Exceptional service in the national interest

Sandia National Laboratories
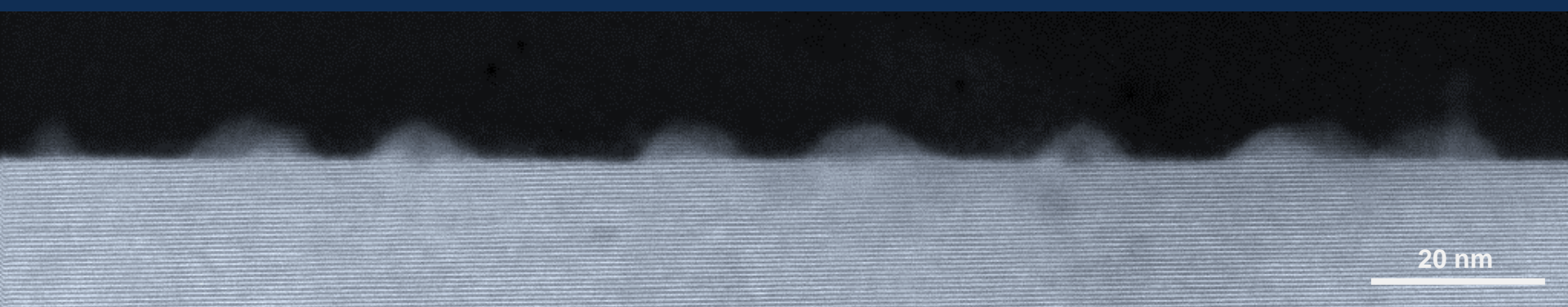
20 nm

InGaN Quantum Dots by Quantum Size Controlled Photoelectrochemical Etching

George T. Wang[1,*], Benjamin Leung[1], Xiaoyin Xiao[1], Arthur J. Fischer[1], Ping Lu1, Miao-Chan Tsai[2], Daniel D. Koleske[1], Michael E. Coltrin[1], Jeffrey Y. Tsao[1]

[1]*Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87047*

[2]*Center of High Technology Materials, University of New Mexico, Albuquerque, NM 87106*
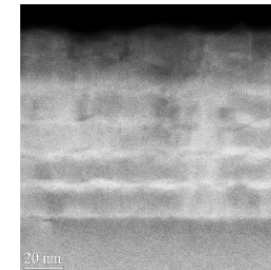
*gtwang@sandia.gov

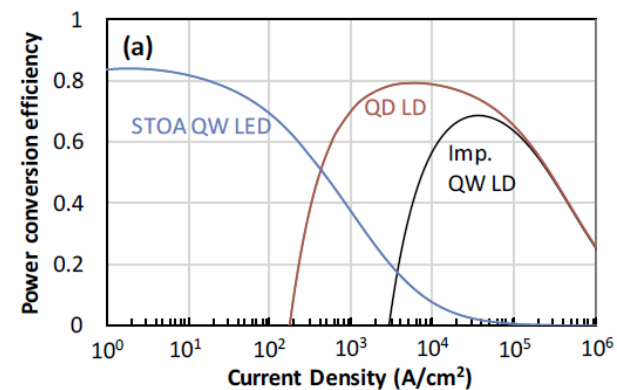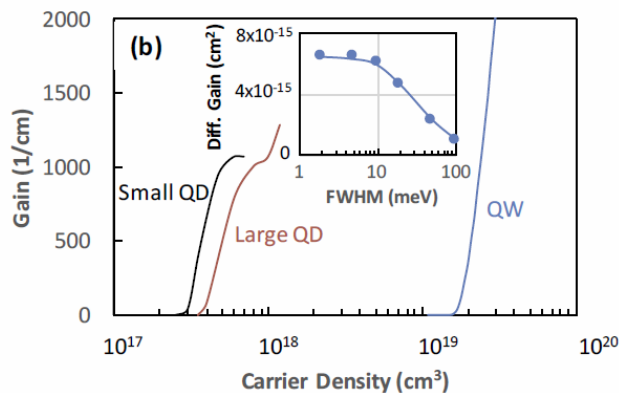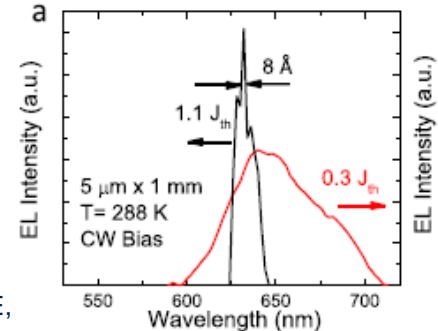# Motivation: InGaN Quantum Dots (QDs) as emitters

Potential advantages vs quantum wells

- Reduced polarization fields (reduced QCSE)

    Schulz & Reilly, PRB 82, 033411 (2010)

- Longer wavelength emission

- Lower lasing thresholds

- Higher efficiencies

- Single photon emission

U. Mich. - Red electrically injected InGaN QD laser
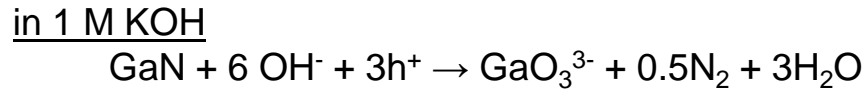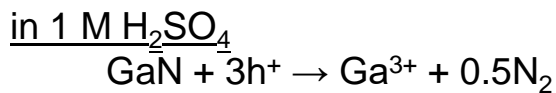

Frost et al., IEEE JQE, **49,** 923 (2013).

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

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

(In)GaN Photoelectrochemical (PEC) Etching

- GaN relatively inert to wet etching, particularly (0001) c-plane

- PEC etching: photogenerated holes oxide surface which is then dissolved

in 1 M H_2SO_4
$$GaN + 3h^+ \rightarrow Ga^{3+} + 0.5N_2$$

in 1 M KOH
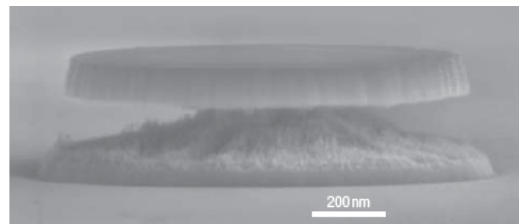$$GaN + 6\ OH^- + 3h^+ \rightarrow GaO_3^{3-} + 0.5N_2 + 3H_2O$$

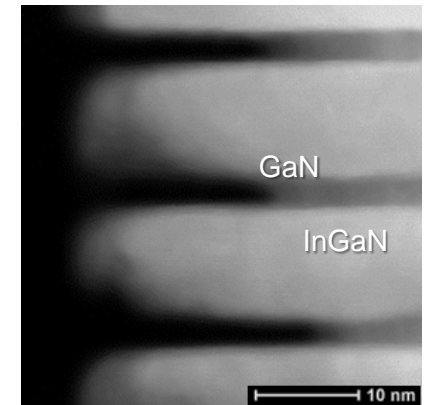Huygens et al., J. ECS **147**, 1797 (2000)

- Laser or lamp excitation (Xe arc lamp, tunable ps Ti:S)

- KOH (~0.1M) typically used as electrolyte for GaN

- Band gap selective (etch InGaN over GaN) based on wavelength used
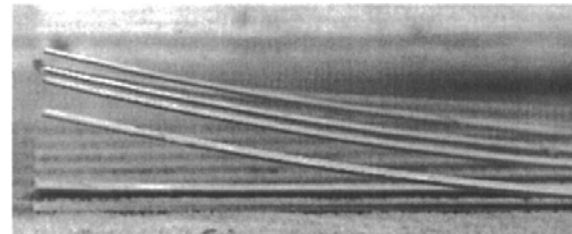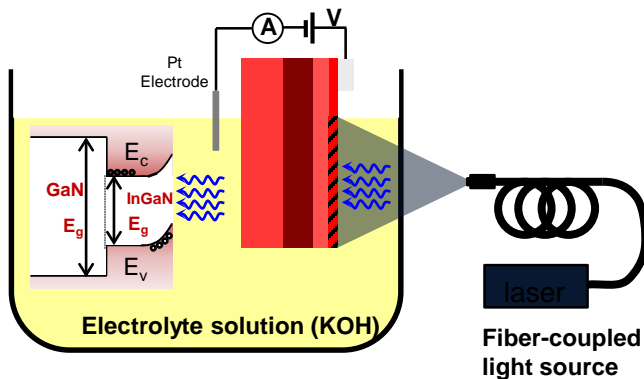
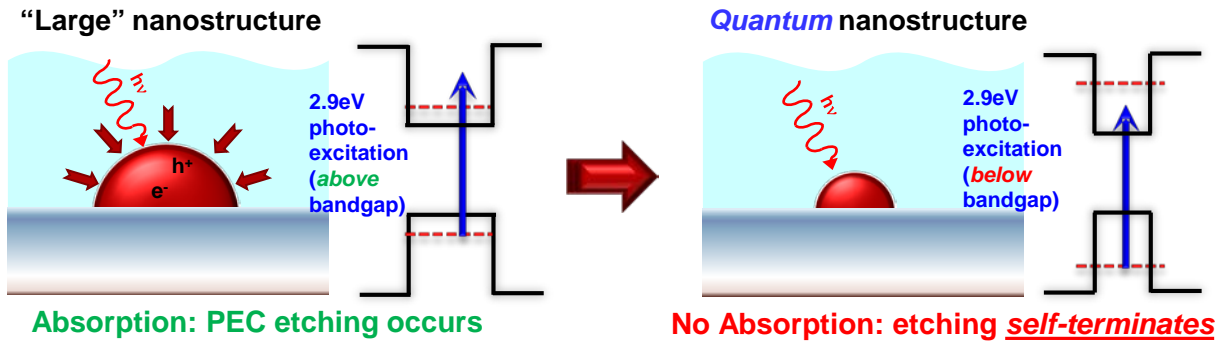
Stonas et al., JVST B **19**, 2838 (2001)

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

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

Controlled fabrication of QDs via PEC etching

Quantum Size Control: Use size quantization to control QD size

"Large" nanostructure

2.9eV photo-excitation (*above* bandgap)

h+
e-

Absorption: PEC etching occurs

***Quantum* nanostructure**

2.9eV photo-excitation (*below* bandgap)

No Absorption: etching _self-terminates_

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

- For QDs, band gap depends on size
- As PEC etch proceeds,
  - QD size gets smaller, band gap goes up
  - Etch should terminate for $E_g > E_{photon}$ pump (no more carriers needed for etch)
- Self-terminating etch process
- Final QD size (band gap) depends on PEC etch wavelength used
- "Monodisperse" QD distributions ??
- Earlier work on "size selective photocorrosion" to shrink size of colloidal CdS QDs using monochromatic light[1,2]
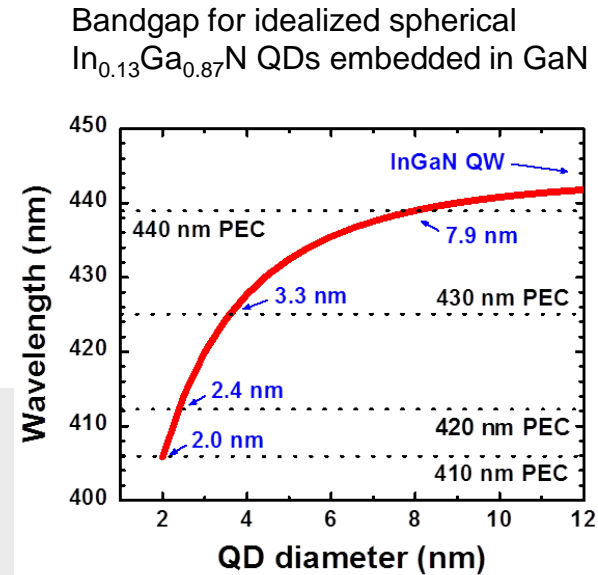
[1]Matsumoto et al., J. Phys. Chem. **100**, 13781 (1996)   [2]Torimoto et al., J. ECS **145**, 1964 (1998)

Starting MOCVD-grown InGaN/GaN samples

Uncapped single InGaN QW

InGaN QW
n-GaN
Sapphire

- ~5 - 20 nm thick $In_{0.14}Ga_{0.86}N$ layer
- No InGaN underlayer is used in this sample
- Uncapped single QW sample (14% In):
  - Amenable to surface characterization of QDs
  - TEM, AFM characterization
  - Luminescence weaker than capped sample

Capped single InGaN QW

GaN cap
InGaN QW
InGaN underlayer
n-GaN
Sapphire

- ~3 nm $In_{0.14}Ga_{0.86}N$ QW, 10 nm GaN cap
- InGaN underlayer (~2% In) used in this sample
- Capped single QW sample (14% In):
  - AFM is not useful for capped samples
  - Luminescence brighter than uncapped samples
- Etch is thought to proceed via pits, dislocations

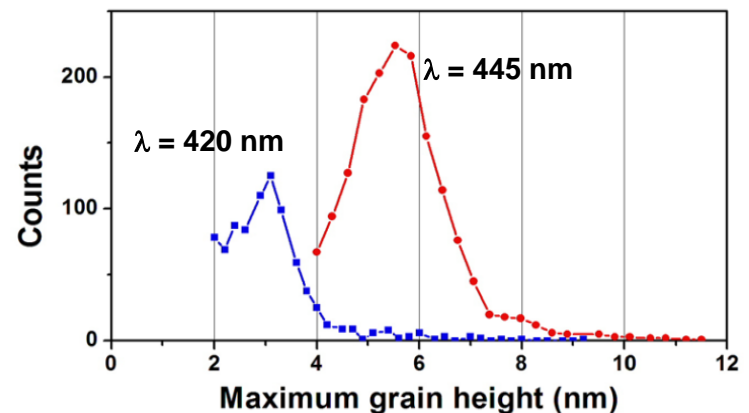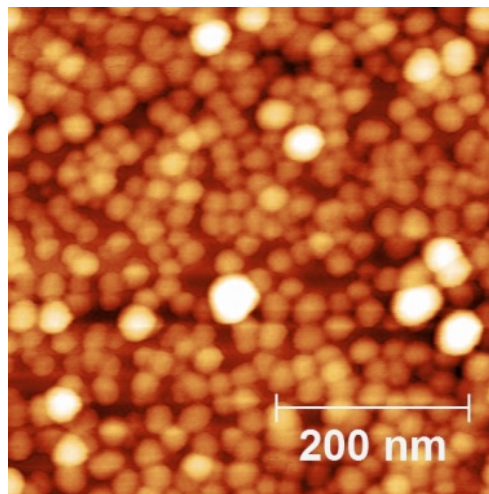# QSC-PEC etched uncapped InGaN layer - AFM Measurements

Uncapped InGaN QW

InGaN QW
n-GaN
Sapphire

- Samples etched two hours at 420 nm and 445 nm
  - 0.2M H_2SO_4 solution (no dark etch)
  - Tunable Ti:sapphire laser (2 ps pulse width, < 1 nm linewidth,
  - 82 MHz pulse repetition rate)
  - Laser power density: ~ 3 mW/cm^2
- Observe formation of (quantum) dots!
  - Very high dot density: ~10^{11}/cm^2
- Some big dots (10-20 nm) remain: due to dislocations?
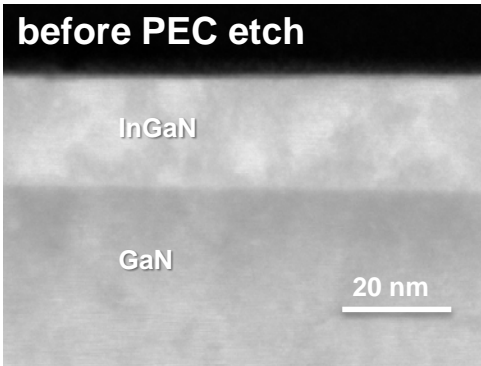- QD size depends on PEC etch wavelength!

PEC etch→ λ = 420 nm
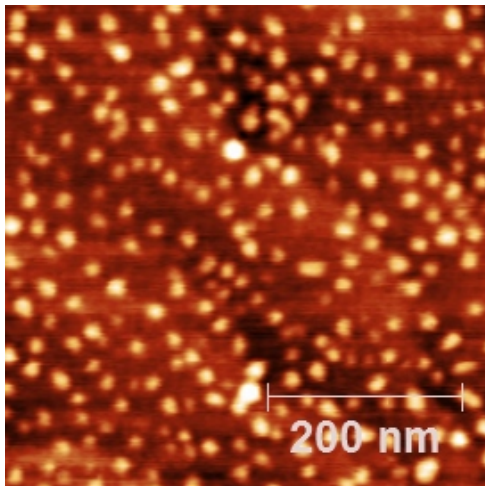
PEC etch → λ = 445 nm

QSC-PEC etched uncapped InGaN layer – Scanning TEM measurements

Uncapped InGaN QW


before PEC etch
InGaN
GaN
20 nm

- 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

After 445 nm PEC etch
20 nm

EDS
445 nm PEC etch
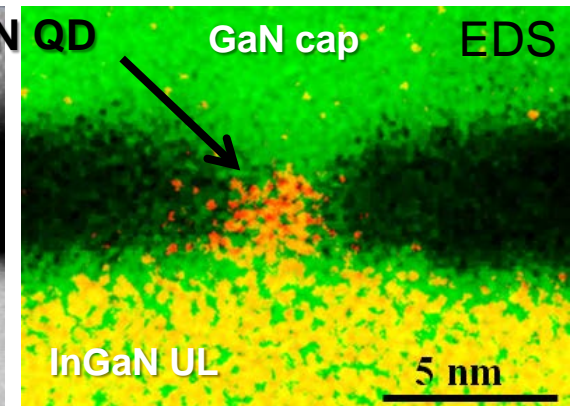20 nm

445 nm
5 nm
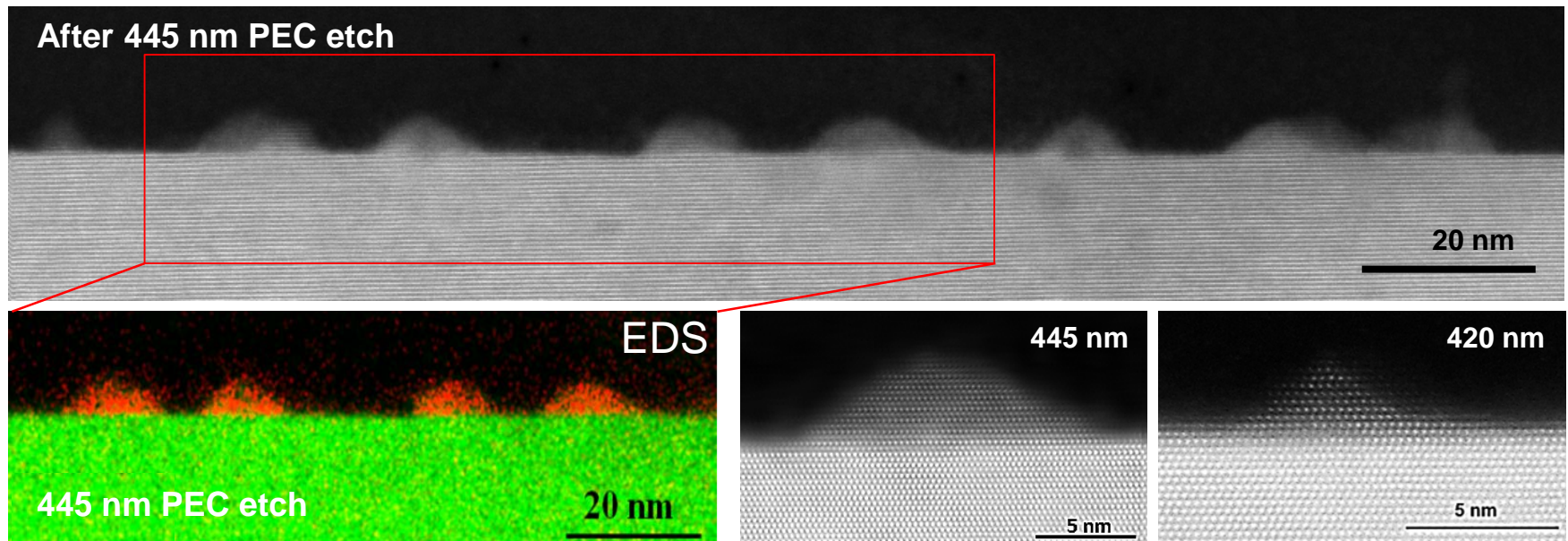
420 nm
5 nm

QSC-PEC capped InGaN layer w/InGaN underlayer – scanning TEM measurements

before PEC etch

GaN cap

InGaN QW
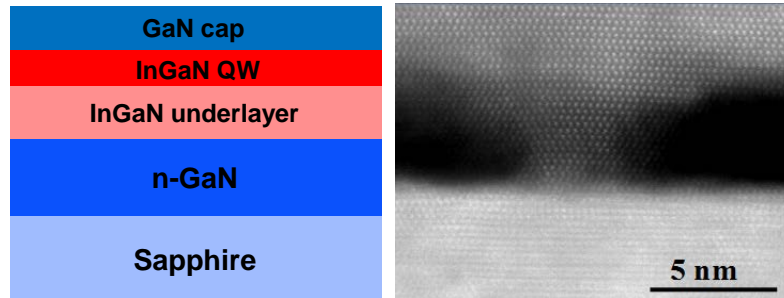
InGaN UL

10 nm
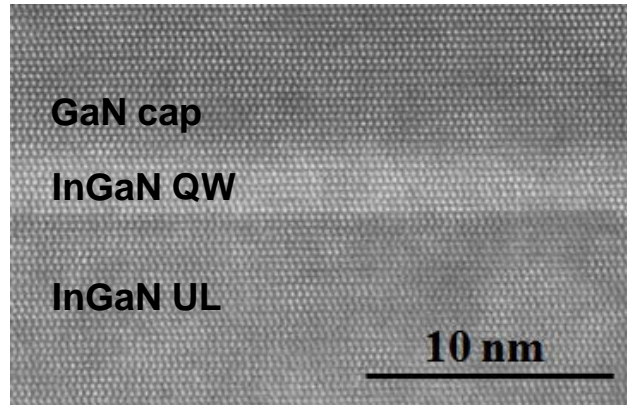
- Sample PEC etched at 420 nm
- Etch appears to break through GaN cap – defects?
- EDS mapping: dots are InGaN
- InGaN QDs are epitaxial to the underlying GaN
- 2% InGaN UL + GaN cap → PL is ~100x brighter
- GaN cap provides (partial) passivation

after PEC etch

InGaN QD   GaN cap   EDS

InGaN UL   5 nm

5 nm

X. Xiao et al., Nano Lett. **14**, 5616−5620 (2014)
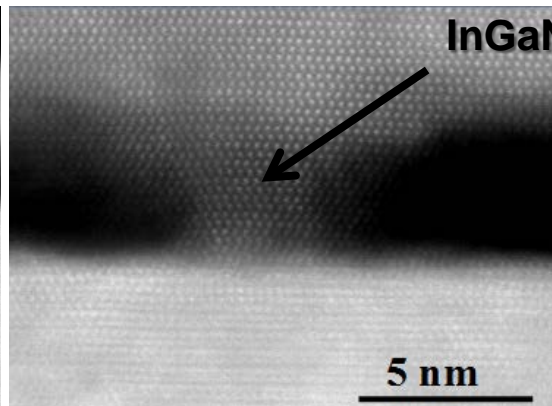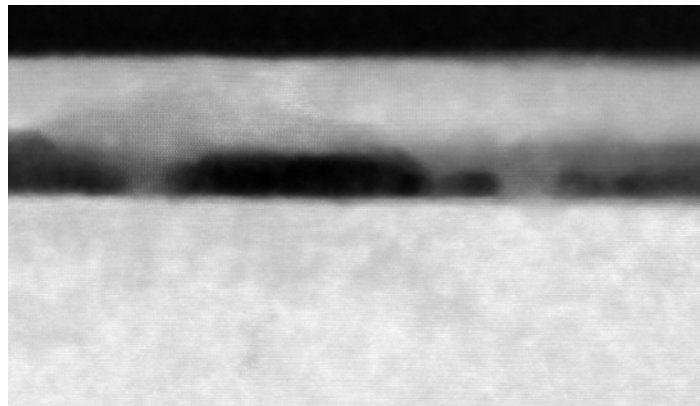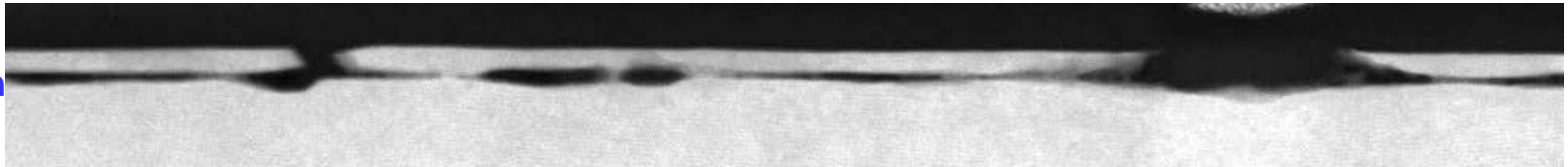
LT Photoluminescence from QSC-PEC etched InGaN QDs

Capped InGaN QDs

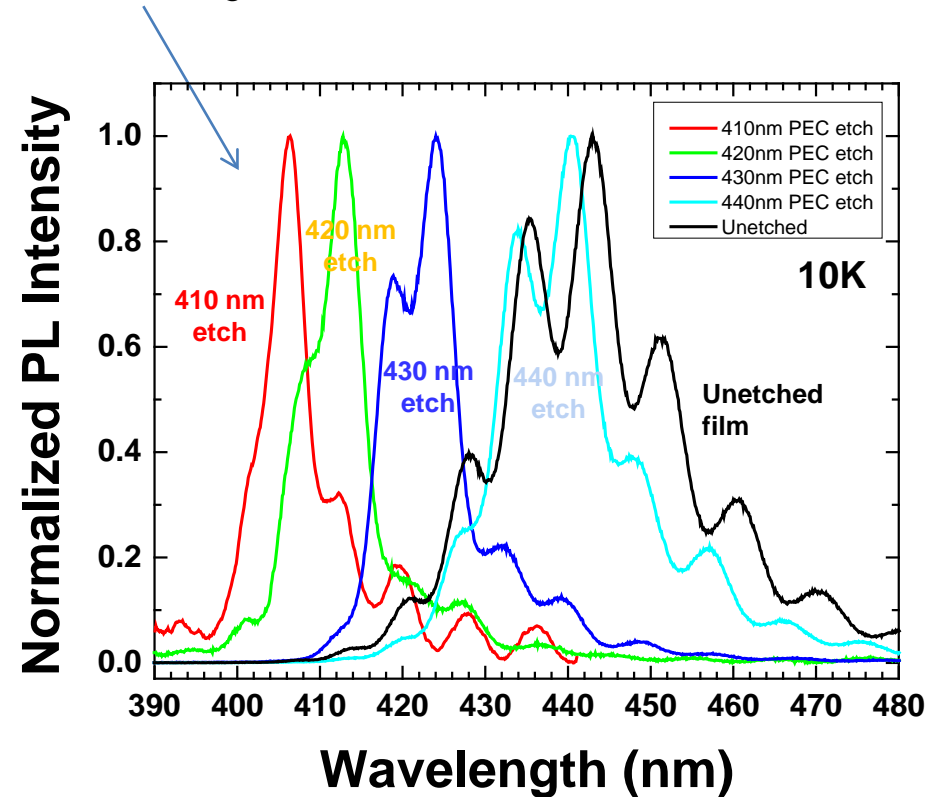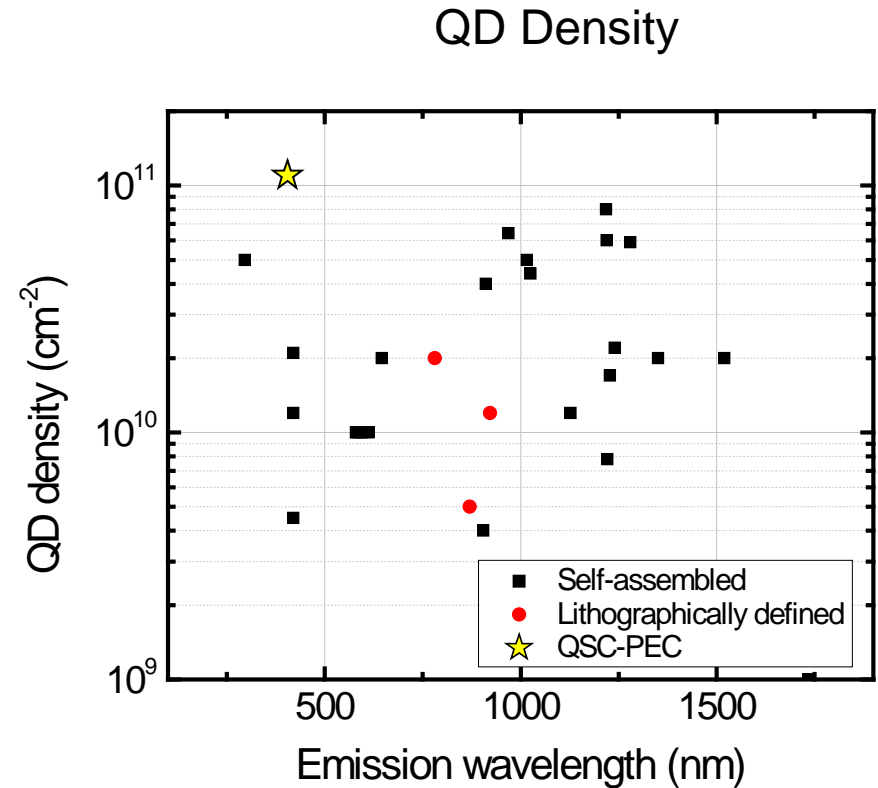|	
GaN cap	
InGaN QW	
InGaN underlayer	
n-GaN	
Sapphire	

5 nm

Photoluminescence (PL) data:

- 375 nm pump (ps pulsed), 10K
- Etched QD PL wavelength correlates with PEC etch wavelength
- PL linewidth: 24 nm (film) → 6 nm (QDs etched at 410 nm)
- Quantum size-controlled PEC etching works!

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

- 410nm PEC etch
- 420nm PEC etch
- 430nm PEC etch
- 440nm PEC etch
- Unetched

10K

410 nm etch
420 nm etch
430 nm etch
440 nm etch
Unetched film

Normalized PL Intensity

Wavelength (nm)

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

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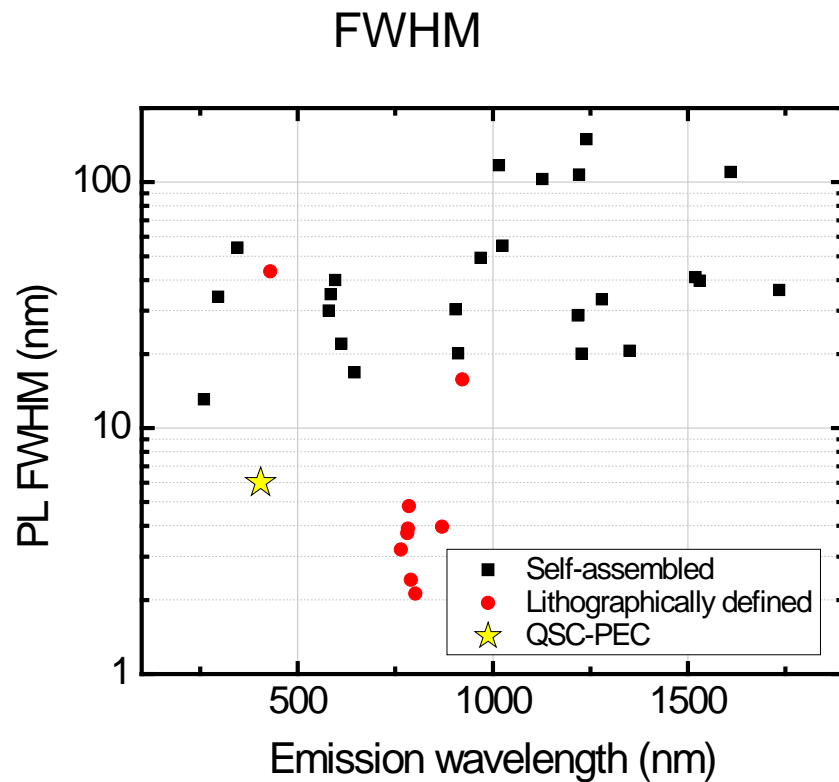
FWHM

QD Density

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

QSC-PEC Etch Time Evolution of InGaN QDs

- Analysis of AFM images shows high density of larger dots initially, with initial small increase in density as dot size shrinks

- Longer etch times suggest <u>self-termination of QSC-PEC etch</u> process with little continuing change in QD emission energy with further etching

- *Next steps: need to capture earlier initial breakup of film, and continue time-dependent etch study at longer times*

QD energy vs PEC etch time
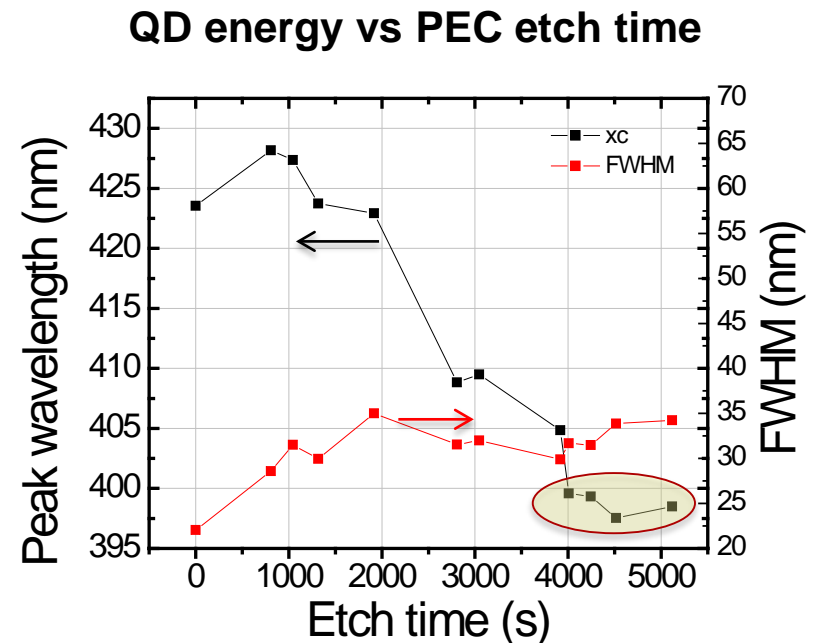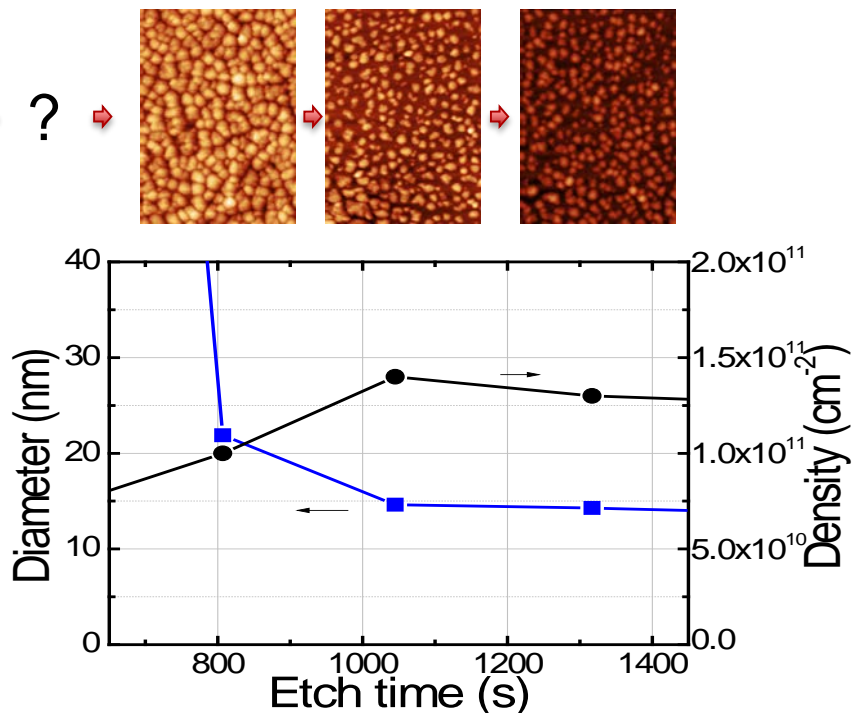
Passivation of QSC-PEC etched QDs via regrowth

- Uncapped InGaN QDs have relatively low quantum efficiency. **Thus, post-etch surface passivation strategies need to be developed.**

- We explored MOCVD **regrowth of GaN, AlGaN (1 nm), and AlGaN/GaN (1/10 nm)** capping layers on <u>unetched InGaN QWs</u> and <u>PEC etched InGaN QDs</u>.
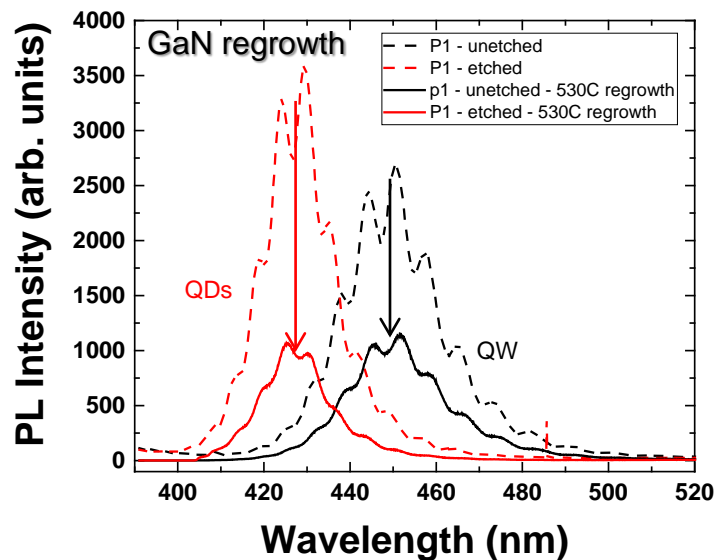
Relative integ. InGaN PL intensity after GaN regrowth

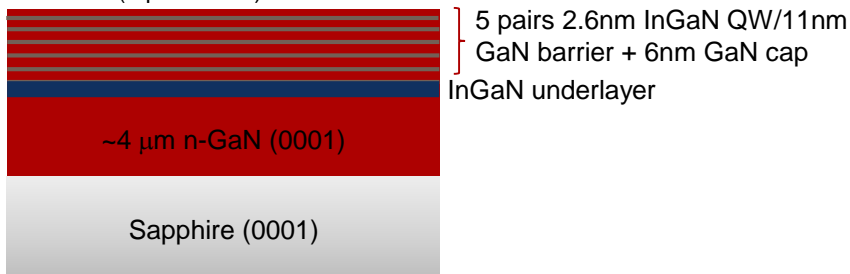|	530°C	600°C	600 ramp to 750°C	750°C
QW (unetched)	0.43	0.8	0.35	0.72
QD (etched)	0.29	0.26	0.1	0.05

- *Regrowth of GaN decreases <u>both QW and QD PL intensity</u>*; worse with increasing regrowth T

- AlGaN and AlGaN/GaN capping showed better but mixed results – unetched InGaN layers show little change and some improvement in QD PL in some AlGaN/GaN samples

Preliminary results: Regrowth of GaN capping layer decreases PL intensity of QWs and QDs. Regrowth of AlGaN/GaN seems more promising, although further study needed.
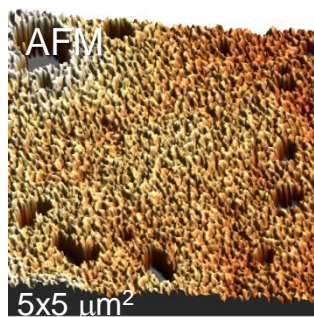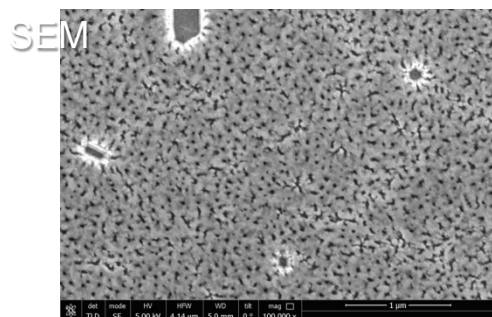
QSC-PEC Etching of InGaN/GaN Multiple Quantum Wells

- QD lasers need multiple layers of QDs to provide sufficient gain

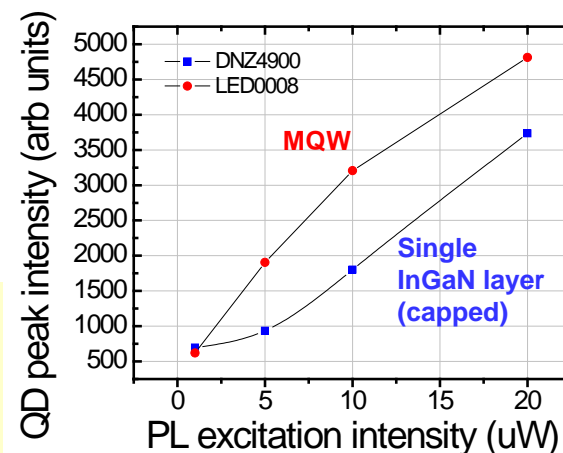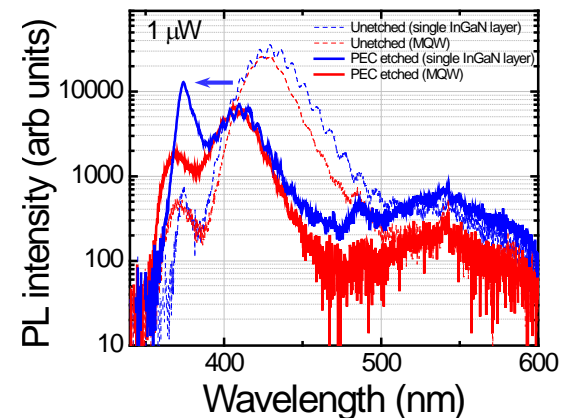- Possible to QSC-PEC etch InGaN/GaN MQWs to provide **multiple layers of capped/passivated QDs?**

LED0008 (5 pair MQW)

5 pairs 2.6nm InGaN QW/11nm GaN barrier + 6nm GaN cap
InGaN underlayer

~4 μm n-GaN (0001)

Sapphire (0001)

PEC etch: 420 nm, 20mW, 1.4V, 0.2M H$_2$SO$_4$, 45min

SEM

AFM

5x5 μm^2

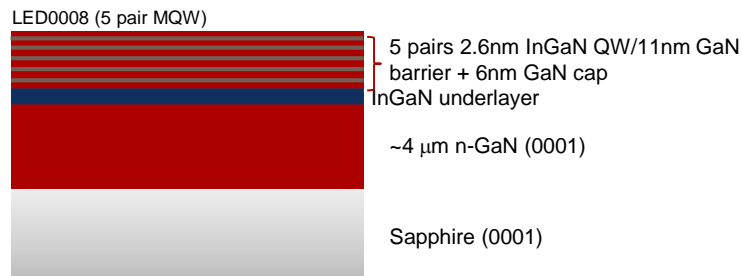**PL blue-shift indicates etching of MQWs into QDs, but PL intensity only slightly higher than single layer capped InGaN QDs (not 5x higher)**

1 μW

Unetched (single InGaN layer)
Unetched (MQW)
PEC etched (single InGaN layer)
PEC etched (MQW)

PL intensity (arb units)

Wavelength (nm)

DNZ4900
LED0008

MQW

Single InGaN layer (capped)

QD peak intensity (arb units)
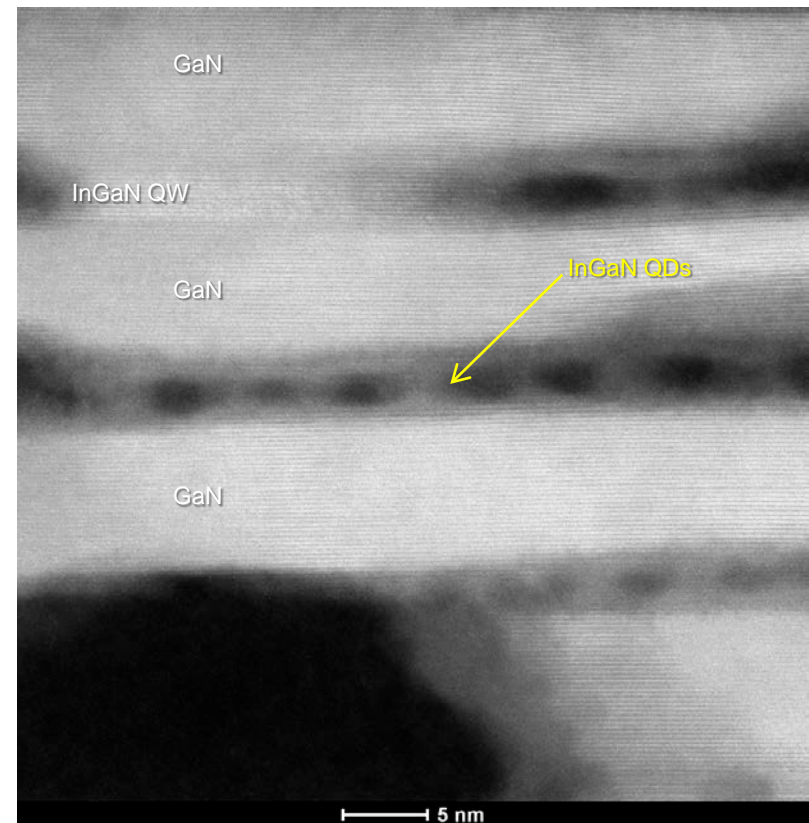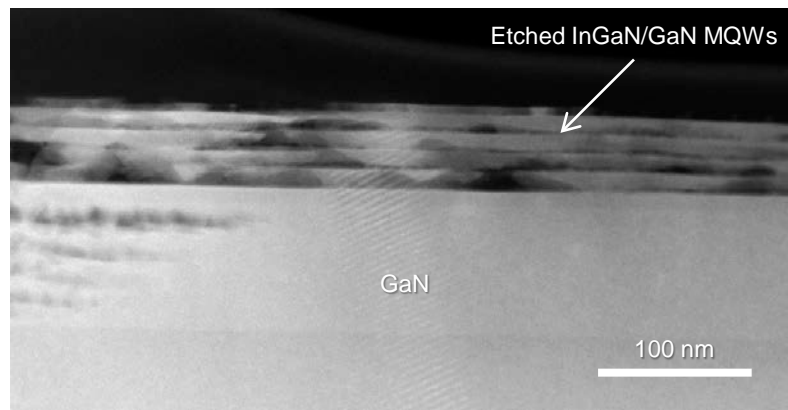
PL excitation intensity (uW)

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

LED0008 (5 pair MQW)

5 pairs 2.6nm InGaN QW/11nm GaN barrier + 6nm GaN cap

InGaN underlayer

~4 μm n-GaN (0001)

Sapphire (0001)

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

Etched InGaN/GaN MQWs

GaN

100 nm

GaN

InGaN QW

GaN

InGaN QDs

GaN

5 nm

STEM by Ping Lu

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 ($\sim 30\text{-}40$ nm)

    - 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

Backup Slides
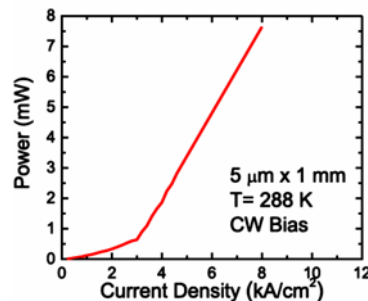
Motivation for InGaN Quantum Dot (QD) Emitters

- **Long wavelength visible emitters:**
  - **Nanostructure (NWs, QDs) can incorporate more indium**
  - **High efficiency yellow, orange, and red emission**
  - **RGB and RYGB emitters require high efficiency yellow to red emitters**
- **Visible QD diode lasers:**
  - **Lasers for lighting is gaining momentum**
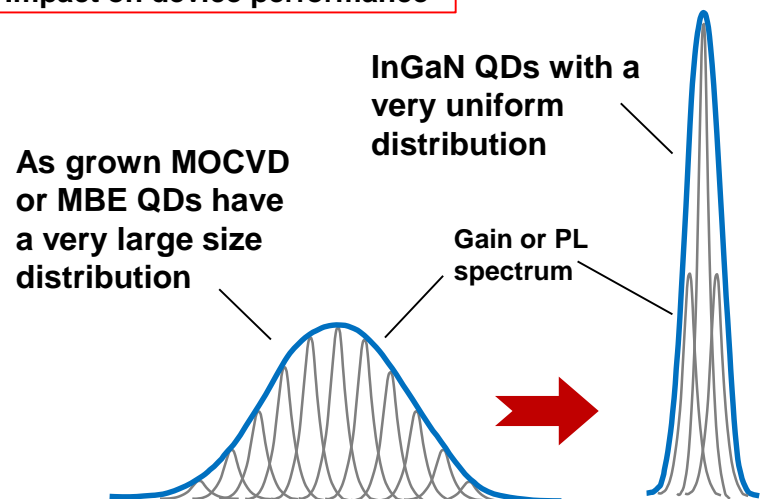 - **Low threshold, high efficiency, better temperature performance**
  - **Monodisperse QDs**

Monodisperse QD Distributions

InGaN QD laser:
- **University of Michigan**
- **Electrically injected**
- **630 nm**
- **$T_o = 236K$**

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

Impact on device performance

InGaN QDs with a very uniform distribution

As grown MOCVD or MBE QDs have a very large size distribution

Gain or PL spectrum

InGaN QD internal quantum efficiency

Capped InGaN QW

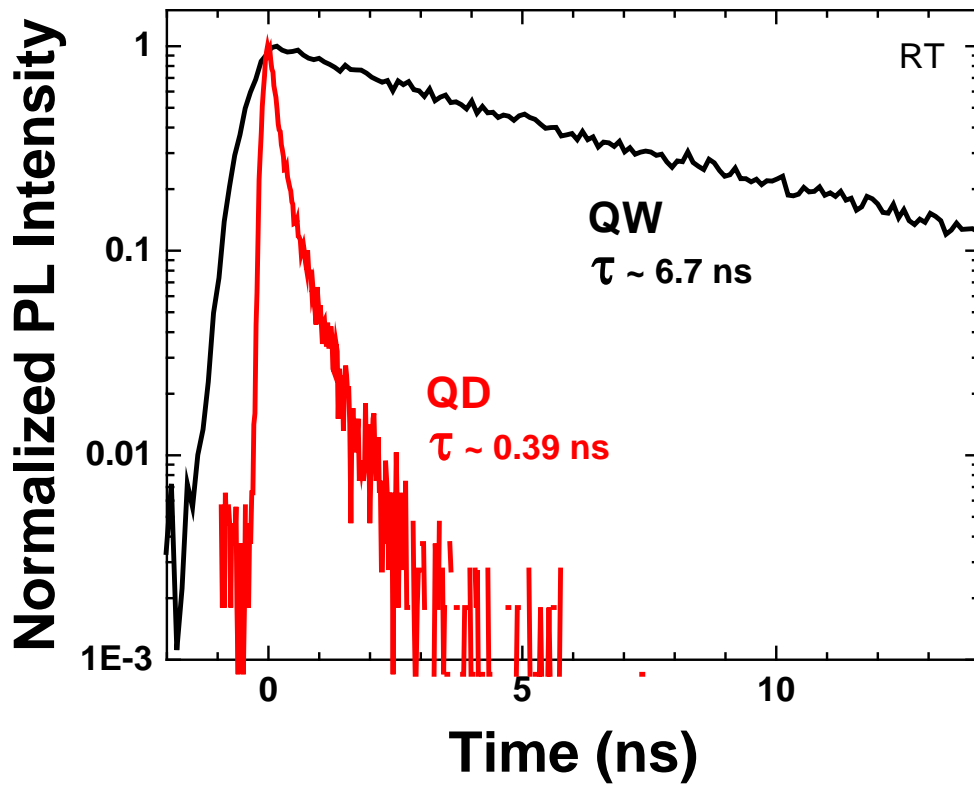| |
|---|
| GaN cap |
| InGaN QW |
| InGaN underlayer |
| n-GaN |
| Sapphire |

- 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
- QDs are expected to have better IQE

QD PL Efficiency — QD PL Efficiency (arb. units) vs Pump Power (mW), showing 10K and RT curves, 2.5X → 40%

Internal Quantum Efficiency — IQE (%) vs Pump Power (mW), showing QD (~40% IQE) and QW (4.2% IQE)
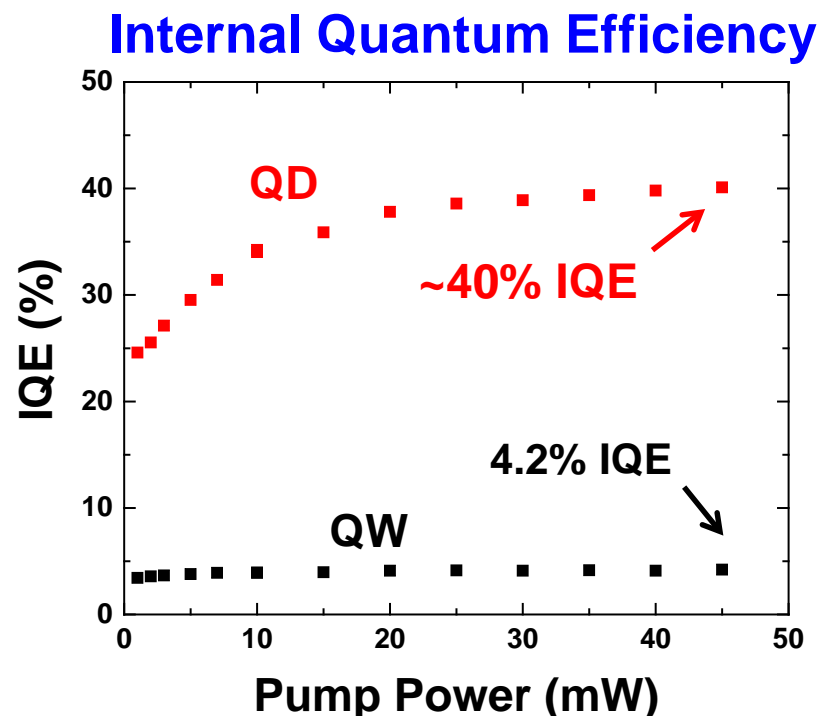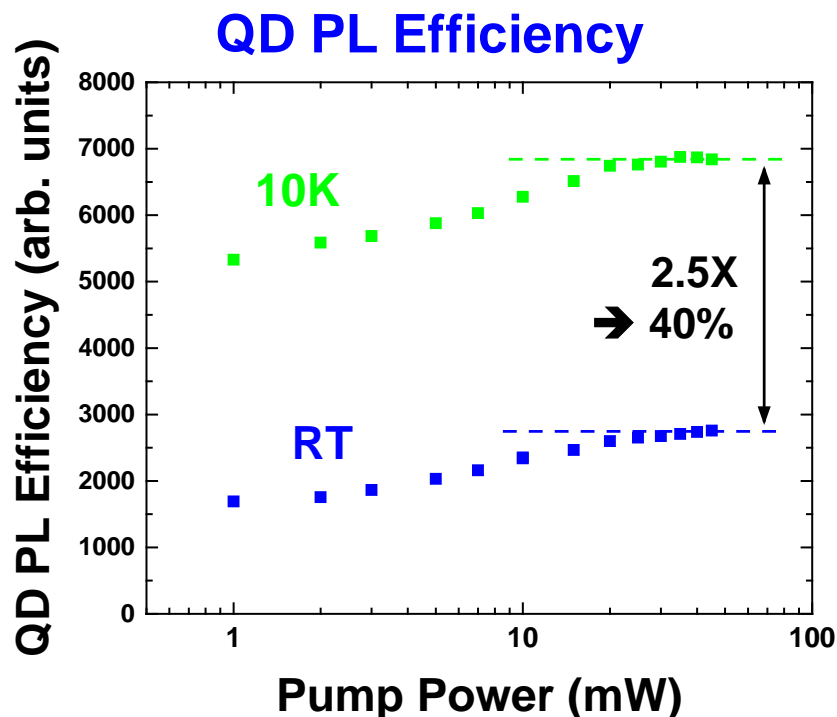
Time-resolved PL data from InGaN QDs

Capped InGaN QW

GaN cap
InGaN QW
InGaN underlayer
n-GaN
Sapphire

TRPL data:

- **405 nm pump (~ 2 ps, pulsed)**
- **Resonant pumping into InGaN**
- **Room temperature TRPL data**
- **Hamamatsu streak camera data**
- **17X change in PL lifetime**
- **Lifetime is expected to be much shorter for QDs**
- **Shows that we have fundamentally changed the InGaN material**
- **QW → QDs**

AFM of QDs
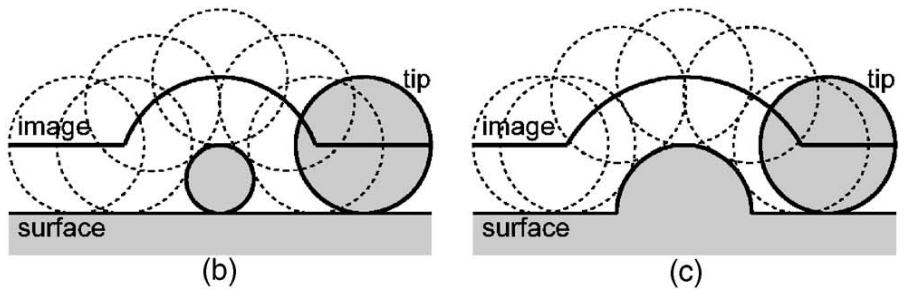
Spherical feature

$$w = 4\sqrt{Rr}.$$

Hemispherical feature
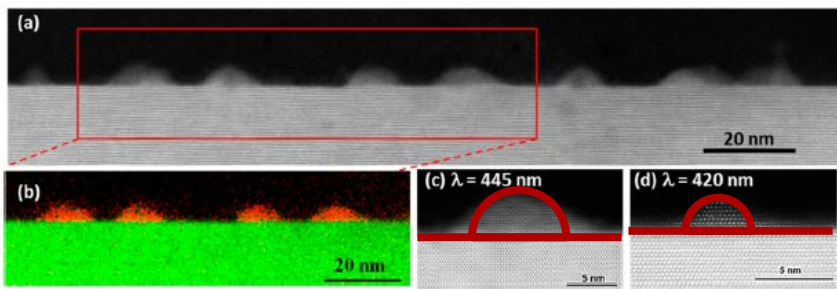
$$w = 2\sqrt{2Rr + r^2}.$$

Convolution, 3 quantities -> image (w),
tip (R), real surface (r),
If know 2, can determine the third

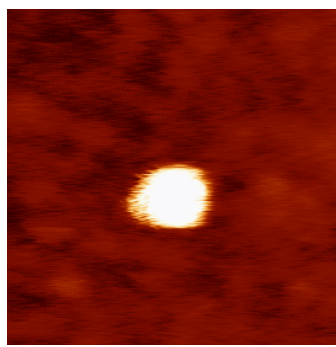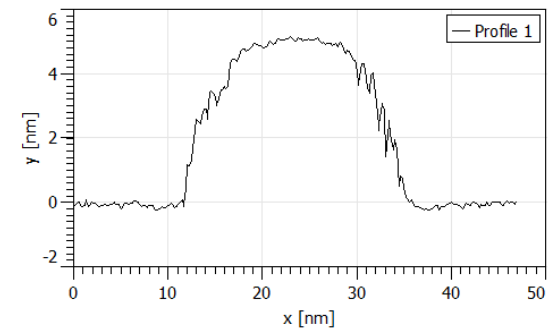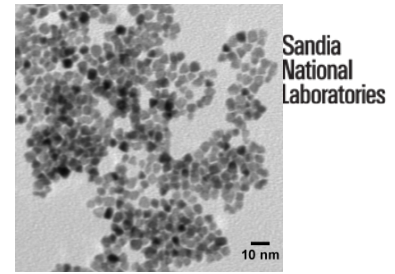AFM image of 5 nm Pt nanoparticle dispersed on silicon

Sandia National Laboratories

100nm x 100nm
512x512 pixels

5.12 nm height
24.33 nm base diameter

For our QDs

(a)

(b)   20 nm

(c) λ = 445 nm   (d) λ = 420 nm

Strength of convolution effect is
determined by *aspect ratio of QDs*

Assuming spherical particle

Tip radius = 7.3nm

Modeling QDs as
hemispheres,
(height = ½ width)

For 7 nm tip size,

*20 nm by AFM measurement
> 10-13 nm QD base diameter*

Actual width (nm)

Measured width (nm)

20
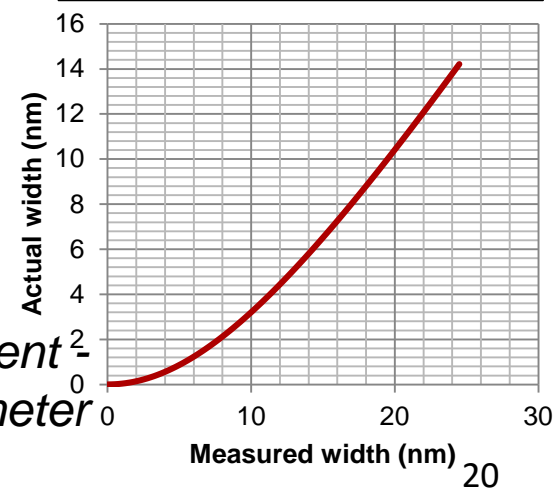
# Quantum Dots as the active region in LDs and LEDs?

- Compared to current InGaN quantum well (QW) active regions, **QD active regions could significantly improve efficiencies of both laser diodes and LEDs**
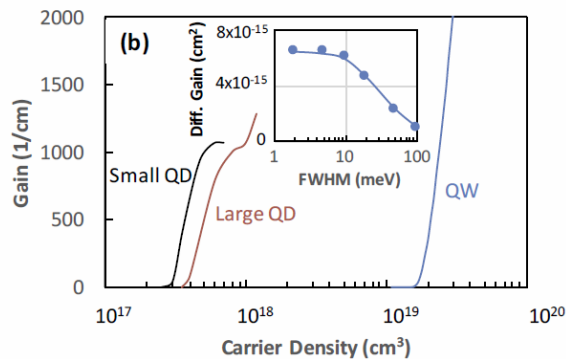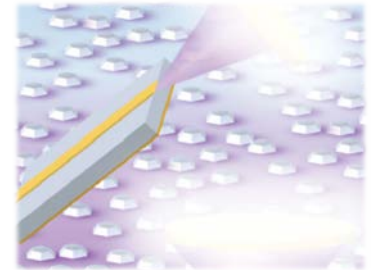
Plot of (a) gain spectra for a single QW at N = 2.5×10^{19} cm^{-3} (blue line), a layer of large QDs at N = 9×10^{17} cm^{-3} (red line), and a layer of small QDs at N = 7×10^{17} cm^{-3} (black line). Plot of (b) peak gain vs. carrier density for a single QW, a layer of large QDs, and layer of small QDs. Inset plots the differential gain of the small QDs vs. as a full-width at half maximum (FWHM) of the inhomogeneous broadening energy.
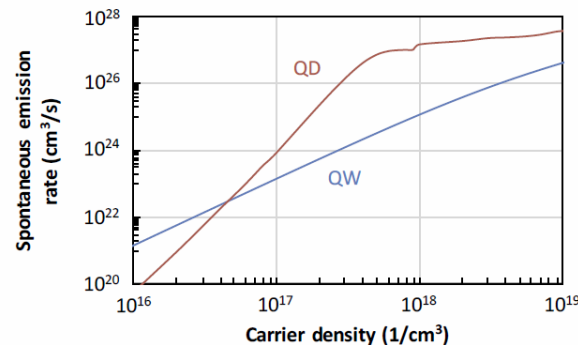
Plot of (a) spontaneous emission rate vs. carrier density for a QW (blue) and QD (red) active region. The QD active layer has higher spontaneous emission rates over the carrier densities of interest. The kink in the curve at ~1×10^{18} cm^{-3} is the onset of carrier filling in the second allowed transition. (Small QDs, 6 layers, 7.2×10^{10} cm^{-2}, 5 meV FWHM, 4 nm base width)
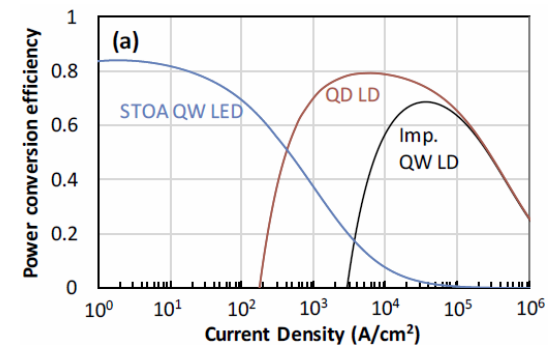
Plot of (a) power conversion efficiency vs. current density of a state-of-the-art (SOTA), QW-based LED (blue line), an improved QW-based LD (black line), and a QD-based LD (red line). The QD LD has extremely low threshold currents and peak efficiencies that rival the QW-based LED.

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

The challenge going forward is to find methods to synthesize QDs to meet the required sizes, inhomogeneous broadening, and densities
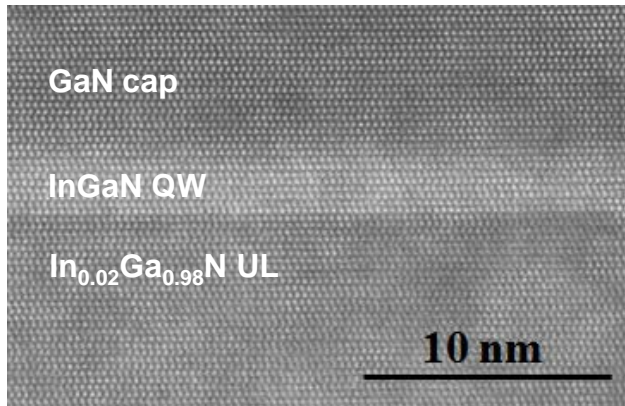
QSC-PEC capped InGaN layer w/InGaN underlayer – scanning TEM measurements

Capped InGaN QW

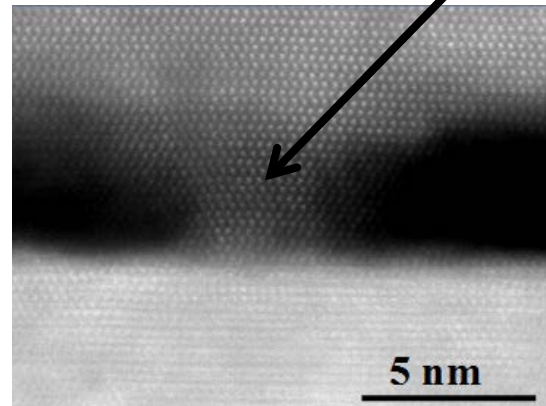| GaN cap |
|---|
| InGaN QW |
| InGaN underlayer |
| n-GaN |
| Sapphire |

- High-angle annular dark-field (HAADF) TEM images
- Sample PEC etched at 420 nm
- EDS mapping shows that dots are InGaN
- InGaN QDs are epitaxial to the underlying GaN
- 2% InGaN underlayer + GaN cap → PL is ~100x brighter
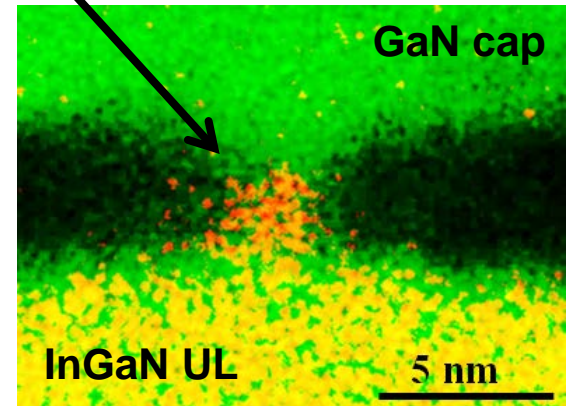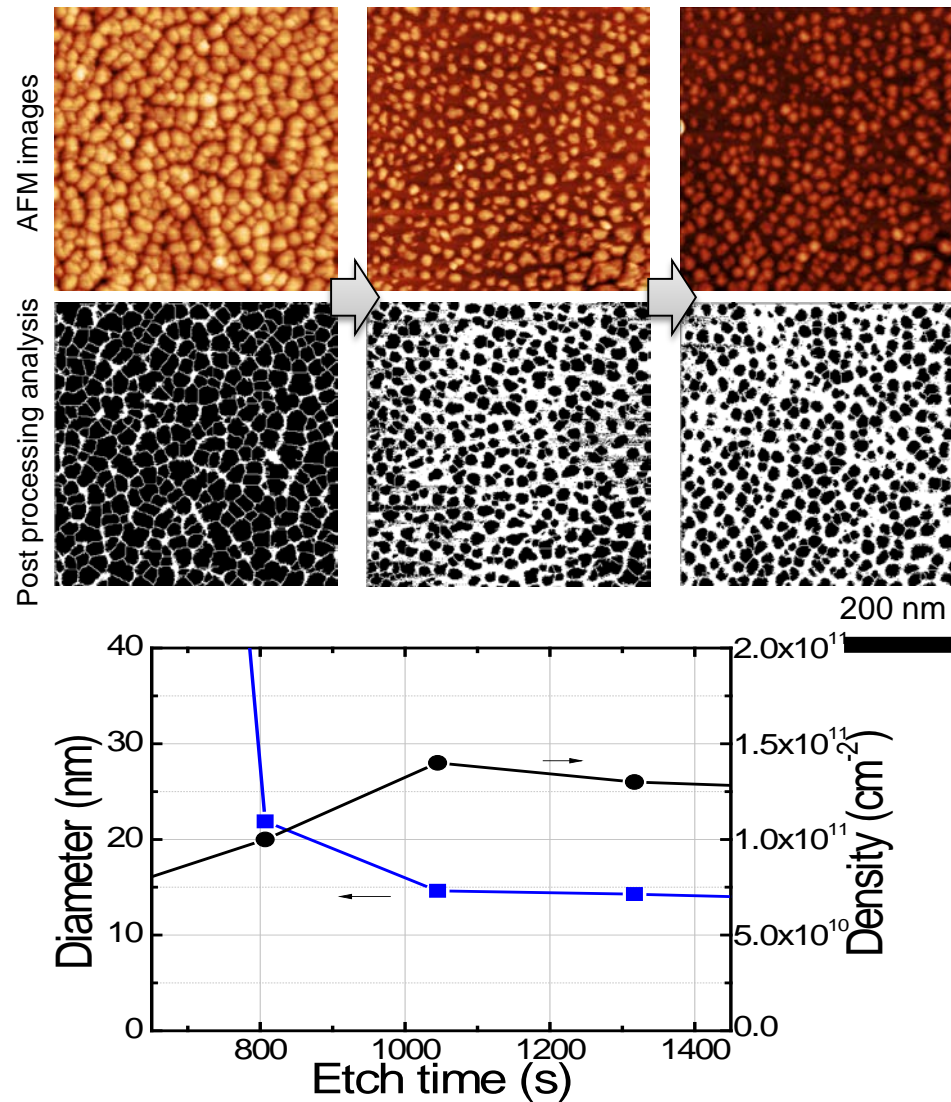- GaN cap provides partial passivation

before PEC etch

GaN cap

InGaN QW

$In_{0.02}Ga_{0.98}N$ UL

10 nm

after PEC etch

InGaN QD

5 nm

after PEC etch
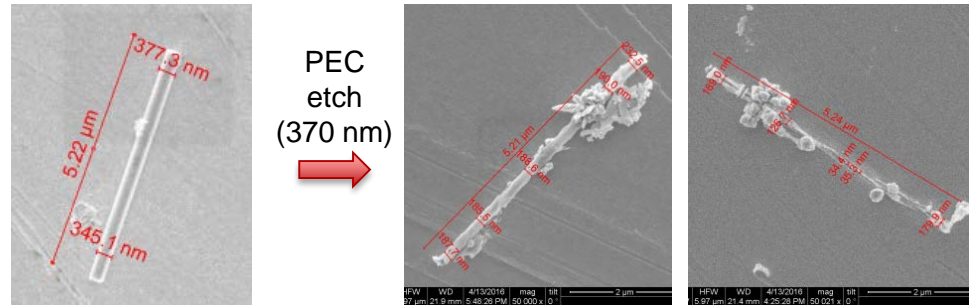
GaN cap

InGaN UL

5 nm

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

# QSC-PEC Etch Evolution of InGaN QDs

PEC etching of GaN nanowire arrays

- GaN nanowires were PEC etched to see if quantum size effects could create diameter controlled 1D quantum wires

PEC etch (370 nm)

- A GaN epilayer was PEC etched to shed light on the results & possible breakup mechanism of film into QDs, _resulting in dense, uniform GaN nanowires_

PEC etch: 370 nm, 4 mW, 1V, 2M H2SO4

45 min

4 hr
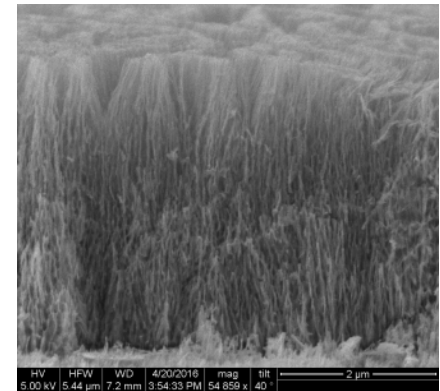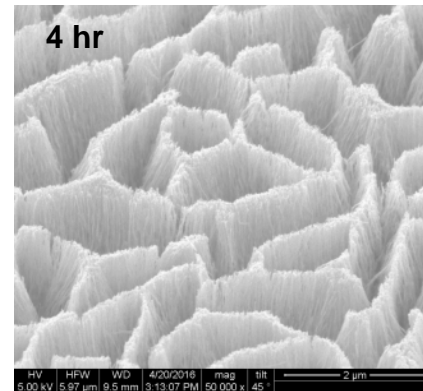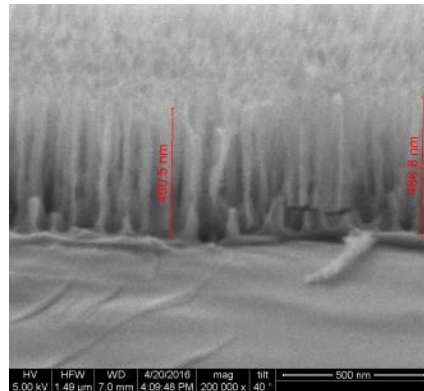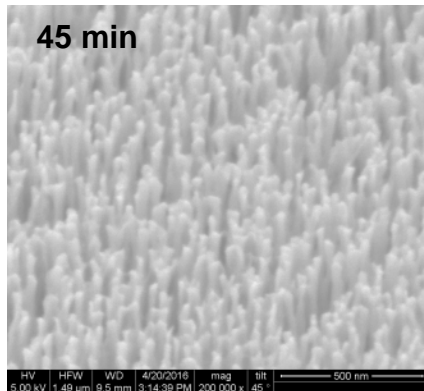
- The density of the nanowires is inconsistent with threading dislocation density of the GaN epilayer (TEM studies needed to confirm)
- _Next: Investigate if nanowire diameter tunable by wavelength of laser (e.g. quantum size effects involved)_

Technical Accomplishment: QSC-PEC etching model

- **Fortran code written to model (1) QD size evolution; due to (2) laser absorption / carrier creation; parasitic-loss terms due to (3) radiative recombination and (4) surface defect recombination; and (5) PEC etching oxidation reaction at the QD surface**

$$\underset{1}{\underline{\dot{N}_{atoms}}} = \underset{2}{\underline{\alpha_{abs}(E_g, N)I_{laser}V(N)}} - \underset{3}{\underline{\rho B_{rad}V(N)}} - \underset{4}{\underline{\rho v_{surf}A(N)}} - \underset{5}{\underline{\rho v_{etch}A(N)}}$$

- **Initial model was developed for the case of spherical QDs**

- **Developed a model for bandgap of _pyramidal dots_ as a function of QD width & height**

QD energy as function of materials system
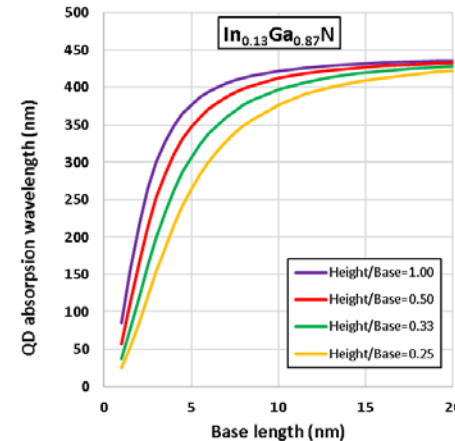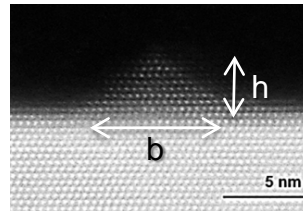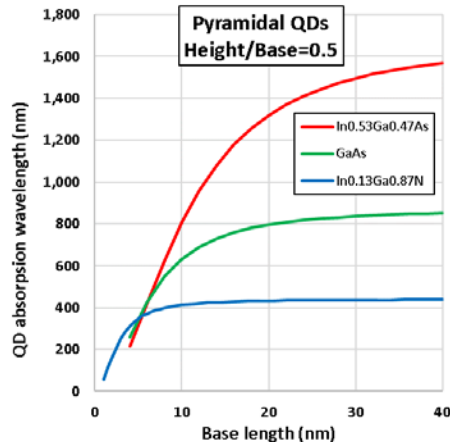
QD energy as function of aspect ratio

- **<u>Future model developments</u>: (1) include Coulombic term in pyramidal QD bandgap model; (2) account for _finite_ barrier confinement energy; (3) estimate or extract from experiment physical parameters in the model; (4) develop model to account for the effect of random alloy fluctuations on final QD size distribution.**