SSLS EFRC
SOLID-STATE LIGHTING SCIENCE
ENERGY FRONTIER RESEARCH CENTER

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III-Nitride Nanowires: Novel Materials for Solid-State Lighting

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NNSA National Nuclear Security Administration

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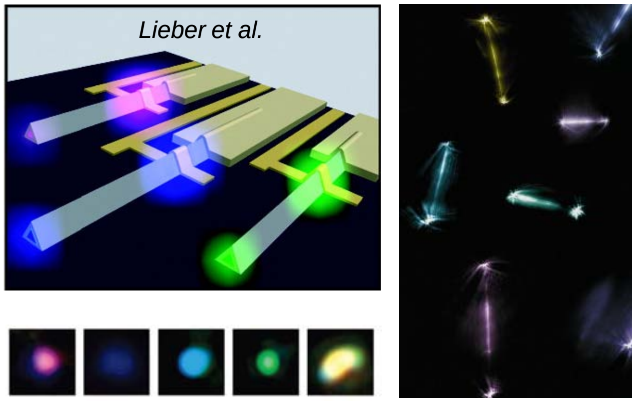
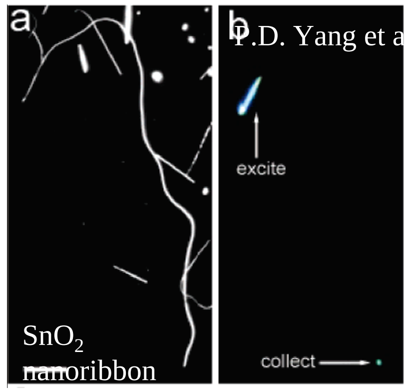
Semiconductor Nanowires (NWs)

Reduced dimensionality, high crystalline quality, high atomic surface/bulk ratio, size (intersects physical characteristic length scales) can lead to enhanced & novel properties



LEDs and lasers

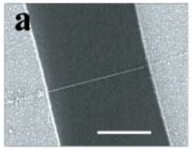
- Nanosized light sources
- Higher efficiency due to lack of defects
- High light extraction

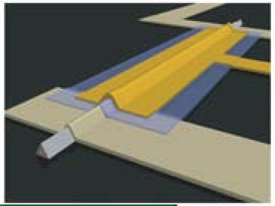


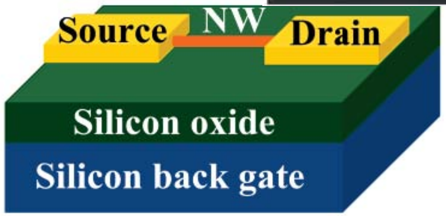
Waveguides and Filters

- coupled with nanowire light sources, building blocks for nanophotonics circuitry

Lieber et al.

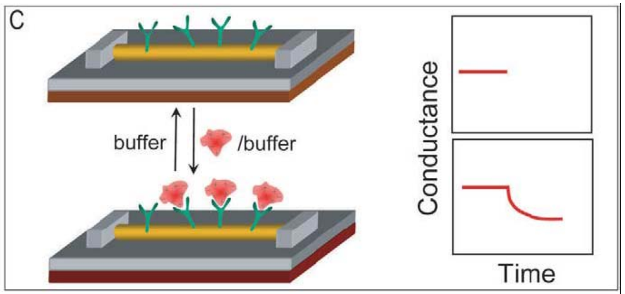






Transistors/HEMTs

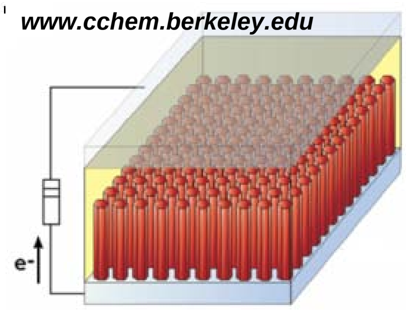
- improved performance characteristics
- small size



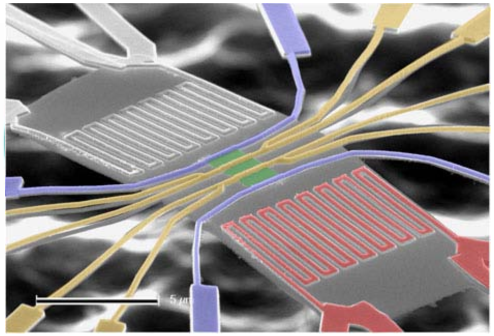
Lieber et al.

Chem/bio-sensors

- large atomic surface/bulk ratio leads nanowire depletion & ultrahigh sensitivity



Lieber et al.



Heath et al.

Energy Harvesting

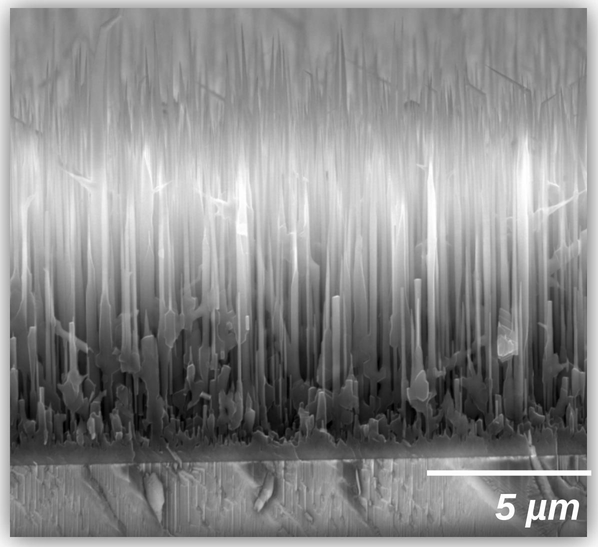
- Nanowire Photovoltaics
- Thermoelectrics
- Piezoelectric energy generation

Sandia National Laboratories

III-Nitride (AlGaInN) nanowires for SSL

Compared to planar films, III-nitride nanowires …

- Have high light extraction efficiencies
- Are strain relaxed
    - can accommodate wider range of alloy compositions (wide color space)
    - typically free of threading dislocations (IQE)
    - can grow on any substrate (cost)
- Are “discrete” – entire structure & changes to the structure can be investigated

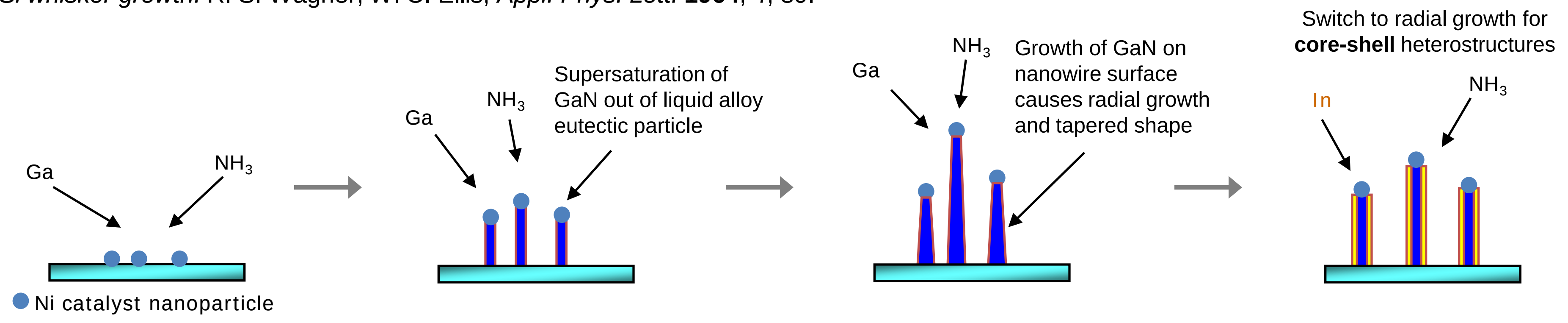


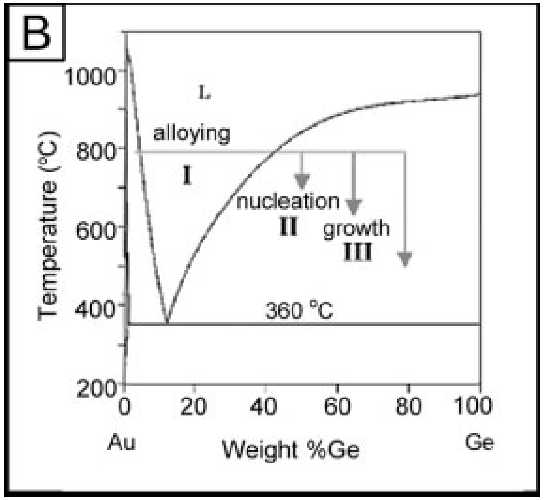
Challenges for nanowire-based LEDs & other devices:

- Understanding & control of synthesis – size, length, alignment, facets, uniformity
- Understanding & control of properties – electrical, optical, thermal, mechanical, etc.
- Device integration – contacts, surface states, single nanowire & vertical integration schemes

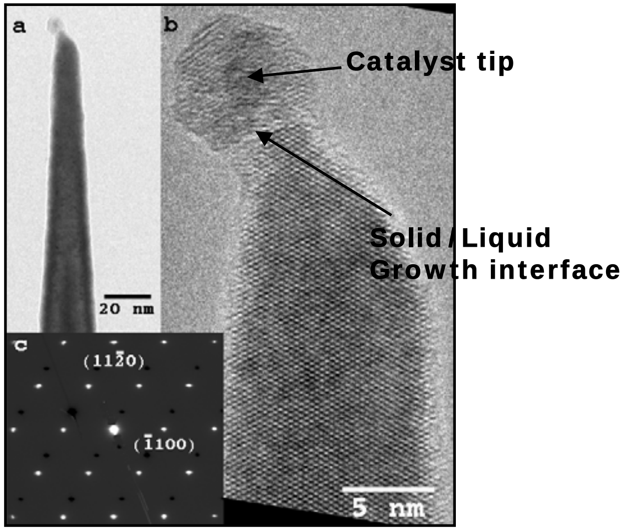
Vapor-liquid-solid (VLS) based nanowire growth

Si whisker growth: R. S. Wagner, W. C. Ellis, *Appl. Phys. Lett.* **1964**, *4*, 89.

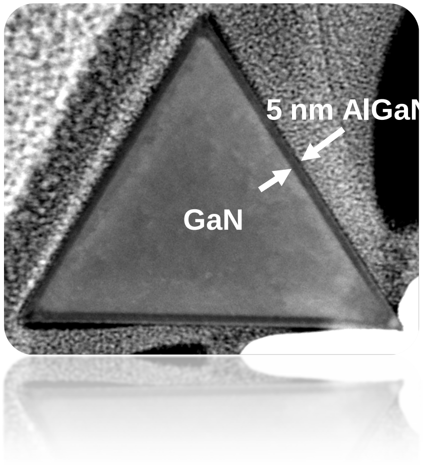




From Xia et al. *Adv. Mater.* ***2003,*** *15, 353.*

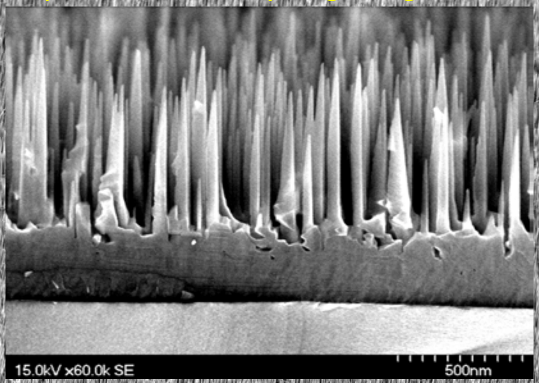


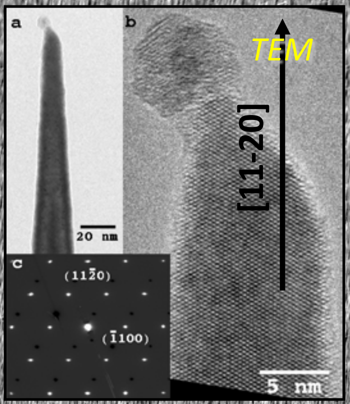
GaN/AlGaN Core-shell NW

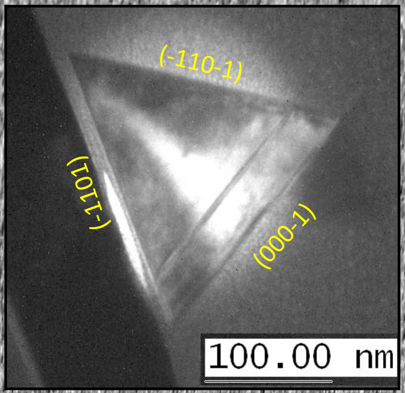


Aligned GaN nanowire growth

Epitaxial vertically aligned growth







- Nanowires grown by Ni-catalyzed MOVPE/MOCVD (VLS)
- Highly-aligned, uniform vertical growth over large areas (2” r-sapphire wafer)
- Controllable densities as high as ~150 nanowires μm^{-2}

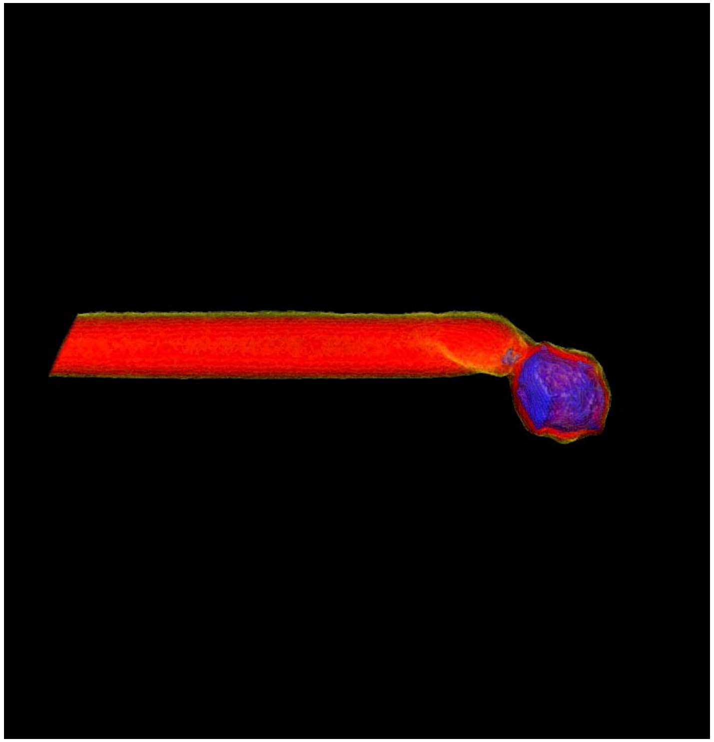
  Q. Li, G. T. Wang, *Appl. Phys. Lett. 93, 043119* (2008)

  Q. Li, J. R. Creighton, G.T. Wang. *J. Crys. Growth 310 3706-3709* (2008)
- Primary [11-20] growth orientation ($\perp$ 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)

3D imaging of core-shell NWs by STEM tomography

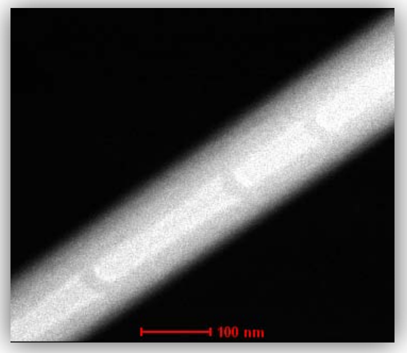
Goal: 3D morphology of heterostructure nanowires

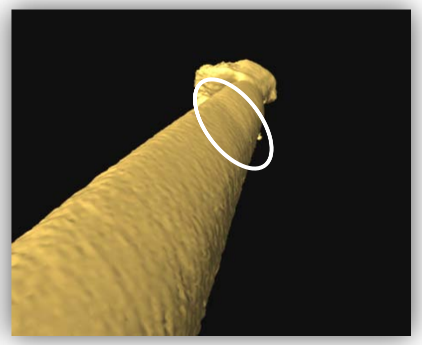


Tilt Range:
-73 to +70 °
144 Images

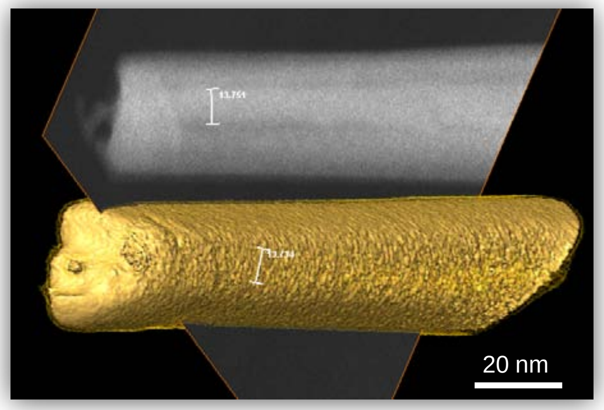
GaN-AlN core-shell NW

50 nm





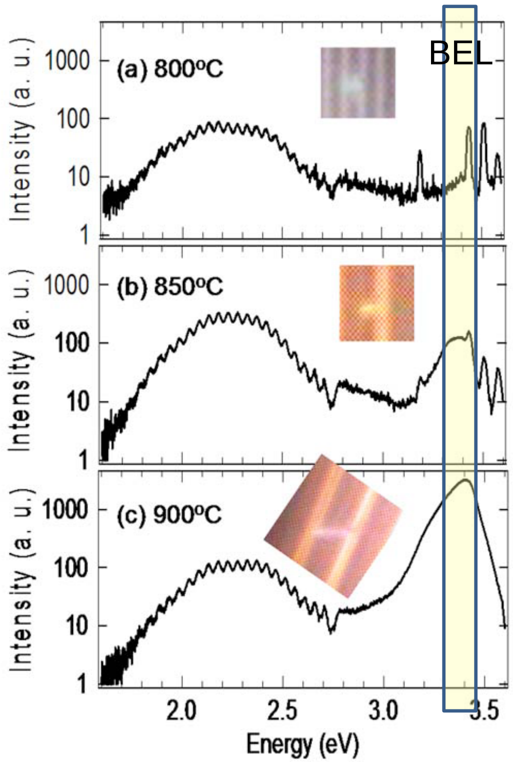
“Breaks” in GaN core from 2D STEM images revealed instead by 3D tomography as *surface notches*

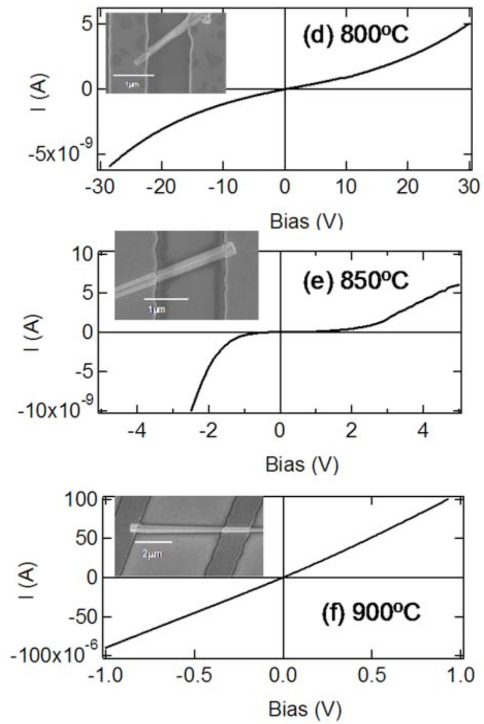


Bright center strip revealed by 3D tomography as extra facet, not GaN core

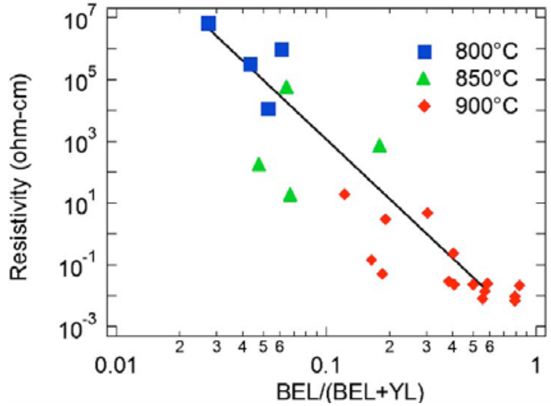
I. Arslan, A. A. Talin, G. T. Wang, J. Phys. Chem. C **112**, *11093. (2008)*

μPL and I-V measurements: Impact of NW growth temperature





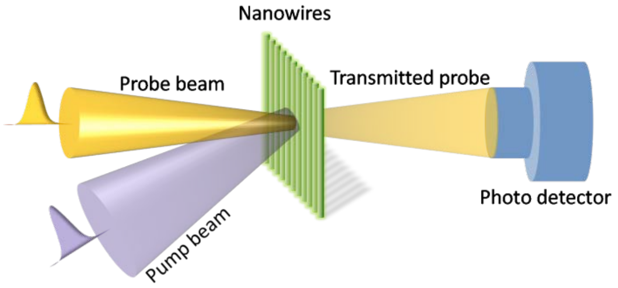
Optical/electrical NW device platform

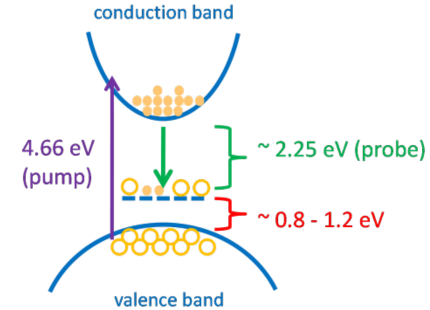


- **~50x** increase in band-edge emission at 900 °C vs 800 °C
- Resistivity **~ 6 orders** of magnitude lower at 900 °C vs 800 °C
- Yellow luminescence (YL) & high resistivity linked to C incorporation in GaN films[1,2]

1 Wickenden, A.E., et al. *J. Crys. Growth 2003*, 54
2 Koleske, D.D., et al. *J. Crys. Growth 2002*, 55

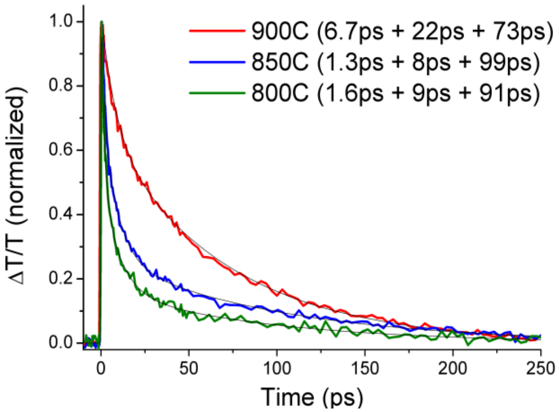
Non-equilibrium carrier dynamics in GaN nanowires

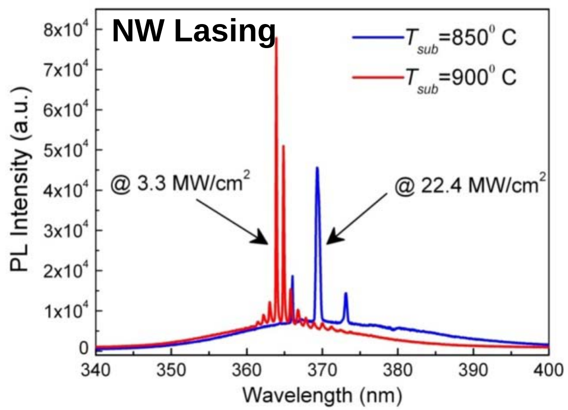




Measures transmission of ultrashort optical pulse (probe) after above-band gap excitation (pump) on a fs timescale

Here, we examine **carrier relaxation** through YL defect states after above-band gap excitation in GaN NWs

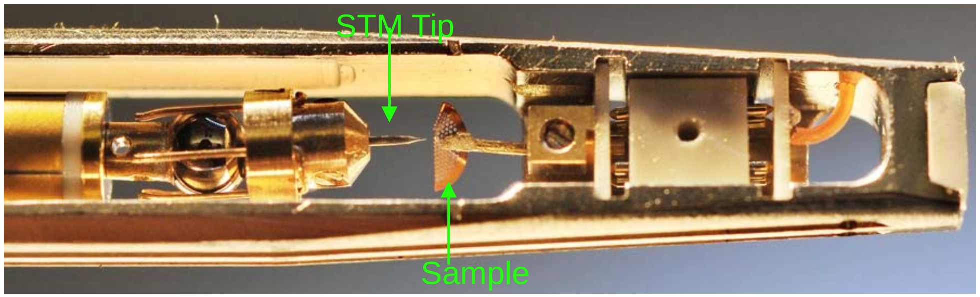


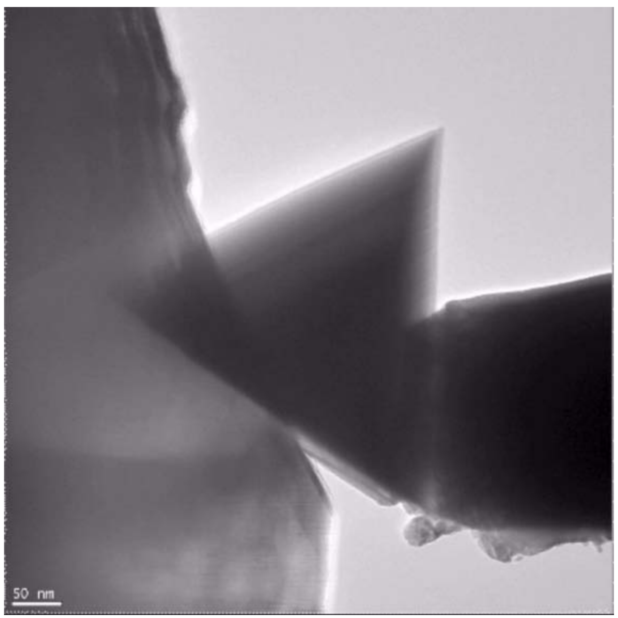


- carrier relaxation rates through YL states increase with decreasing growth temperature due to additional impurity sites that are present at lower growth temperatures.
- defect states also influence the lasing threshold in GaN NWs
- control of the growth temperature can be used to optimize GaN NW-based devices.

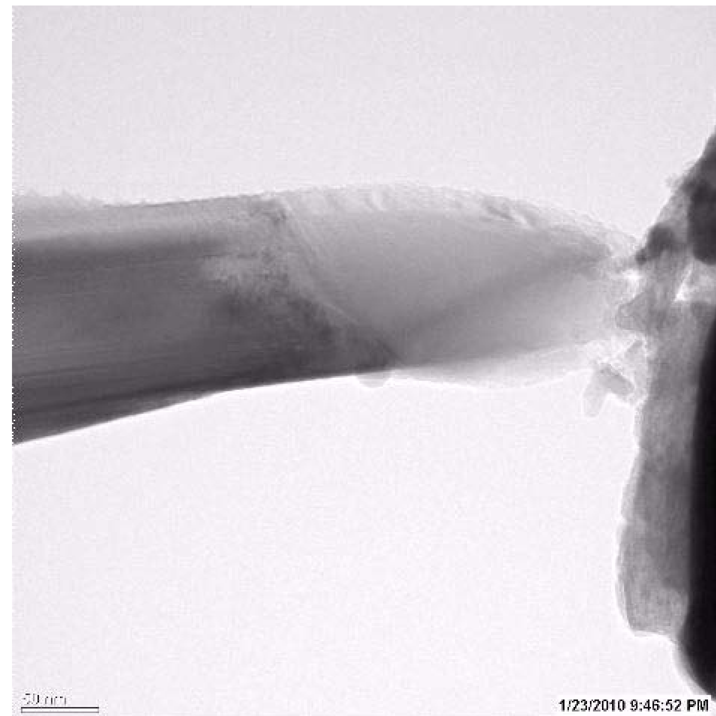
Semicond. Sci. Tech. (2010); *Phys. Stat. Solidi(b)* (2009)

In-situ TEM studies – nanowire electrical breakdown





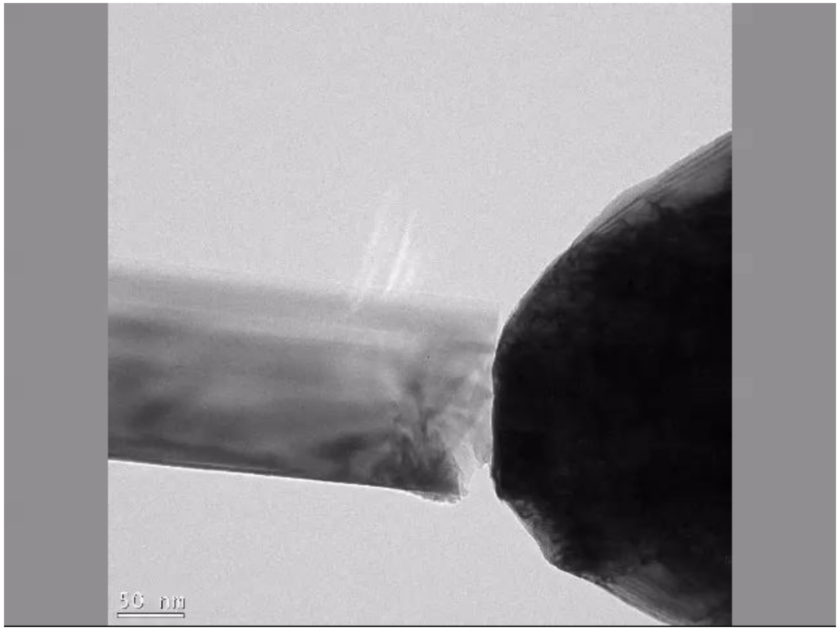
NW decomposition via Joule heating
(relevant for NW devices)



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

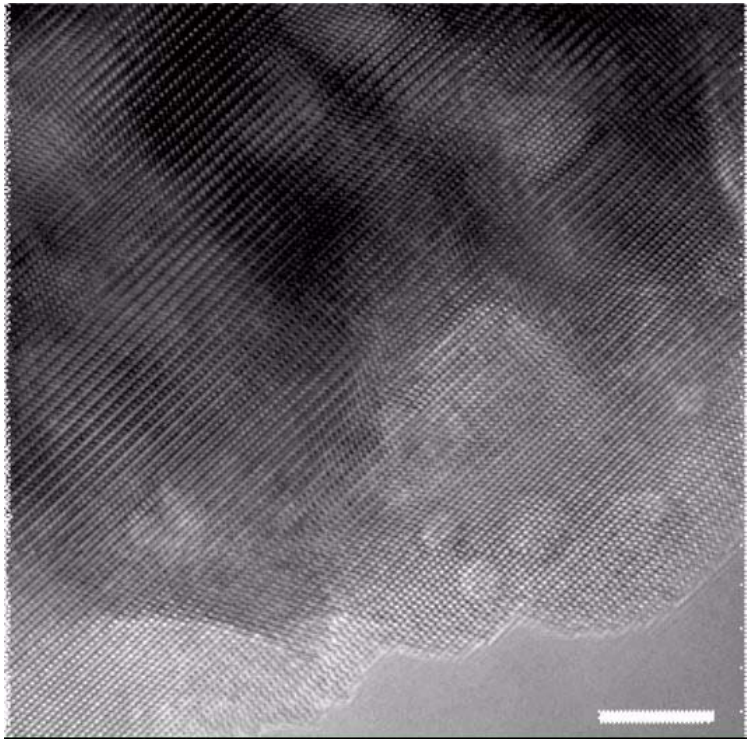
In-situ TEM studies

In-situ deformation



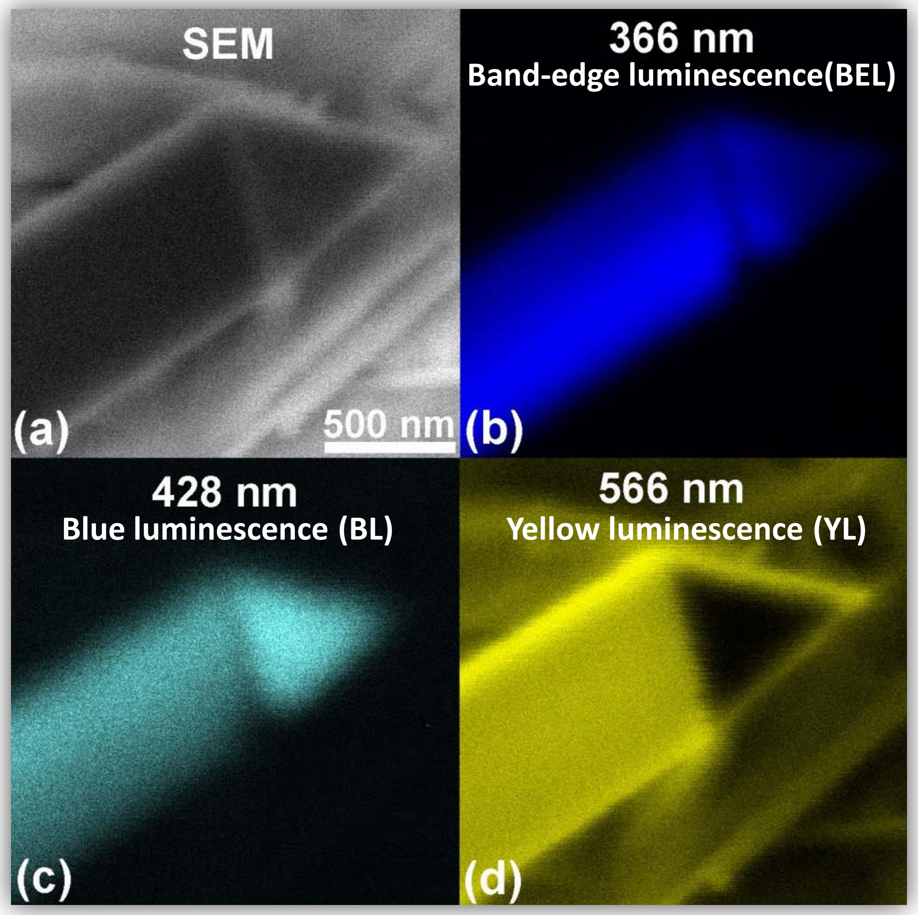
- Dislocation-free NW undergoes non-recoverable plastic deformation
- Mediated by dislocation formation, grain boundary sliding

Void/bubble migration



- “Bubbles” migrate under beam irradiation
- Origin unknown – possible N_2 / H_2 gas?

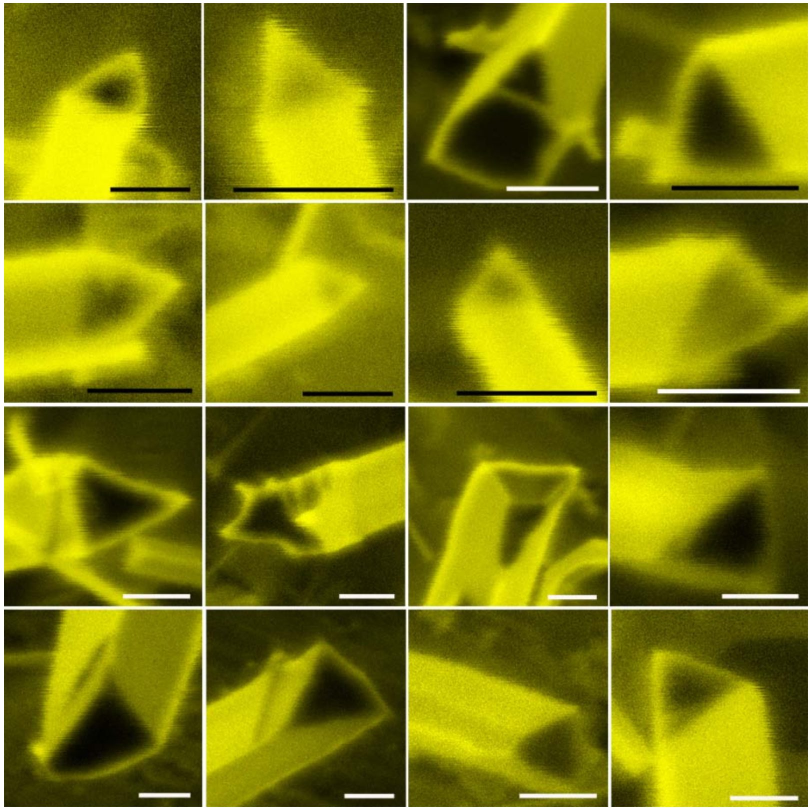
Spatially-resolved CL study of GaN NWs

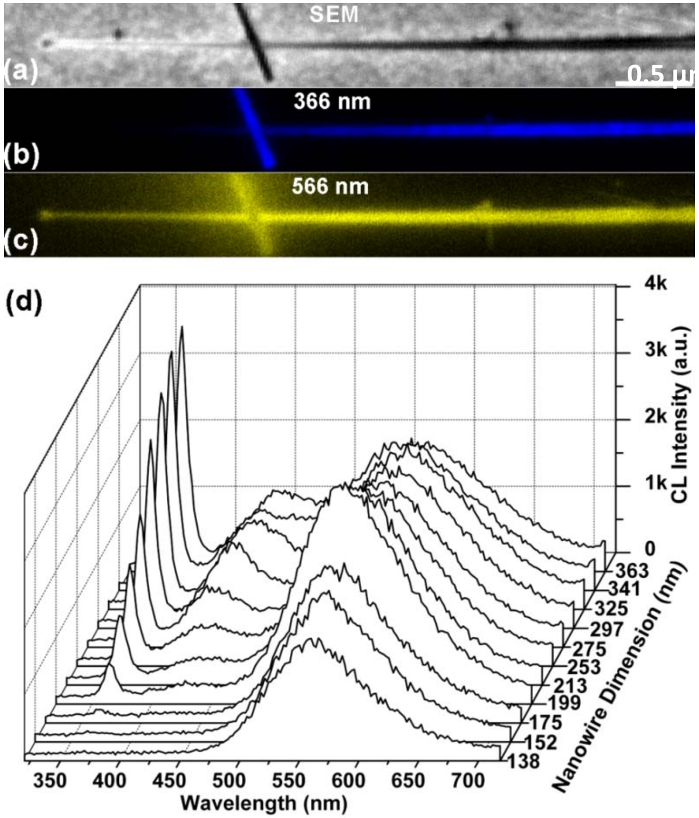


Nanoscale CL imaging: **Cross-section GaN NW**

- 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
- Well-known 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

YL surface layer causes "pinch-off" of BEL

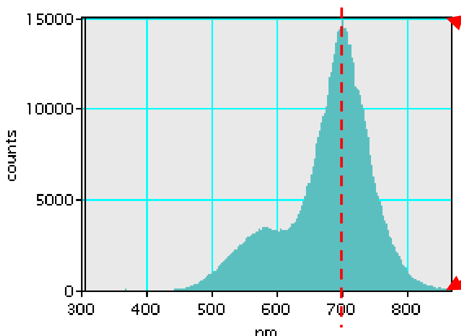


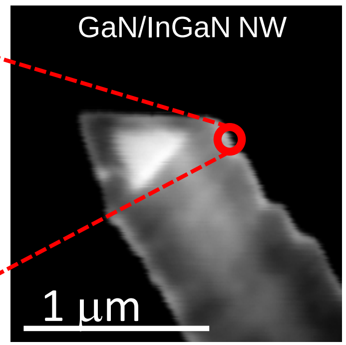


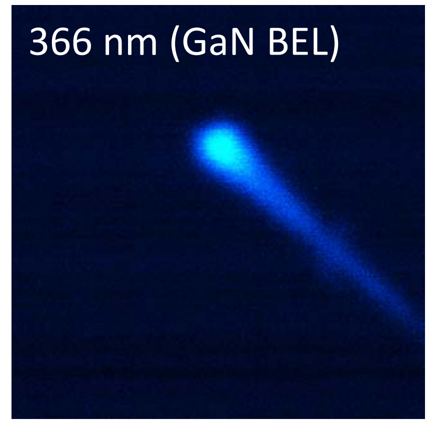
- Tapered nanowire shows "pinch-off" effect
- Spectra taken along tapered NW length, shows "critical diameter" of ~160 nm

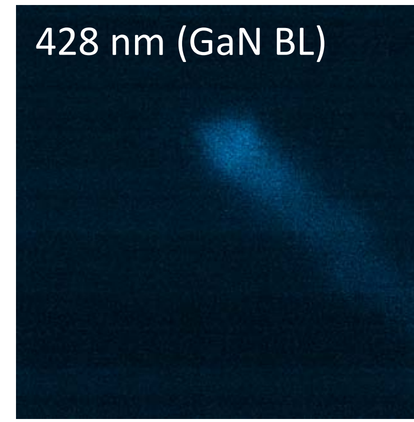
High Indium Incorporation in GaN/InGaN core-shell NWs

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

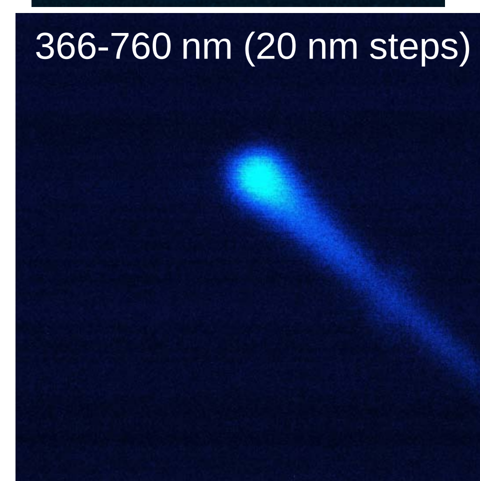


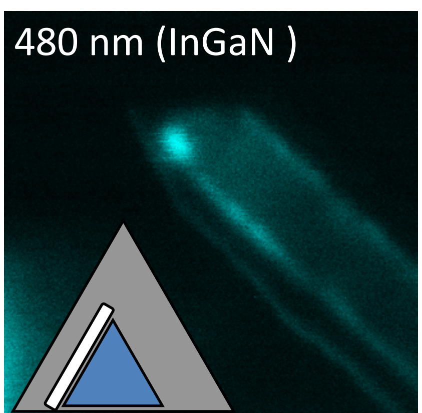


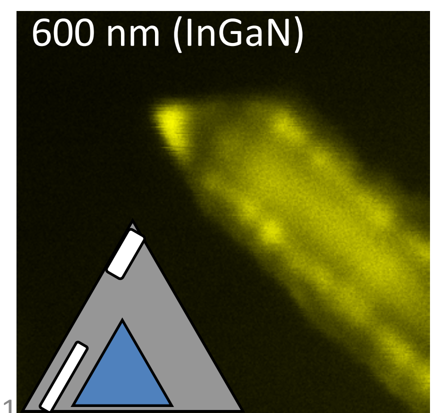


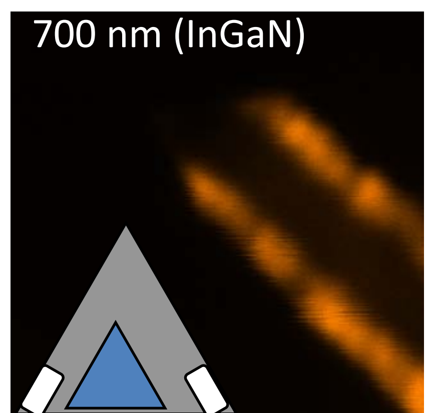


Growth conditions: GaN core – 900 ˚C, 10 min.
InGaN shell – 760 ˚C, 60 min.



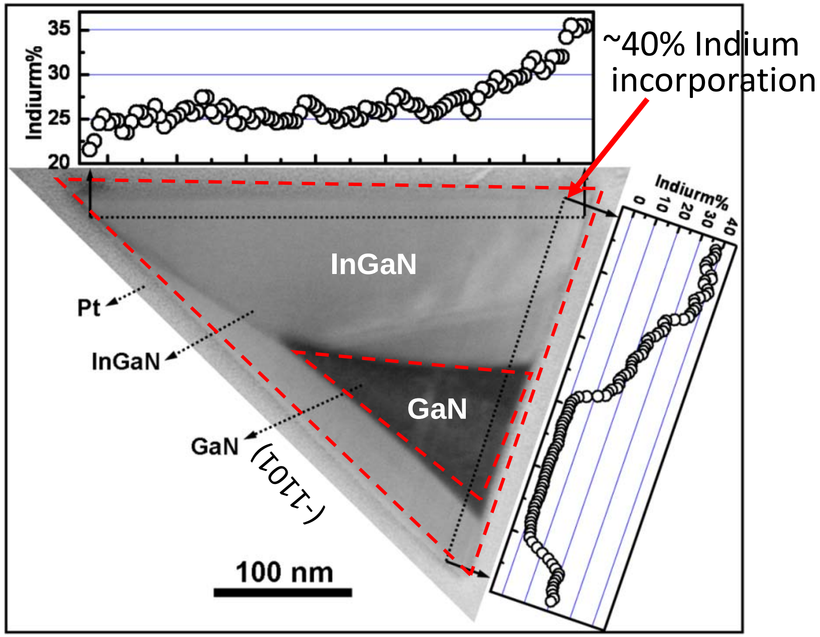


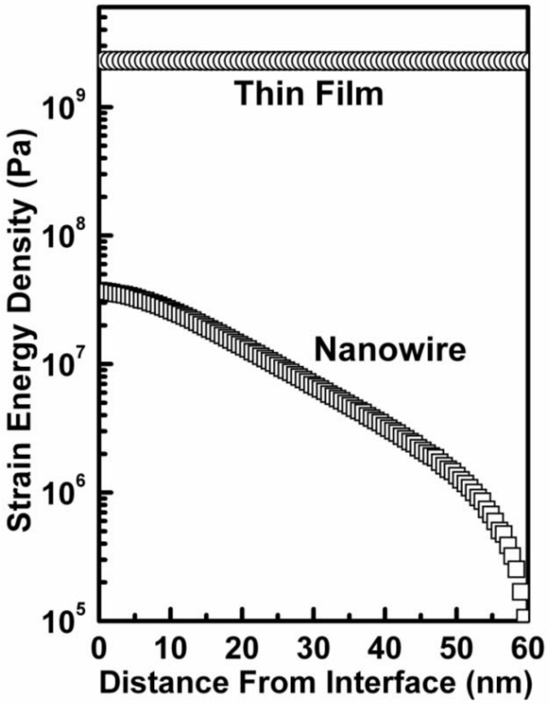




In incorporation in GaN/InGaN core-shell NWs

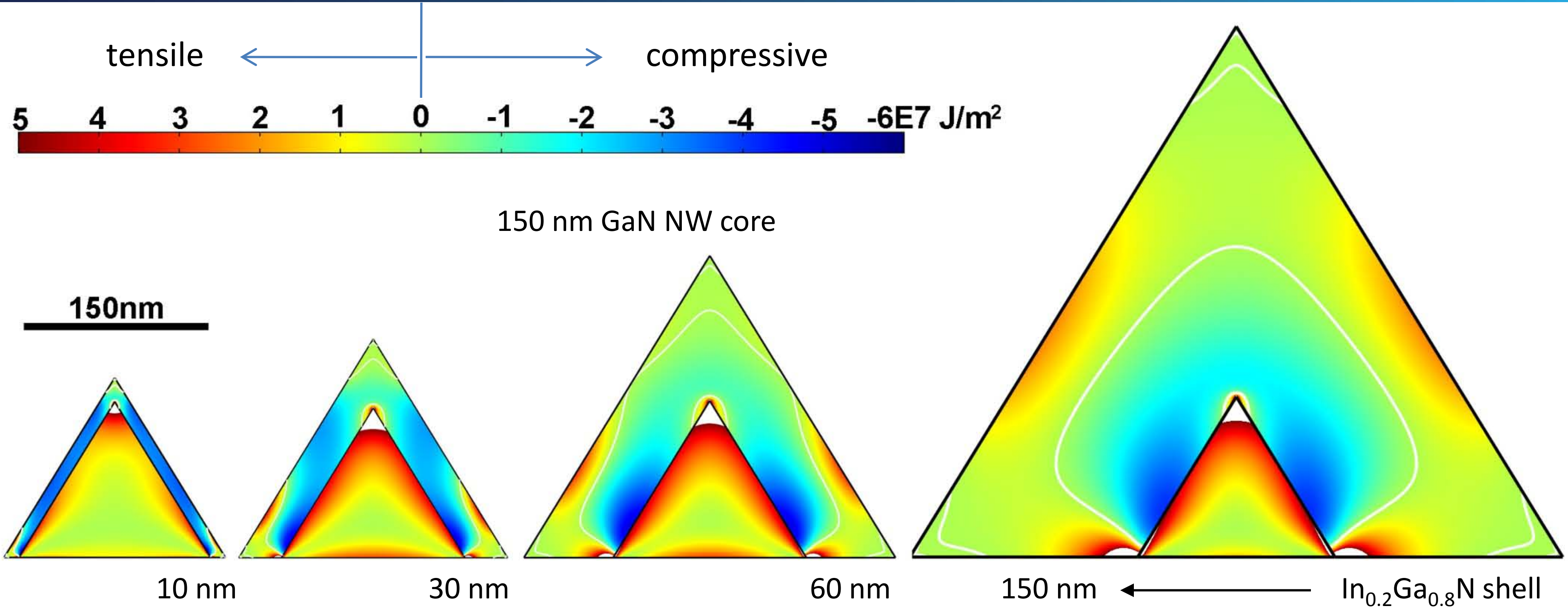
EDX(STEM)





- InGaN shell growth highly facet-dependent -- no growth on (000-1) c-plane facet
- In concentration increases away from GaN/InGaN interface, highest at corners
- No dislocations observed despite very high In concentration
- Strain in InGaN NW shell much lower than for InGaN thin film

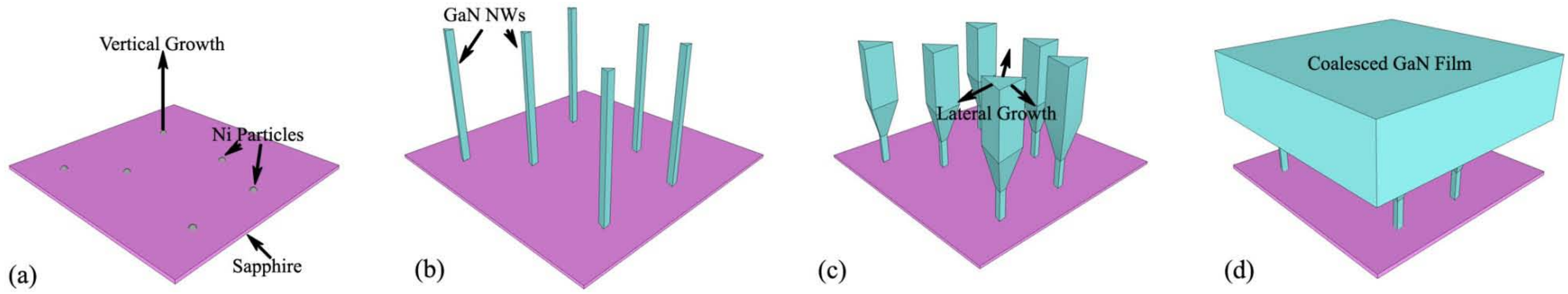
Strain-dependent In incorporation in GaN/InGaN core-shell NWs



- Finite element models show compressive/tensile strain in GaN core and InGaN shell
- Compressive strain dominates in thinner shells, decreases away from interface and becoming tensile for thicker shells
- Higher In incorporation correlated with lower (compressive) strain regions

Nanowire-templated lateral epitaxial growth (NTLEG) of high quality GaN

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



Ni nanoparticle formation | **Vertical nanowire growth** | **Lateral growth** | **Full coalescence**

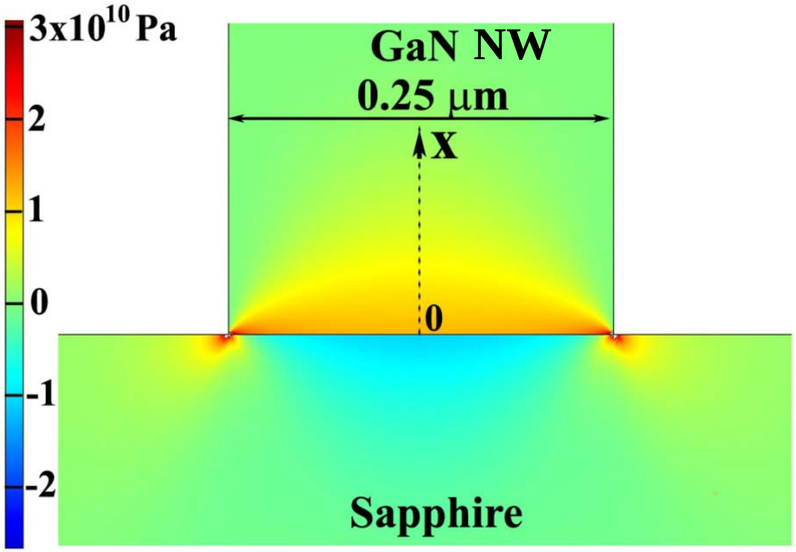
<u>Advantages of NTLEG approach vs. epitaxial lateral overgrowth</u>

- High quality dislocation-free nanowires as growth template
- *NWs as 3D-compliant nanoscale bridges connecting film & substrate, relieving strain in the film & reducing defects (nanoheteroepitaxy)*[1]
- No high defect density "window/stripe" areas
- <u>Low cost</u> (comparable to standard GaN growth on sapphire)
  - Sapphire can be used (potentially even Si)
  - No patterning
  - Single growth step

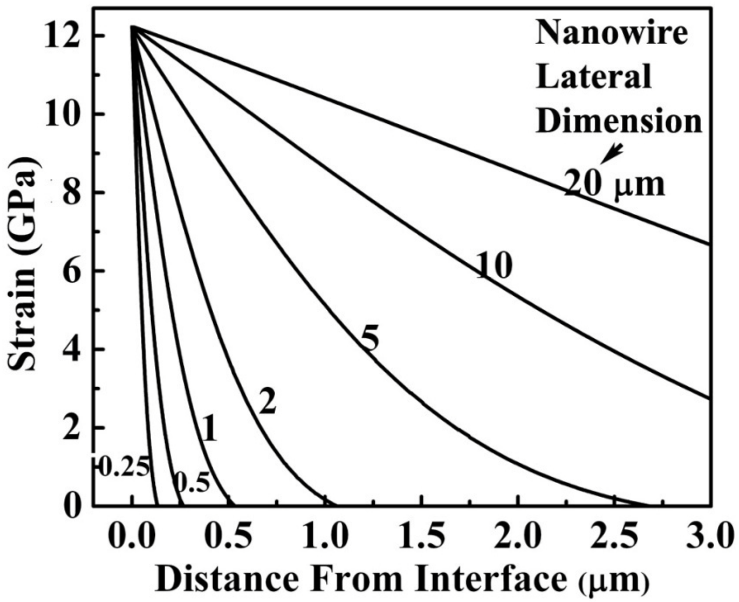
Q. Li, Y. Lin, J.R. Creighton, J. Figiel, G.T. Wang, *Adv. Mat.*, **21** 2416–2420 (2009)

[1] D. Zubia, S. D. Hersee, *Journal of Applied Physics* ***1999**, 85, 6492.*

NTLEG – Nanowire-substrate strain modeling



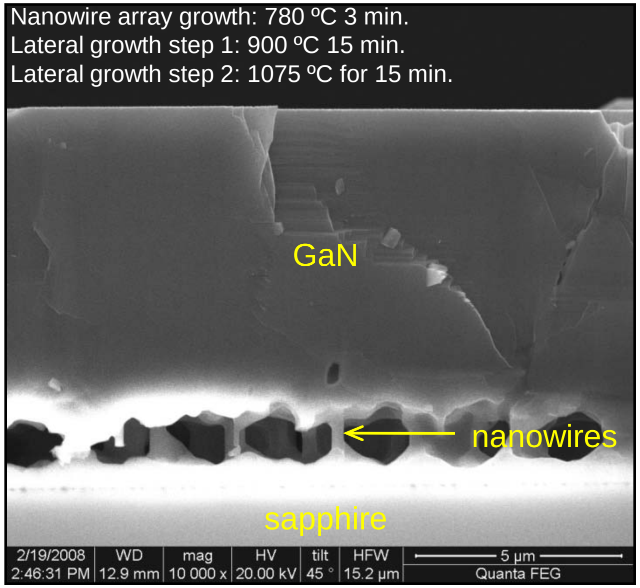
Strain distribution in 250 nm wide GaN NW on sapphire
(15% lattice mismatch between a-plane GaN & r-plane sapphire)



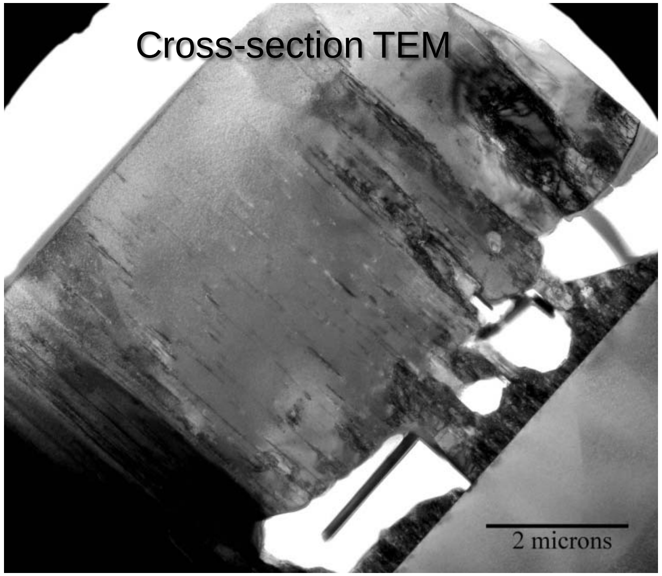
Line plots of the strain decay along the NW center line

- Finite element analysis shows *strain rapidly decays away from nanowire/sapphire interface.*
- The strain decay length (length where strain ~ 0) is ~one-half of the lateral NW dimension
- Shows theoretical basis for strain relief in the NTLEG film, which is distant from strain field caused by lattice/thermal mismatches

NTLEG – Growth & Characterization a-GaN film



Cross-section SEM



Selected previous planar a-plane GaN on r-plane sapphire work:

Method on *r*-sapp	TDD (cm-2)	SFD (cm-1)	XRD FWHM (11-20)[1]	Source
NTLEG (This work)	~$1x10^9$	$1.5x10^5$	540	This work (Q. Li et al. Adv. Mat., 21, 2416–2420 (2009))
LT nucl. Layer	~$3x10^{10}$	$4x10^5$	1040	M. D. Craven et al., Appl. Phys. Lett., 81, 469.(2002)
” “	~$7x10^{10}$	$7x10^5$	1290	A. Chakraborty et al. Appl. Phys. Lett., 89, 041903 (2006)
SiNx Nanomask	$9x10^9$	$3x10^5$	1040	A. Chakraborty et al. Appl. Phys. Lett., 89, 041903 (2006)
Single-step LEO	10^7-10^8 (wings)	10^4-10^5	610	Imer et al. (2007), JCG 306, 330 (2007)
Sidewall LEO	10^6-10^7	10^3-10^4	295	Imer et al. (2007), JCG 306, 330 (2007)

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

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Conclusions

- Electrical & optical studies reveal impact of nanowire growth conditions on properties
- Spatially resolved CL reveals a yellow luminescence surface layer in GaN NWs. YL-related defects may be mobile & migrate to the surface region during growth
- GaN NWs good platform for InGaN growth -- up to 40% In incorporation is observed with no observed dislocations, due to reduced compressive strain
- Aligned growth and NW strain-relaxation leveraged to grow planar GaN films (NTLEG)

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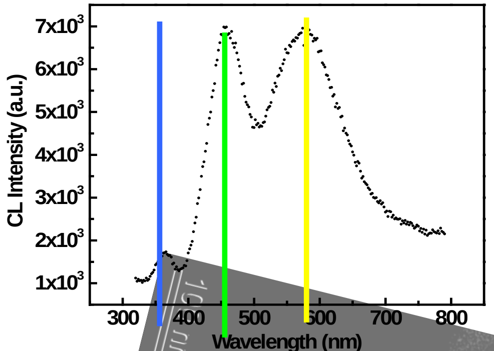
Multiquantum well InGaN/GaN nanowires



- CL shows two main InGaN peaks around 460 nm & 580 nm