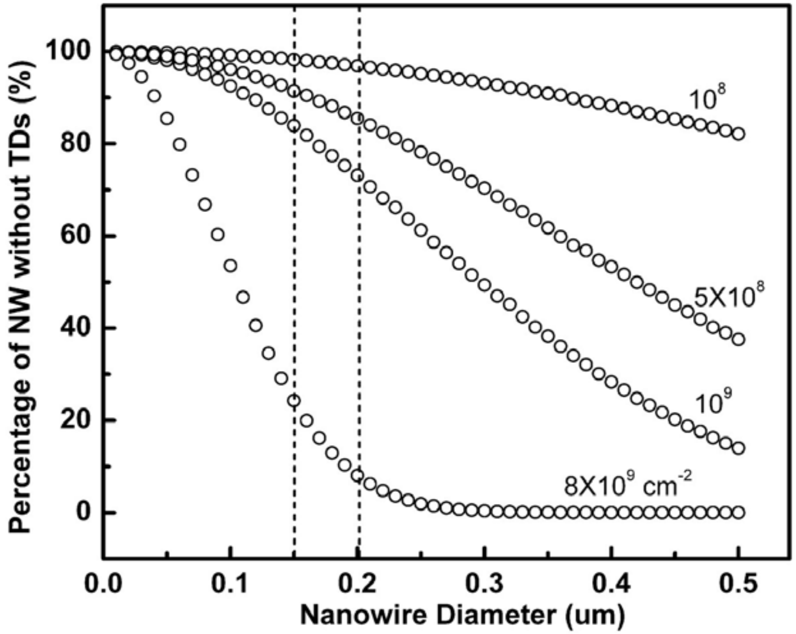




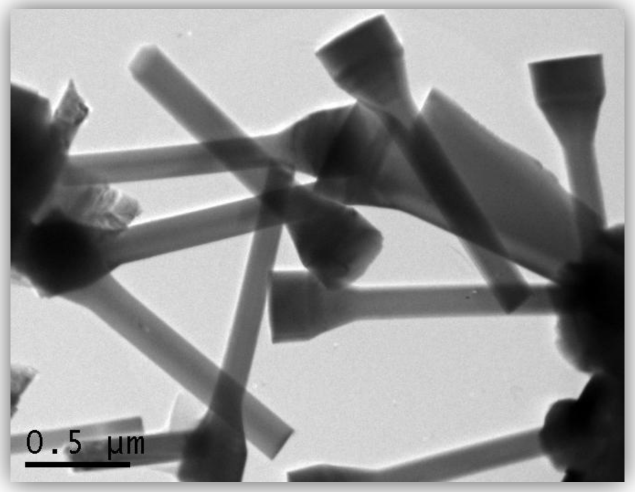
Q. Li et al., *Optics Express* **19**, 25528 (2011)

Nanorod threading dislocations as function of diameter

Monte Carlo simulation



Bright-field TEM



Nanorods etched from ~5e8 cm^{-2} planar LED

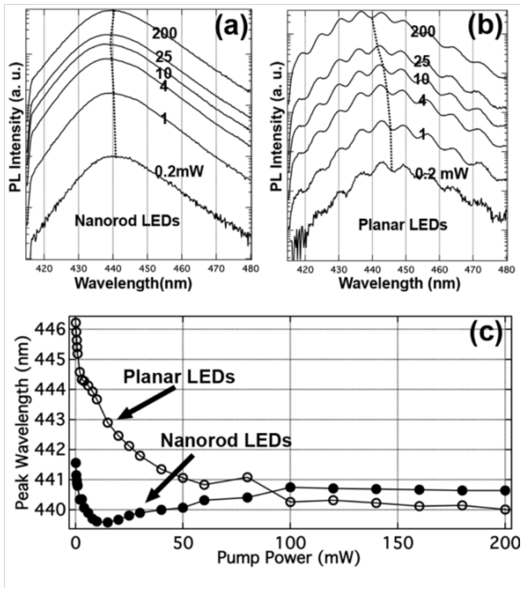
- Etched nanorods inherit the dislocation density of the parent film
- However, as the diameter approaches zero, the *fraction* of nanorods with one or more dislocations also approaches zero! [# TDs per rod ~ (TDD)×($A_{cross\text{-}section}$)]
- *~94% of nanorods ~150 nm in diameter from TDD~5e8 cm^{-2} film dislocation free!*

Optical performance – axial nanowire LEDs vs. planar LEDs

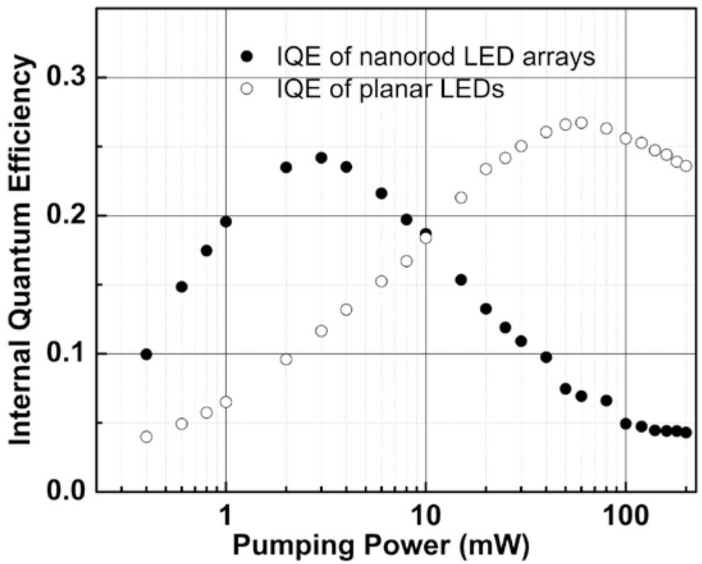
413 nm pump (InGaN selective)

PL, IQE measurement K. Westlake, M. Crawford

InGaN peak position vs pump power



IQE – nanowire vs Film



- XRD shows ~16±4% strain reduction in InGaN QWs in nanowire LEDs

  XRD measurement courtesy Steve Lee

- Little wavelength shift at higher pump powers for nanowire LEDs (no/reduced QCSE)

- nanowire LED: comparable IQE to planar LED but peak IQE occurs at much lower pumping power (enhanced light absorption, heating)

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

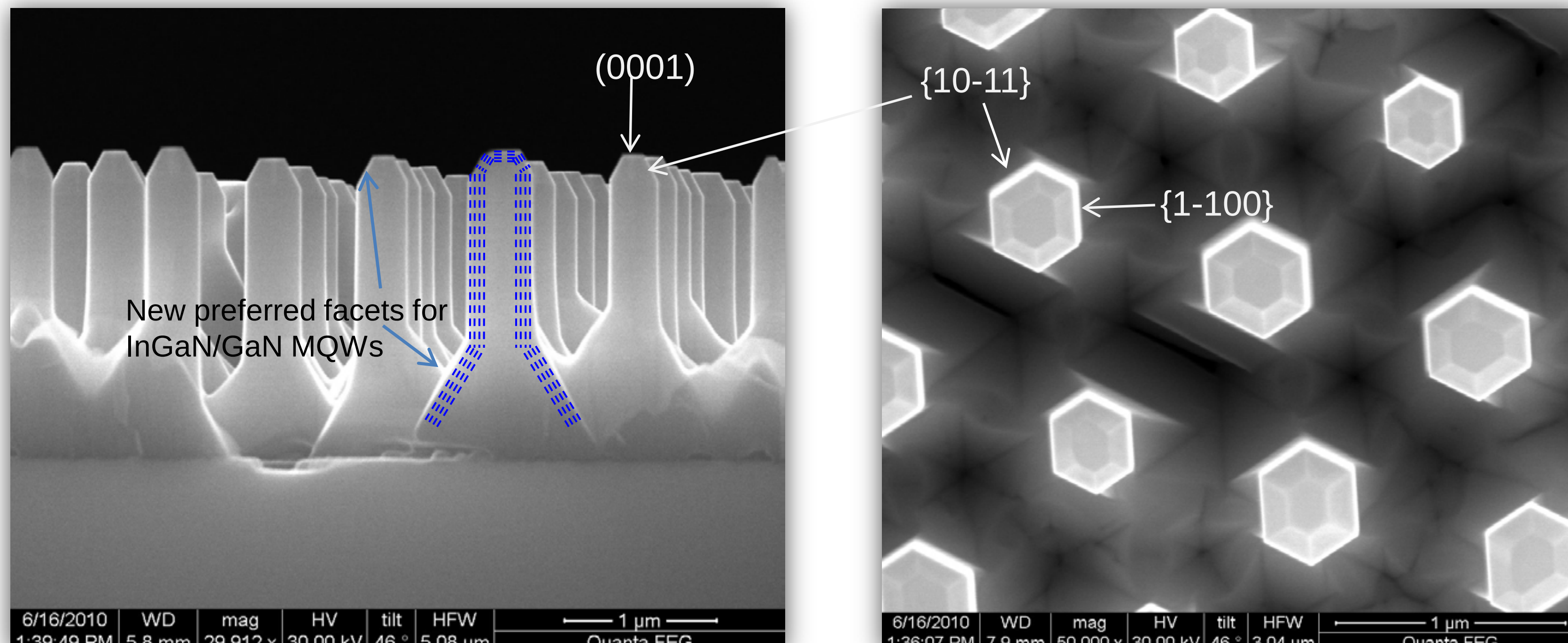
Sandia National Laboratories

Radial core-shell InGaN/GaN MQWs on top-down NWs

<u>Radial core-shell heterostructures</u>

- Much higher active area than axial or planar structures
- Reduced strain InGaN growth for higher In incorporation

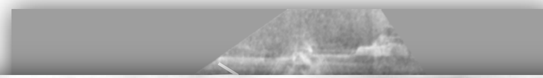
After 5-period MQW GaN/InGaN shell growth

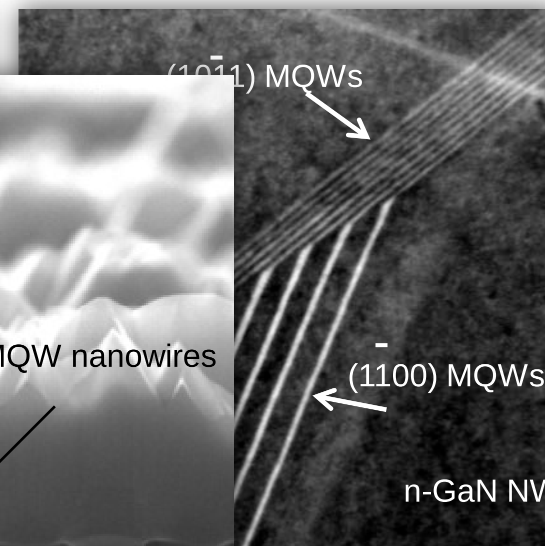


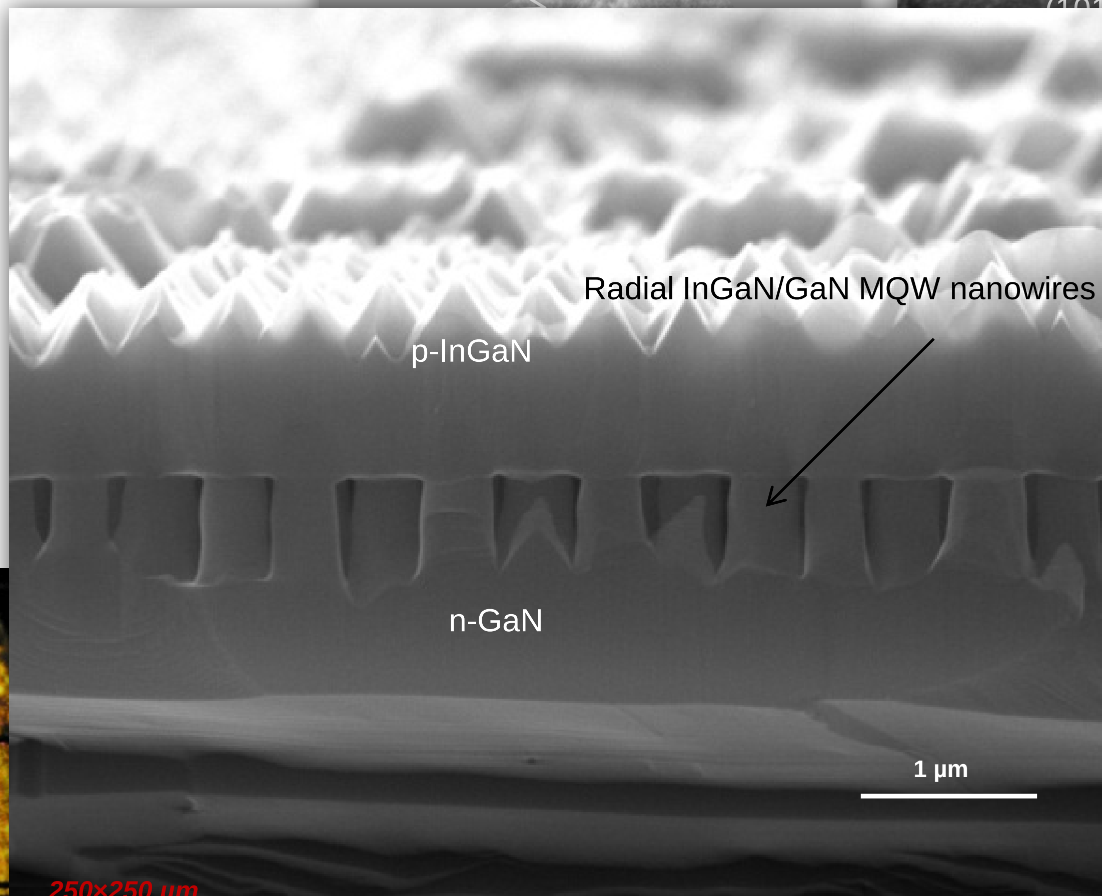
New semipolar facets form with InGaN/GaN MQW growth

SSLS EFRC

Highlight: Electrically injected core-shell nanowire based "3D" LED emitting at yellow-red wavelengths

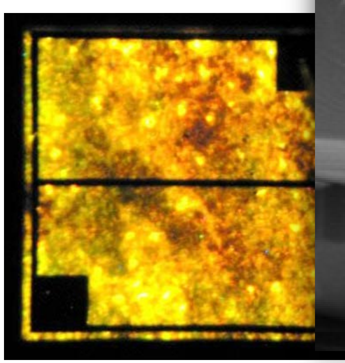






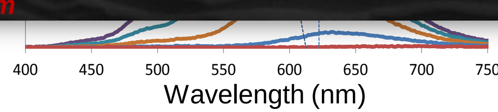
otechnology, published online

troluminescence!



nst) red

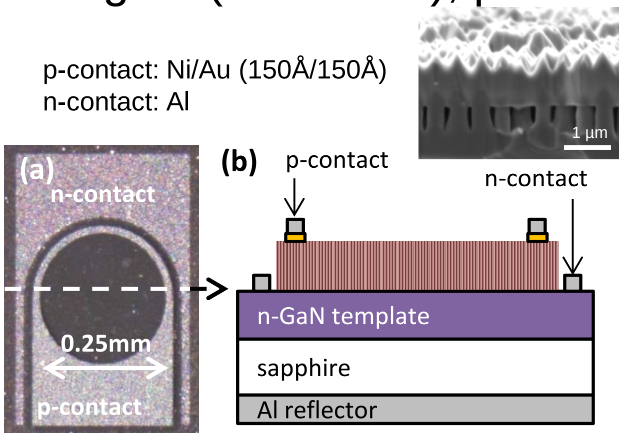
(shift) yellow



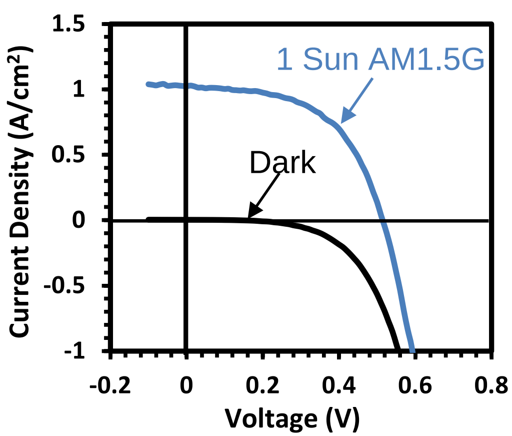
III-nitride nanowire arrayed solar cell

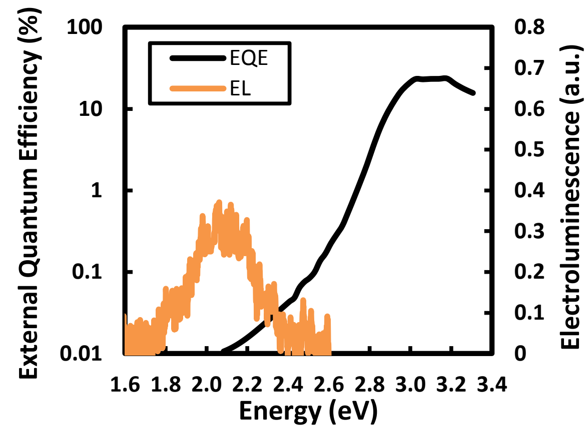
- III-nitride solar cells: InGaN bandgap (0.7-3.4 eV) covers solar spectrum; high rad. resistance

- Nanowire solar cells: increased light scattering/absorption, short carrier collection lengths (core-shell), potentially smaller bandgap cell (higher In content InGaN layers)



J. Wierer et al., *Nanotechnology*, in press





- *First vertically integrated III-nitride nanowire solar cell*

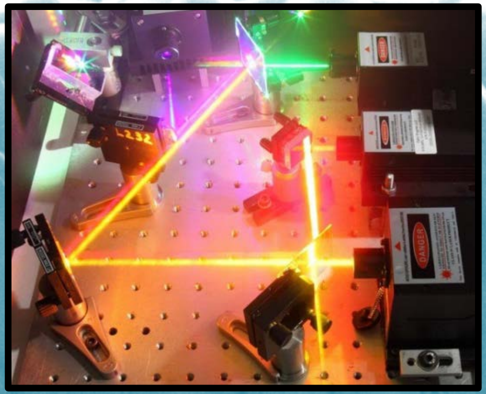
Previous Work: Single III-nitride NW solar cell:
Dong, Y. et al., *Nano Lett.* **9** 2183 (2009)

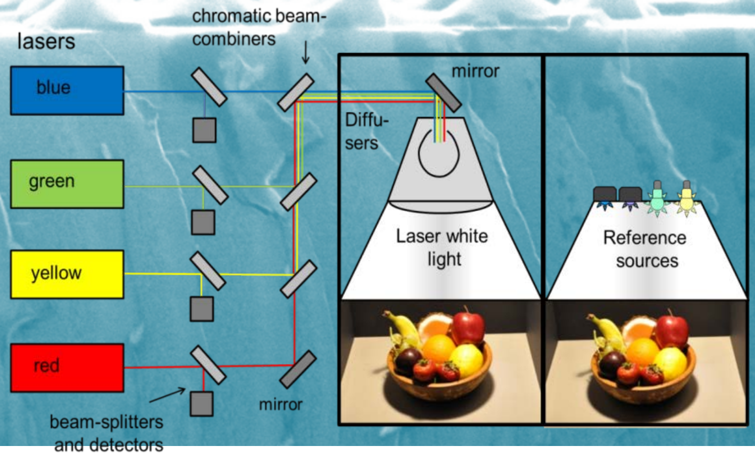
- Peak EQE ~23% at 3.0 eV; Photoresponse to 2.1 eV (590 nm), lowest bandgap reported for III-nitride solar cell; V_{OC} ~ 0.5 V; FF ~ 54%; Power conversion efficiency ~0.3% (shorting from defects in nanowire templates)

Nanowire Lasers

Why Nanowire Lasers?

- ***Nanowire forms a low loss optical cavity***
- ***Low threshold and low power due to small mode volume***
- ***Possibility of high efficiency lasers at green and yellow wavelengths***
- ***Potential applications including electronic/optical integration, sensing, imaging, lithography, lighting***
- ***Lasers may circumvent droop problem in LEDs***

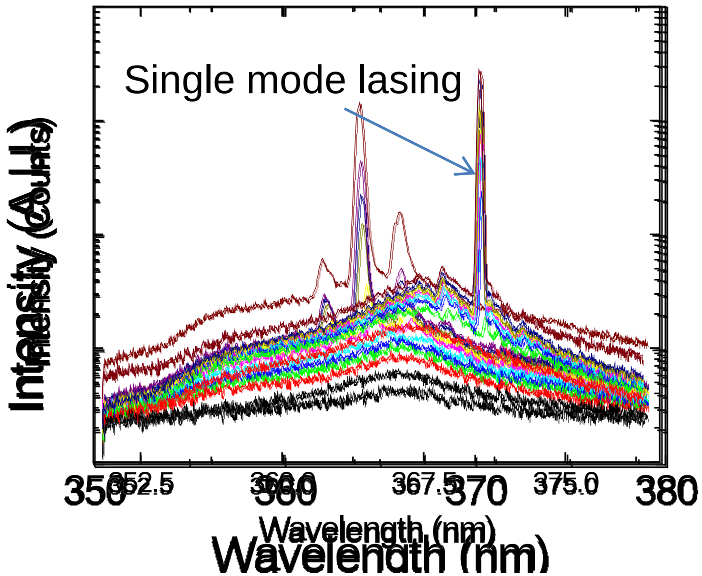


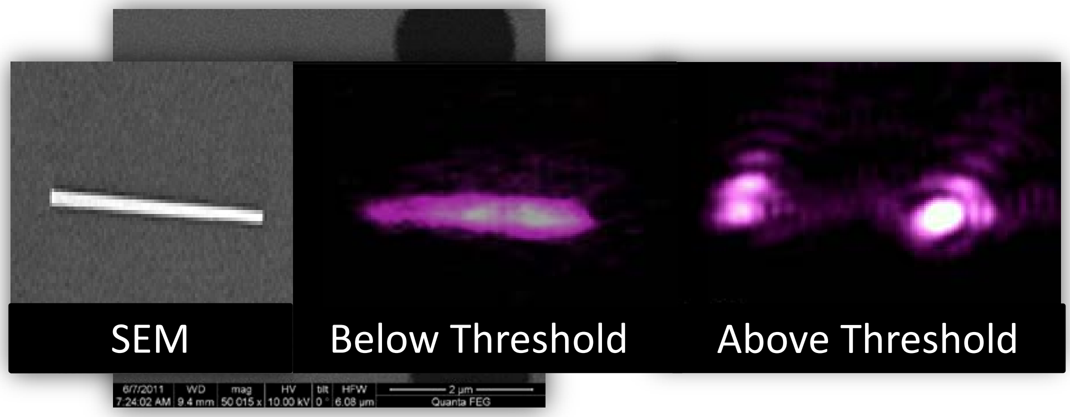


A. Neumann et al, *Optics Express*, **19**, A982-A990 (2011)

Single mode GaN nanowire laser

- Single-mode lasers are desirable (no mode-hopping, lower threshold & noise)





Nanowire dimensions: ~**130nm** x 4.7µm
Nanowire dimensions: ~**500 nm** x 4.7µm

Single-mode, Narrow-Linewidth (<0.1 nm), 15dB Side Mode Suppression Ratio, and **Low Threshold** (~250 kW/cm²)
Multi-mode: Threshold ~500 kW/cm²

Modeling shows that by reducing the dimensionality of the wire the number of competing modes is reduced, leading to single-mode lasing.

Summary

- Nanowire based architectures have several potential advantages over planar-based SSL
- Numerous scientific & technical challenges for nanowire-based SSL
- Our efforts to address these challenges combine nanowire synthesis/fabrication, nanocharacterization, and devices
- Research highlights
  - Growth and properties of bottom-up III-nitride nanowires
  - New top-down nanowire fabrication for controlled geometries, lower point densities, vertical device integration
  - Top-down nanowire LEDs/solar cells/lasers

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