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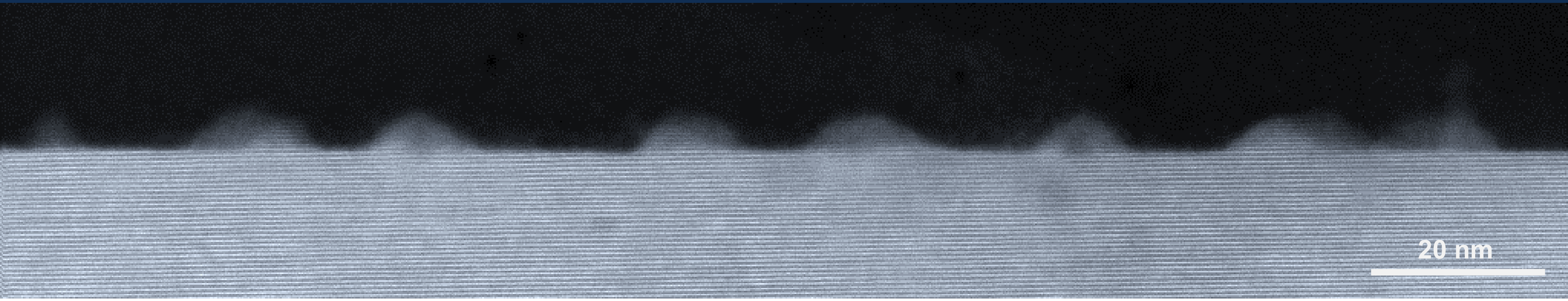

InGaN Quantum Dots by Quantum Size Controlled Photoelectrochemical Etching

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

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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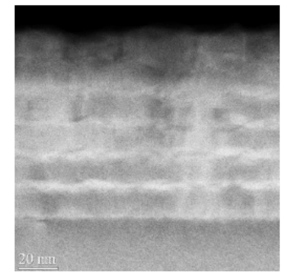
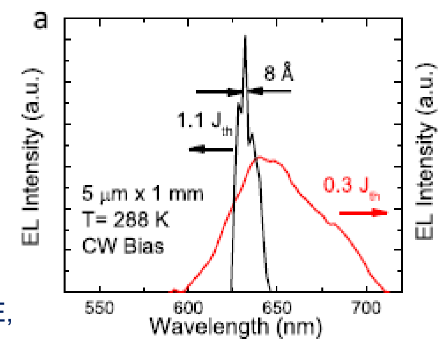
Motivation: InGaN Quantum Dots (QDs) as emitters

Potential advantages vs quantum wells

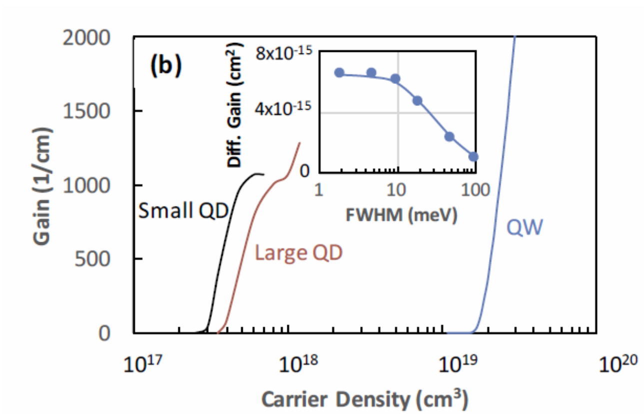
- Single photon emission
- Reduced polarization fields (reduced QCSE)
  Schulz & Reilly, PRB 82, 033411 (2010)
- Longer wavelength emission
- Lower lasing thresholds
- Higher efficiencies

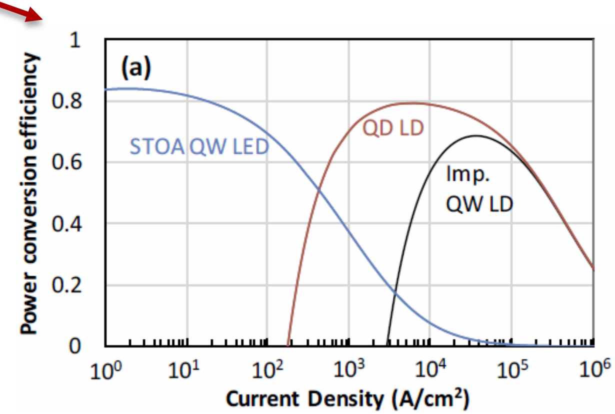
U. Mich. - Red electrically injected InGaN QD laser





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





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

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

(In)GaN Photoelectrochemical (PEC) Etching

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

<u>in 1 M H_2SO_4</u>

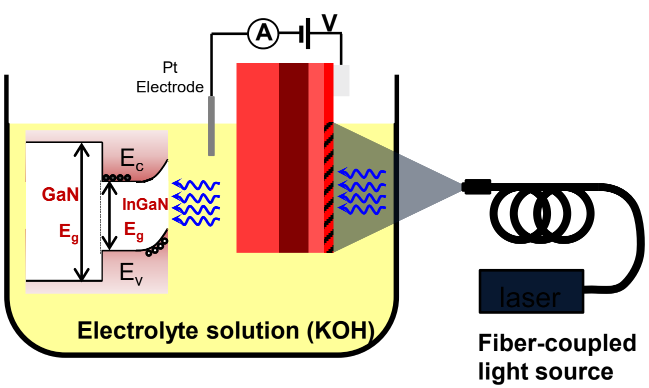
$$GaN + 3h^{+} \rightarrow Ga^{3+} + 0.5N_2$$

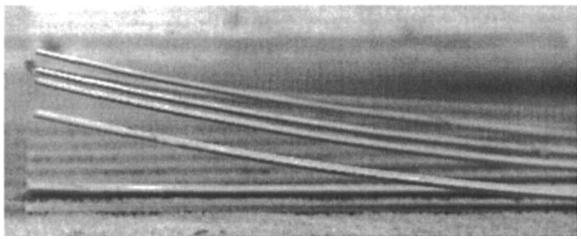
<u>in 1 M KOH</u>

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

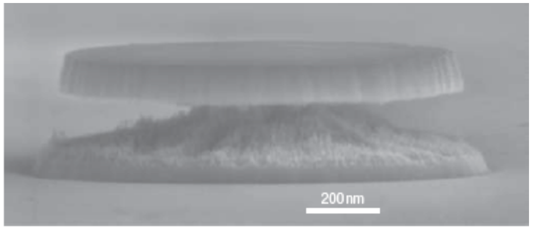
Huygens et al., J. ECS **147**, 1797 (2000)

- 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

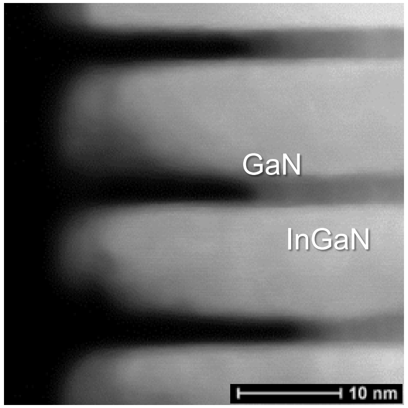




Stonas et al., JVST B **19**, 2838 (2001)



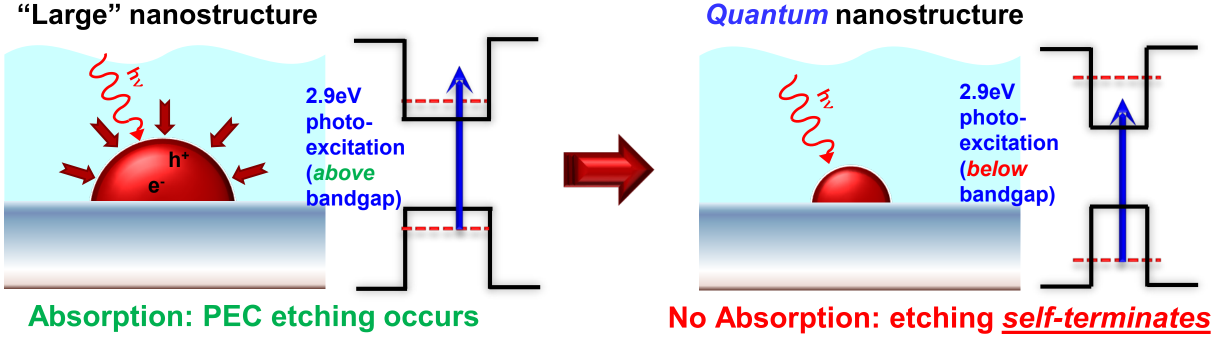
Tamboli et al., Nat. Phot. **1**, 61 (2007)

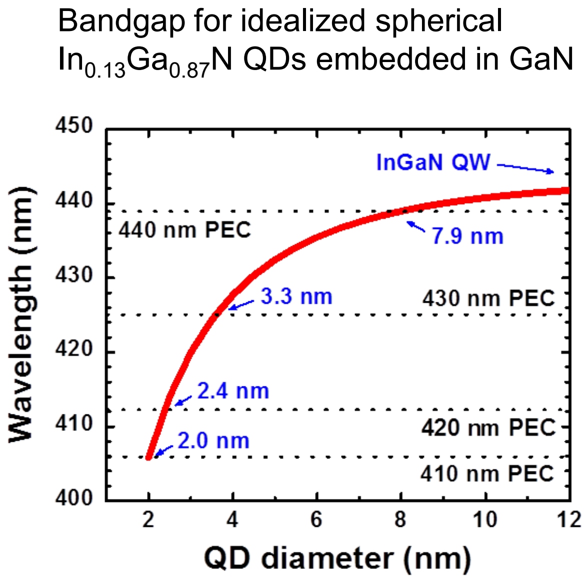


Xiao et al, Elec. Acta 162, 163 (2015)

Controlled fabrication of QDs via PEC etching

Quantum Size Control: Use size quantization to control QD size



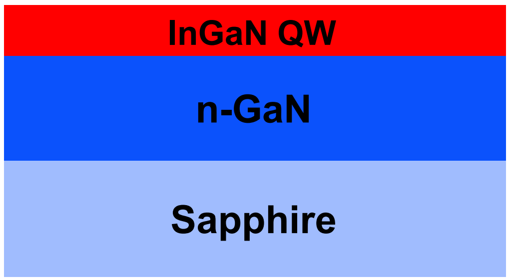


- For QDs, band gap depends on size
- As PEC etch proceeds,
  - QD size gets smaller, band gap goes up
  - Etch should terminate for $E_g > E_{photon}$ pump (no more carriers needed for etch)
- Self-terminating etch process
- Final QD size (band gap) depends on PEC etch wavelength used
- “Monodisperse” 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**



- Uncapped 5 - 20 nm thick $In_{0.14}Ga_{0.86}N$ layer:
  - Amenable to surface characterization of QDs
  - TEM, AFM, PL characterization
  - Luminescence weaker than capped sample

Capped **single InGaN QW**

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

QSC-PEC etched uncapped InGaN layer - AFM Measurements

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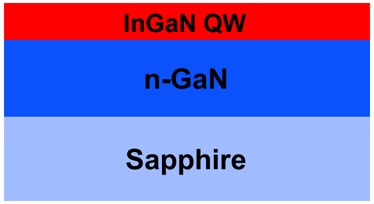
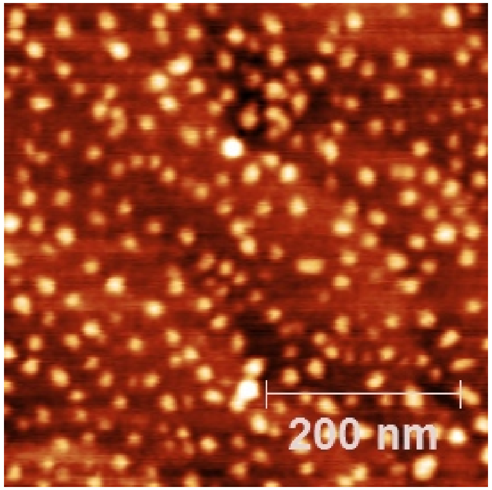
Uncapped InGaN QW

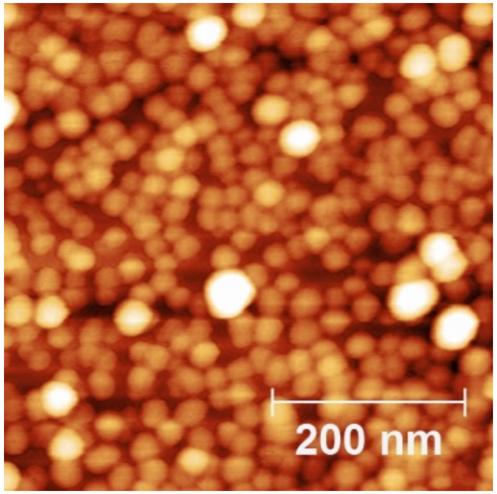


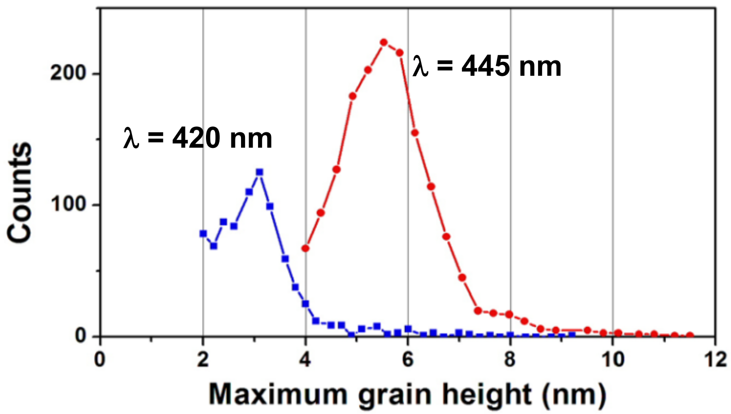
- Samples etched two hours at 420 nm and 445 nm
  - 0.2M H_2SO_4 solution (no dark etch)
  - Tunable Ti:sapphire laser (2 ps pulse width, < 1 nm linewidth,
  - 82 MHz pulse repetition rate)
  - Laser power density: ~ 3 mW/cm^2
- Observe formation of (quantum) dots!
  - Very high dot density: ~$10^{11}/cm^2$
- 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

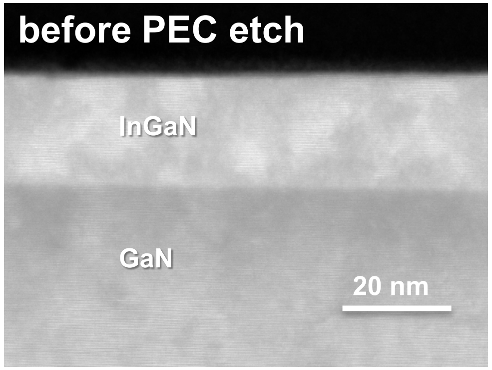




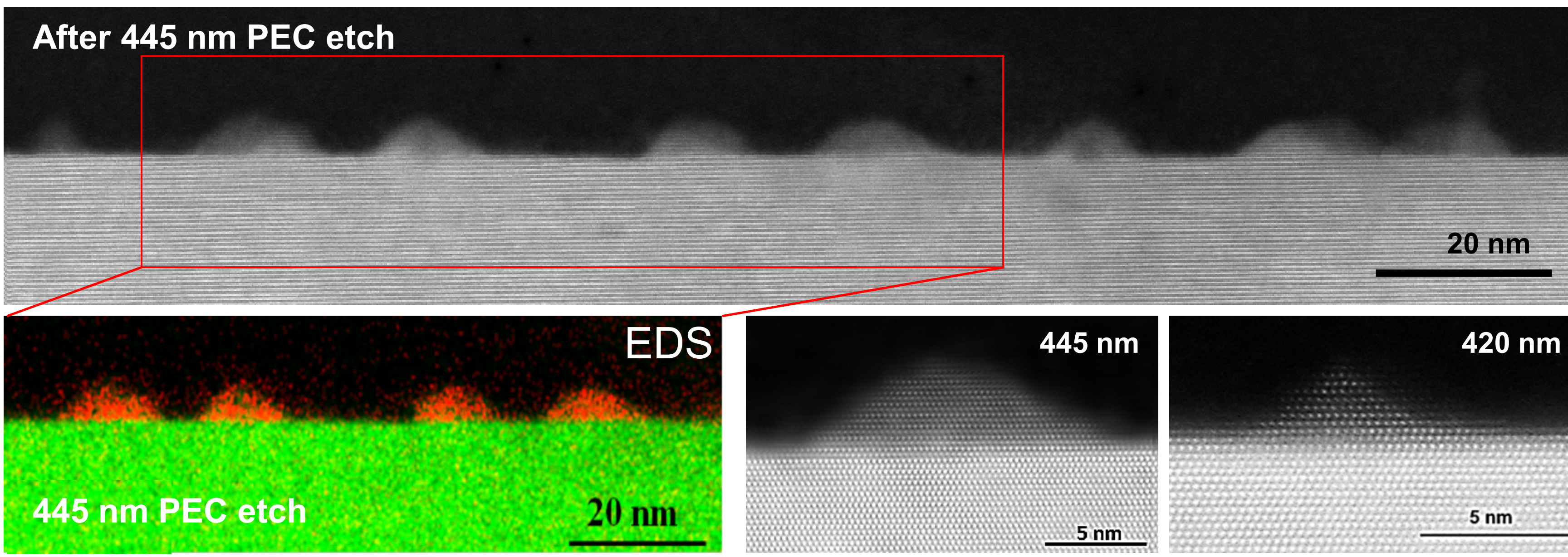
X. Xiao et al., Nano Lett. **14**, 5616−5620 (2014)

QSC-PEC etched uncapped InGaN layer – Scanning TEM measurements

Uncapped InGaN QW



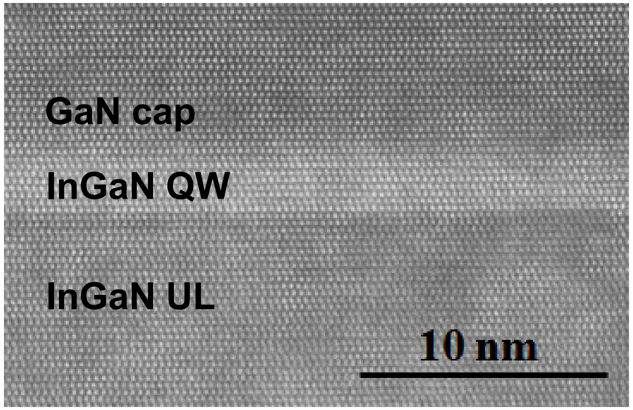
- Cross-sectional high-angle annular dark-field (HAADF) scanning TEM images
- Samples etched at 420 nm and 445 nm
- Energy dispersive (EDS) x-ray mapping
  - QDs on surface are InGaN (Red = In, Green = Ga)
- InGaN QDs are epitaxial to the underlying GaN
- No underlayer, no cap → PL is not very bright



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

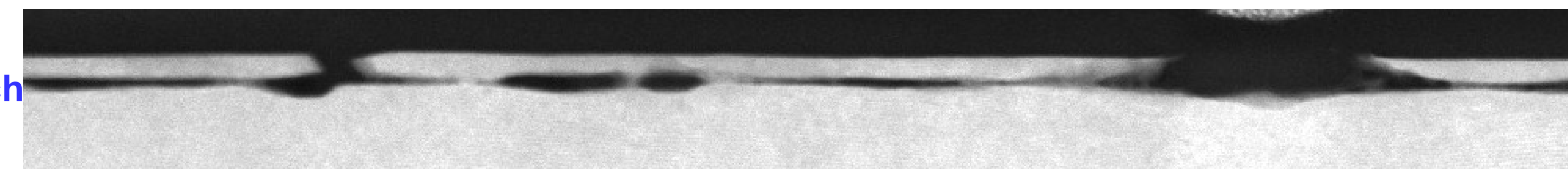
QSC-PEC capped InGaN layer w/InGaN underlayer – scanning TEM measurements

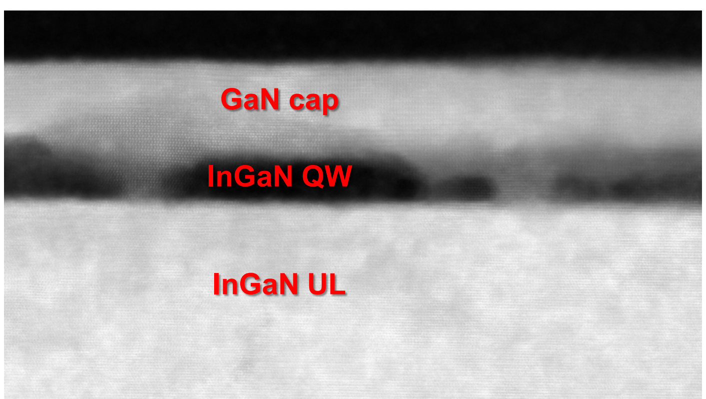
before PEC etch

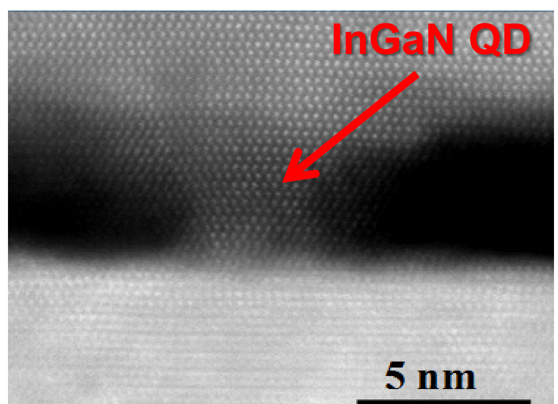


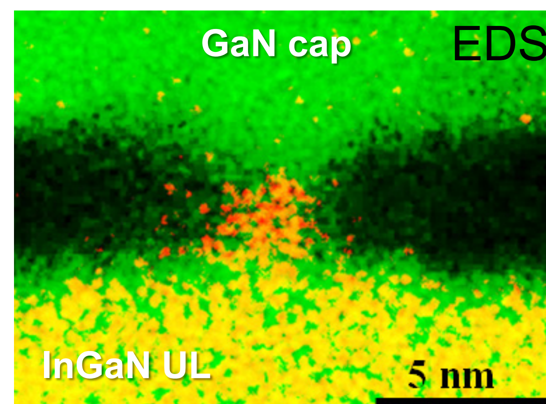
- Sample PEC etched at 420 nm
- Etch appears to break through GaN cap – defects?
- EDS mapping: dots are InGaN
- **2% InGaN UL + GaN cap → QD PL is ~100x brighter**
- GaN cap provides (partial) passivation

after PEC etch









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

LT Photoluminescence from QSC-PEC etched InGaN QDs

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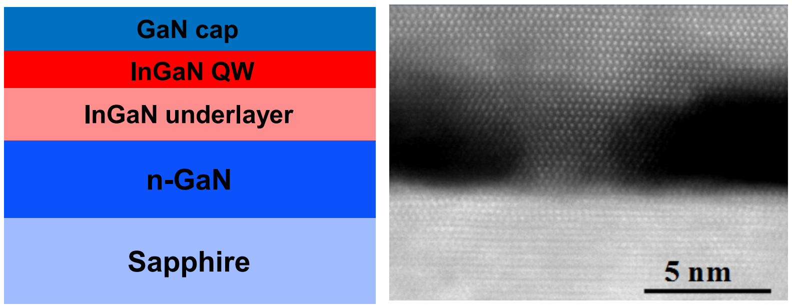
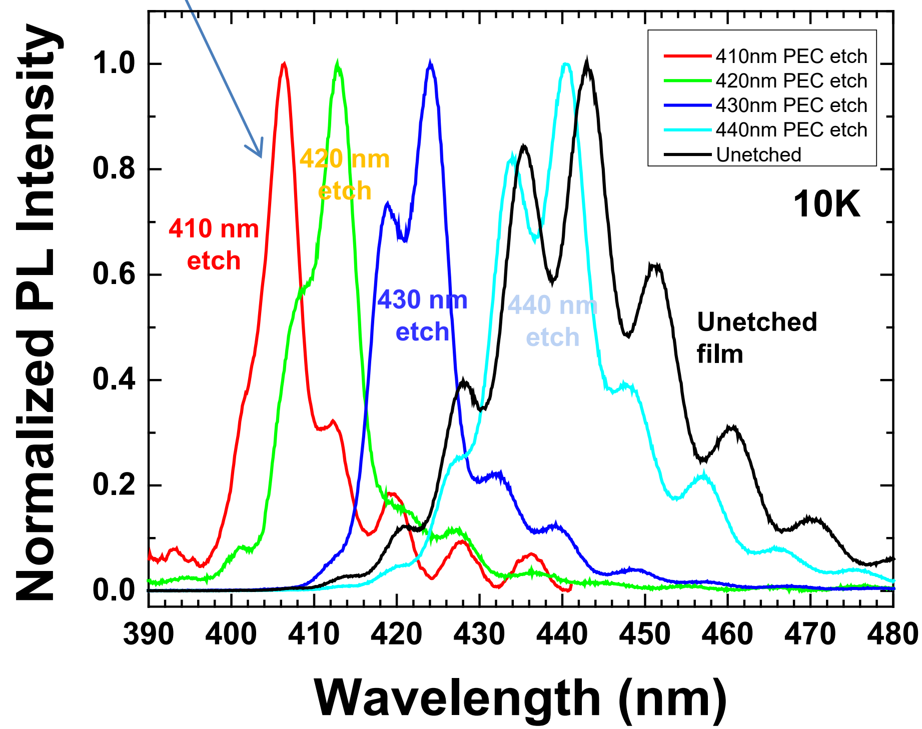
Capped InGaN QDs



Photoluminescence (PL) data:

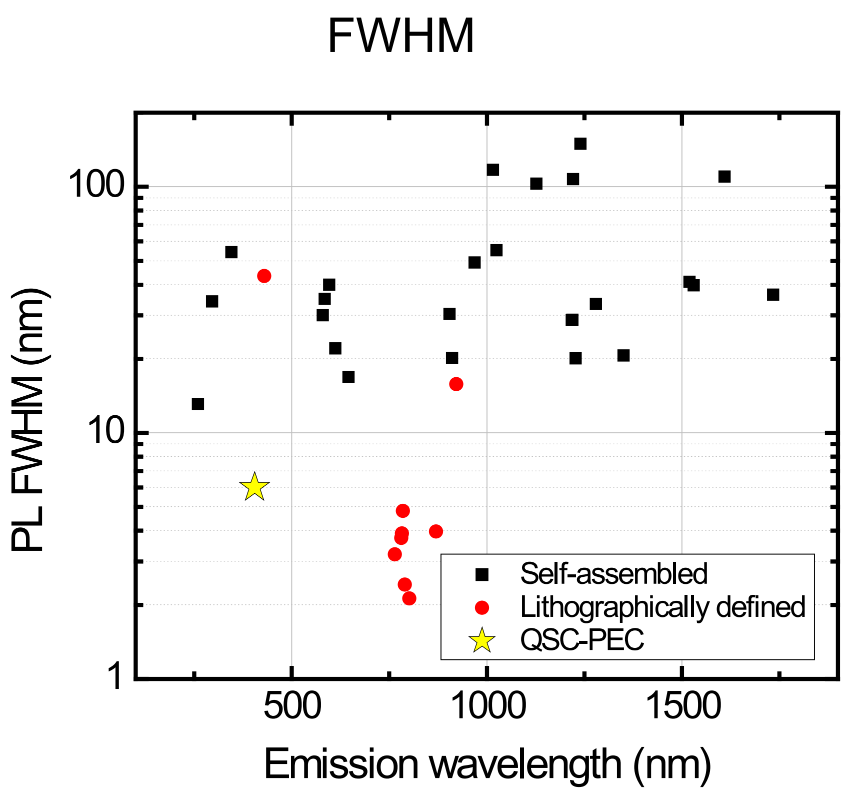
- 375 nm pump (ps pulsed), 10K
- Etched QD PL **wavelength correlates** (but doesn't exactly coincide) **with PEC etch wavelength**
- PL linewidth **decreases with decreasing etch wavelength**: 24 nm (film) → 6 nm (QDs etched at 410 nm)
- **Quantum size-controlled PEC etching works!**

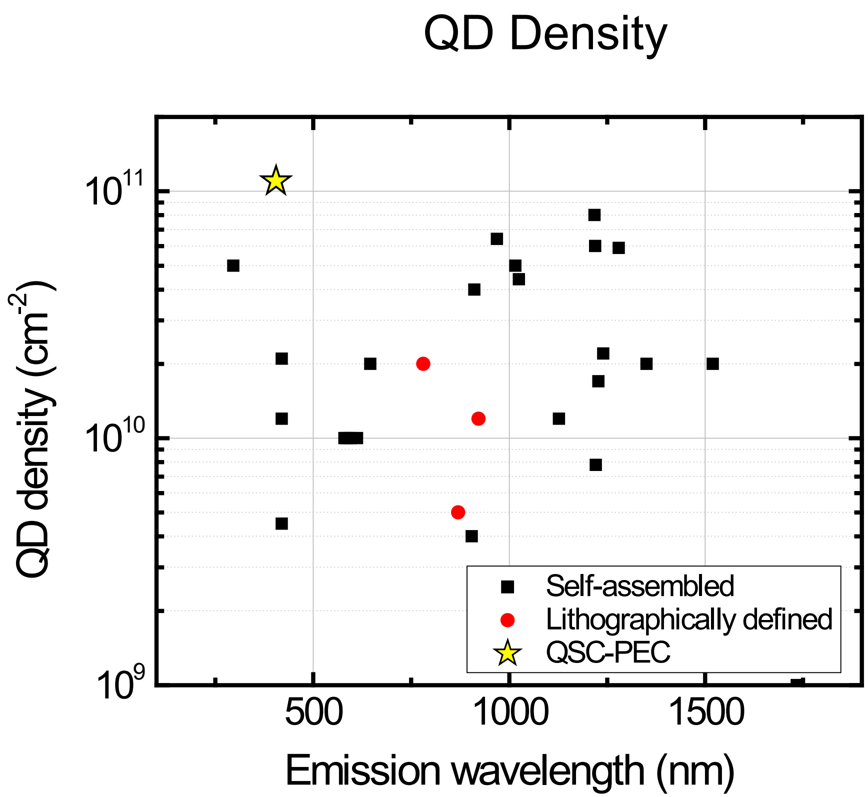
As narrow as **6 nm** FWHM is consistent with a narrowing of the QD size distribution



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

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

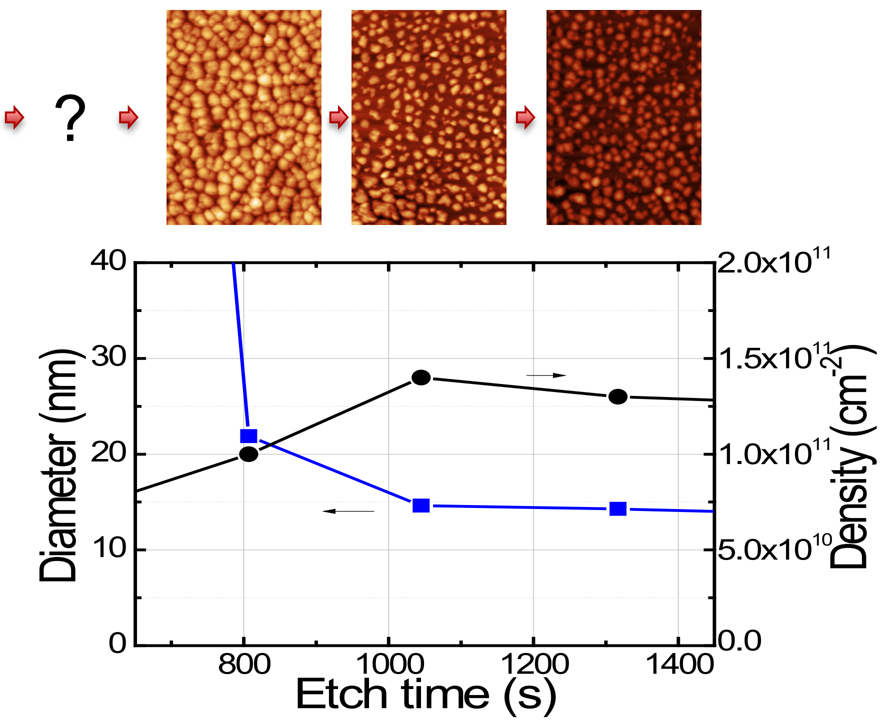




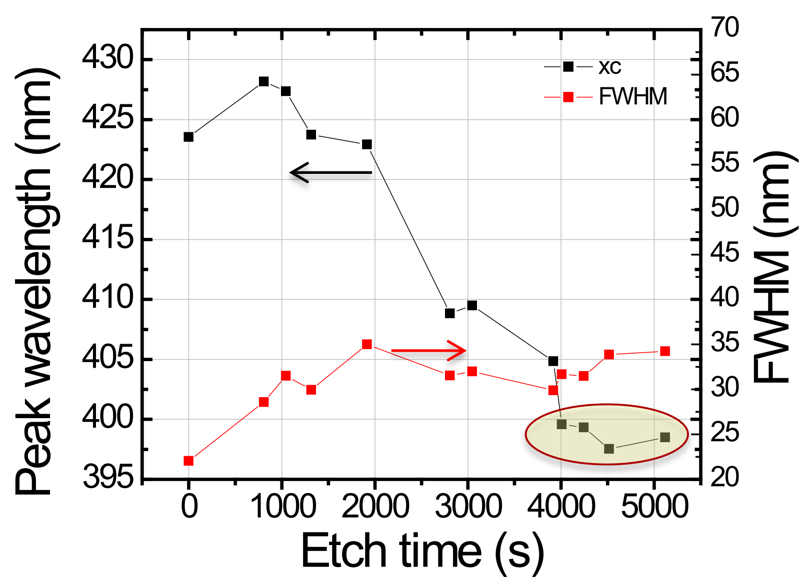
Compared to previous grown and lithographically etched QDs, QSC-PEC etched InGaN QDs have narrow FWHM PL and high density

QSC-PEC Etch Time Evolution of InGaN QDs

- AFM shows high density of larger dots initially, with initial small increase in density as dot size shrinks
- Longer etch times suggest self-termination of QSC-PEC etch process with little continuing change in QD emission energy with further etching

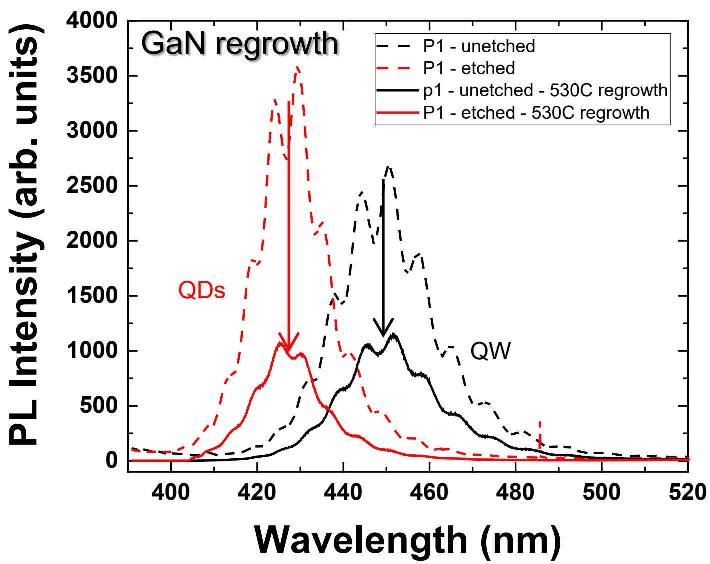


QD energy vs PEC etch time



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.**
- 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

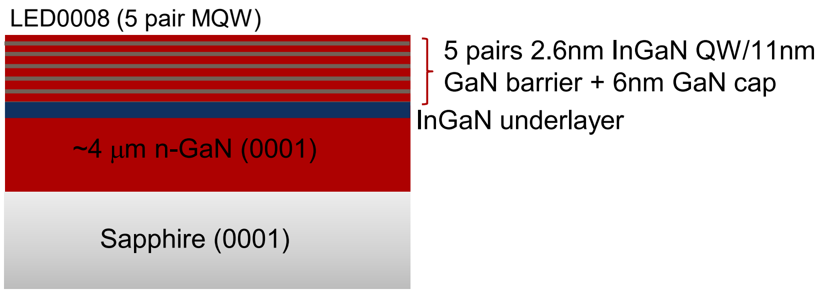
	530°C	600°C	600 ramp to 750°C	750°C
QW (unetched)	0.43	0.8	0.35	0.72
QD (etched)	0.29	0.26	0.1	0.05

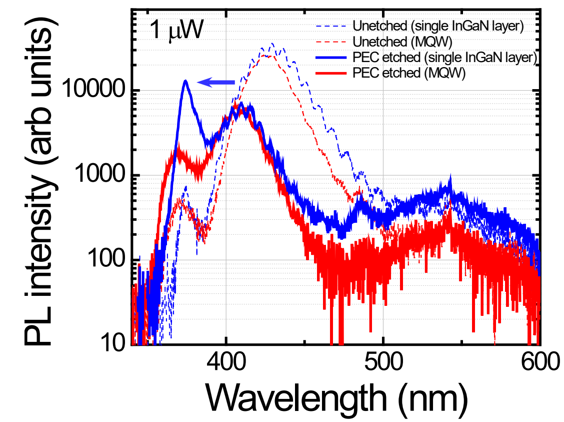
- *Regrowth of GaN decreases <u>both QW and QD PL intensity</u>*; worse with increasing regrowth T
- AlGaN and AlGaN/GaN capping showed better but mixed results – unetched InGaN layers show little change and some improvement in QD PL in some AlGaN/GaN samples

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.

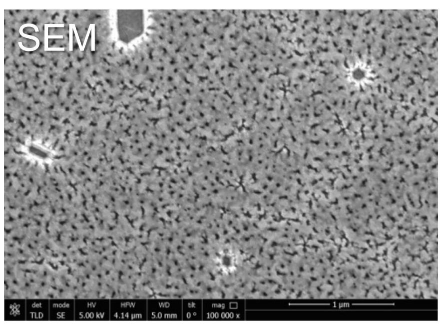
QSC-PEC Etching of InGaN/GaN Multiple Quantum Wells

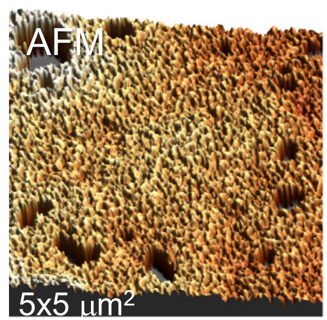
- QD lasers need multiple layers of QDs to provide sufficient gain
- Etch InGaN/GaN MQWs to provide **multiple layers of capped/passivated QDs?**

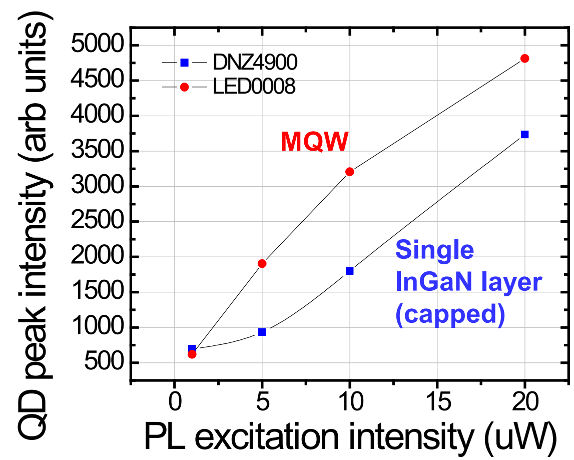




PEC etch: 420 nm, 20mW, 1.4V, 0.2M H_2SO_4, 45min



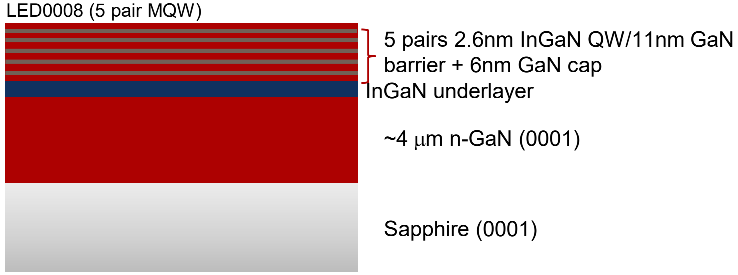




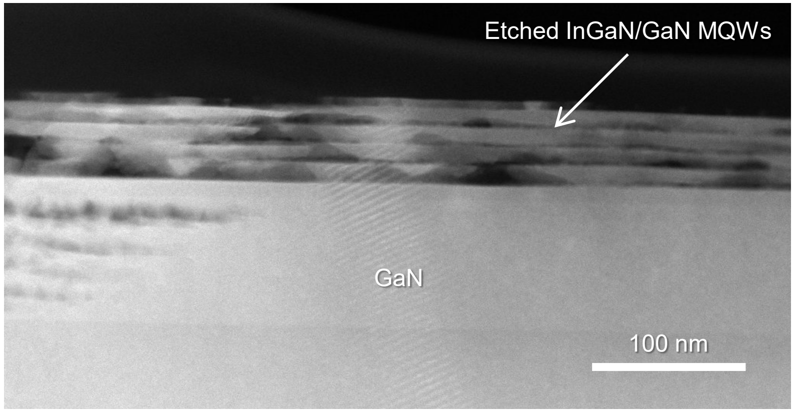
PL blue-shift indicates etching of MQWs into QDs, but PL intensity only slightly higher than single layer capped InGaN QDs (not 5x higher)

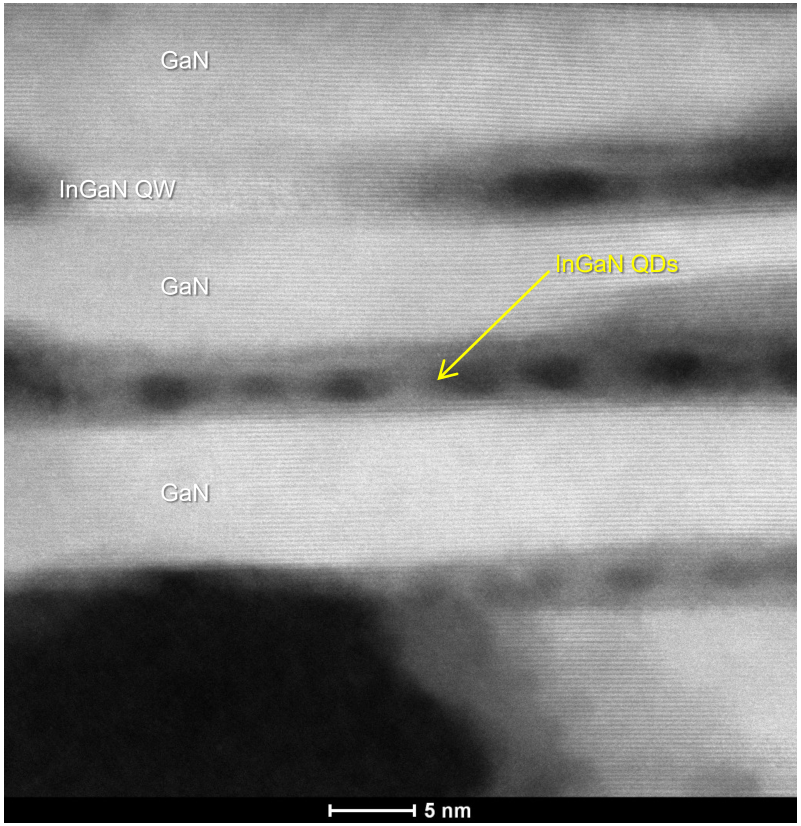
QSC-PEC Etching of InGaN/GaN Multiple Quantum Wells

- 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



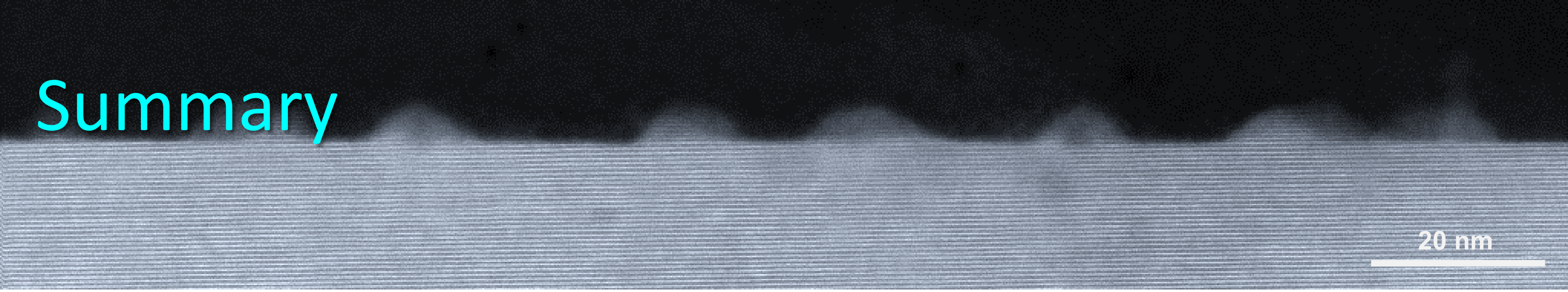
PEC etch: 420 nm, 20mW, 1.4V, 0.2M H_2SO_4, 45min





STEM by Ping Lu

Summary



- Demonstrated controlled fabrication of InGaN QDs from epitaxial layer using quantum-size controlled PEC etching
  - AFM data indicates extremely high QD density (~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)
  - 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

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Backup Slides

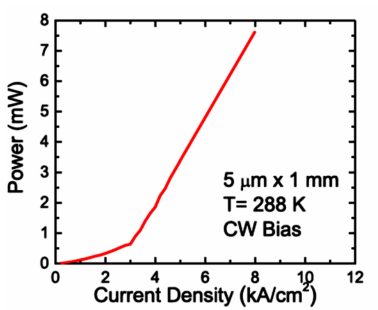
Motivation for InGaN Quantum Dot (QD) Emitters

- **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**

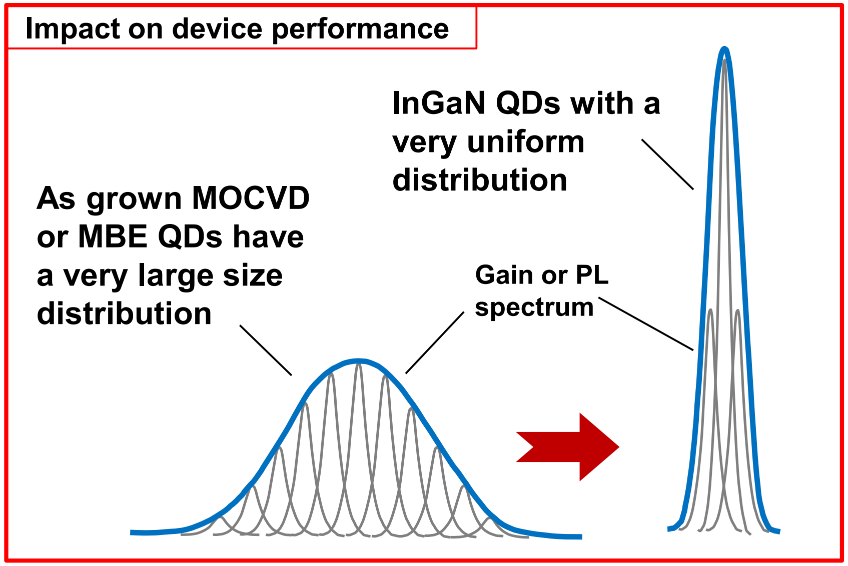
InGaN QD laser:

- **University of Michigan**
- **Electrically injected**
- **630 nm**
- **T_o = 236K**

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



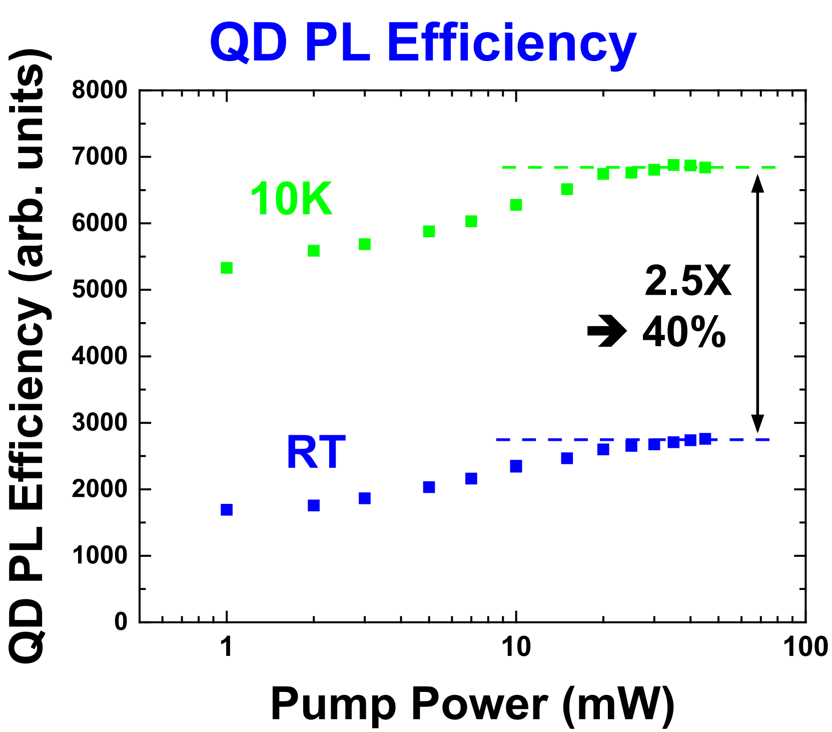
Monodisperse QD Distributions

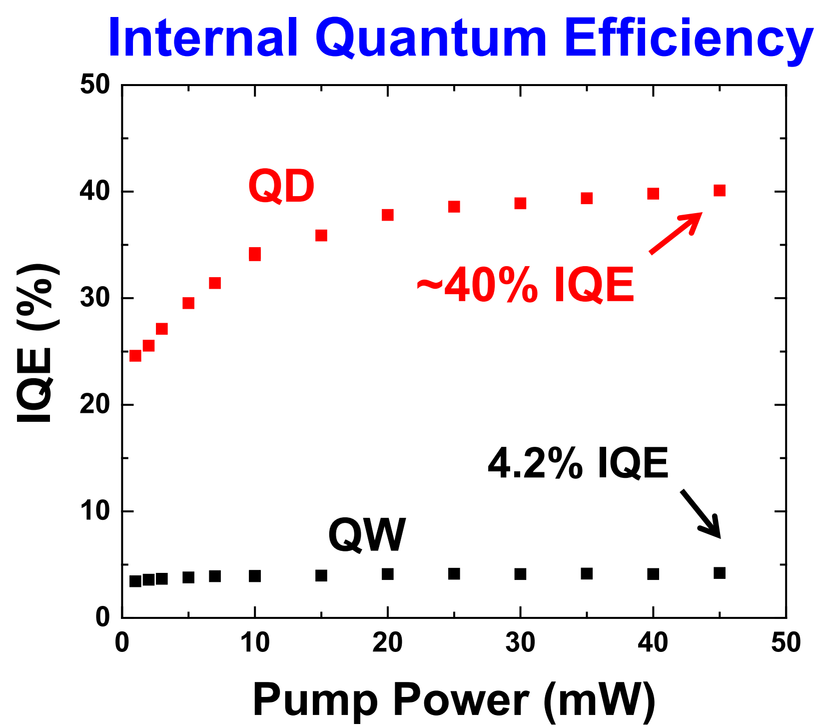


InGaN QD internal quantum efficiency

Capped InGaN QW

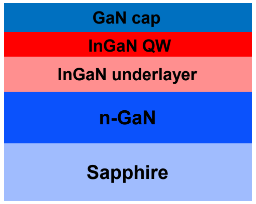
- Compare 10K and RT PL efficiency
- Assumes 10K PL is 100% efficient
- PL Intensity drops by >100X after QD etching
- IQE goes up by almost 10X after QD etching
- QDs are expected to have better IQE

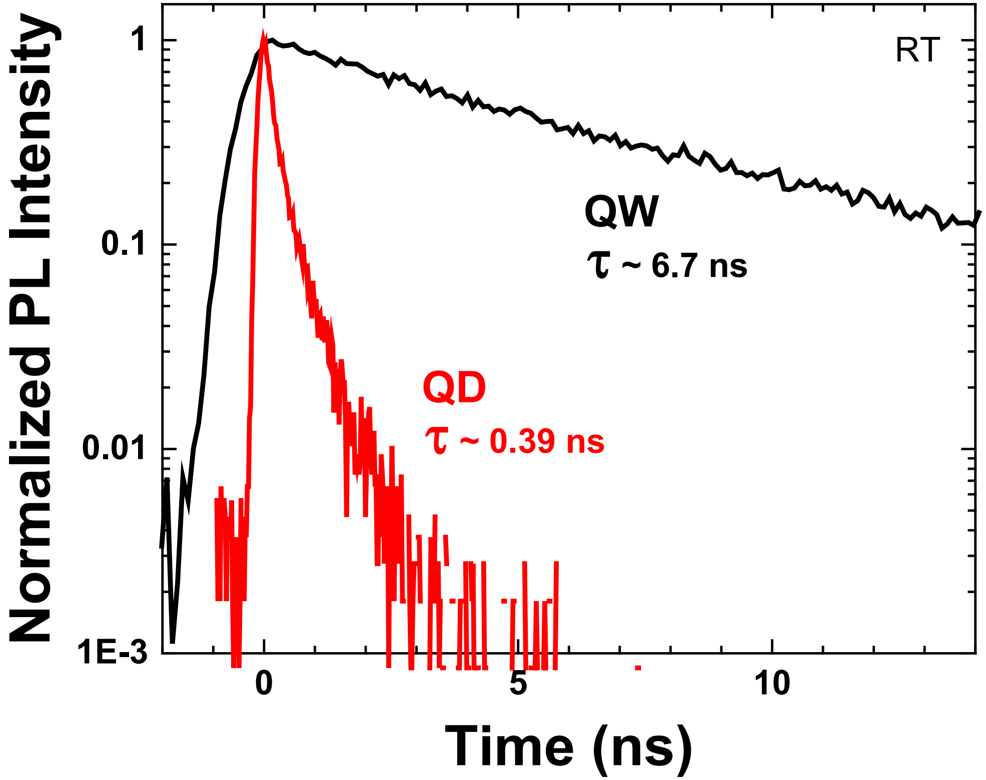




Time-resolved PL data from InGaN QDs

Capped InGaN QW

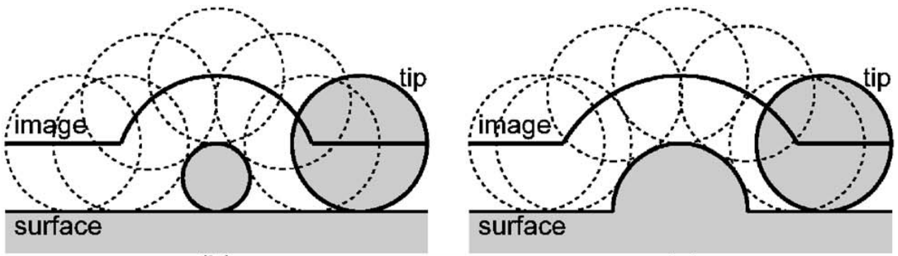




TRPL data:

- 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



(b) Spherical feature

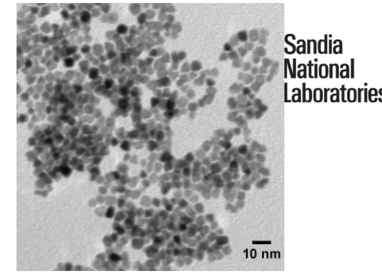
$$w = 4\sqrt{Rr}.$$

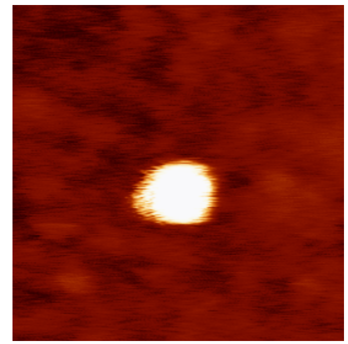
(c) Hemispherical feature

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

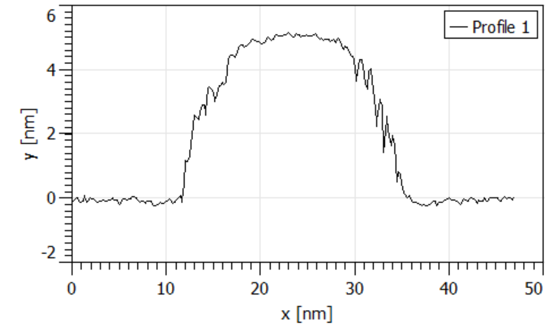
Convolution, 3 quantities -> image (w), tip (R), real surface (r), If know 2, can determine the third

AFM image of 5 nm Pt nanoparticle dispersed on silicon



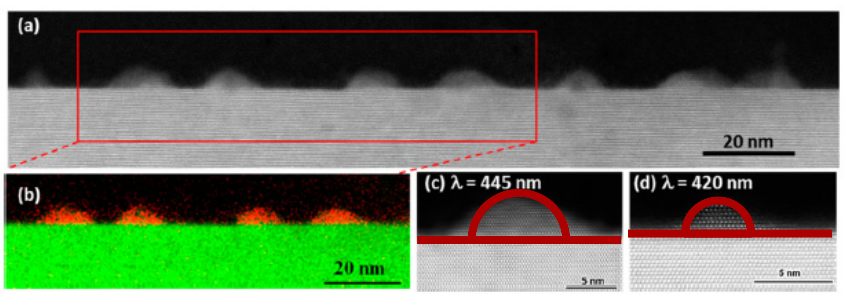


100nm x 100nm
512x512 pixels



5.12 nm height
24.33 nm base diameter

For our QDs

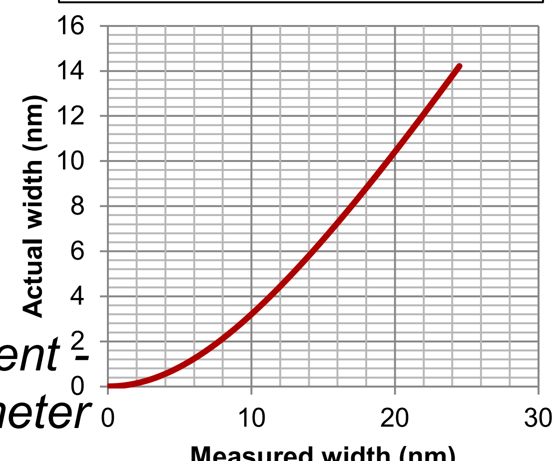


Assuming spherical particle

Tip radius = 7.3nm

Modeling QDs as hemispheres, (height = ½ width)

For 7 nm tip size,



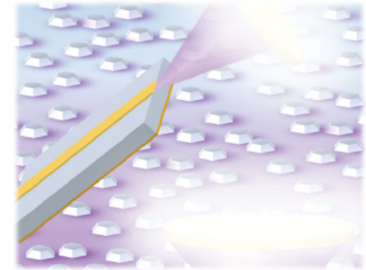
Strength of convolution effect is determined by *aspect ratio of QDs*

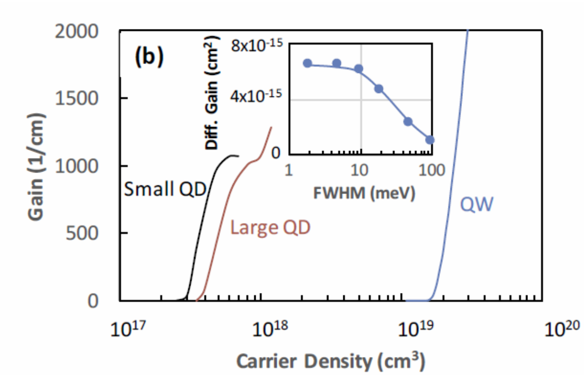
20 nm by AFM measurement -> 10-13 nm QD base diameter

Quantum Dots as the active region in LDs and LEDs?

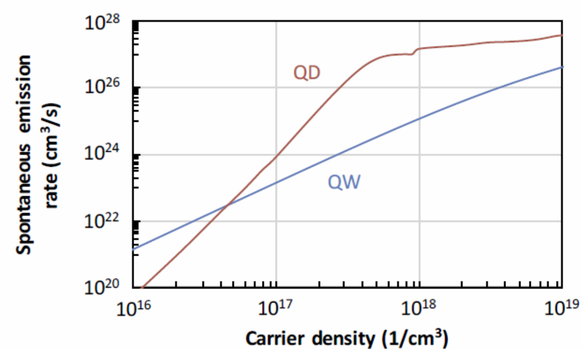
Sandia National Laboratories

- Compared to current InGaN quantum well (QW) active regions, **QD active regions could significantly improve efficiencies of both laser diodes and LEDs**

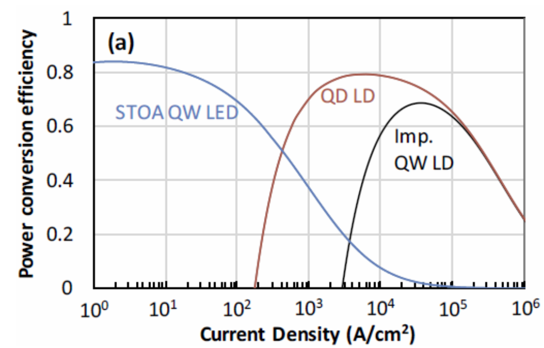




Plot of (a) gain spectra for a single QW at N = 2.5x10^{19} cm^{-3} (blue line), a layer of large QDs at N = 9x10^{17} cm^{-3} (red line), and a layer of small QDs at N = 7x10^{17} cm^{-3} (black line). Plot of (b) peak gain vs. carrier density for a single QW, a layer of large QDs, and layer of small 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 ~1x10^{18} cm^{-3} is the onset of carrier filling in the second allowed transition. (Small QDs, 6 layers, 7.2x10^{10} cm^{-2}, 5 meV FWHM, 4 nm base width)



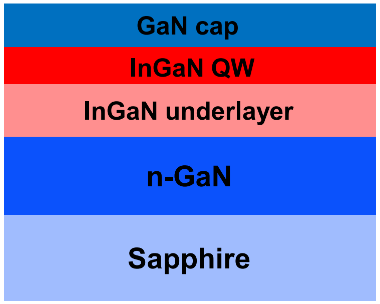
Plot of (a) power conversion efficiency vs. current density of a state-of-the-art (SOTA), QW-based LED (blue line), an improved QW-based LD (black line), and a QD-based LD (red line). The QD LD has extremely low threshold currents and peak efficiencies that rival the QW-based LED.

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

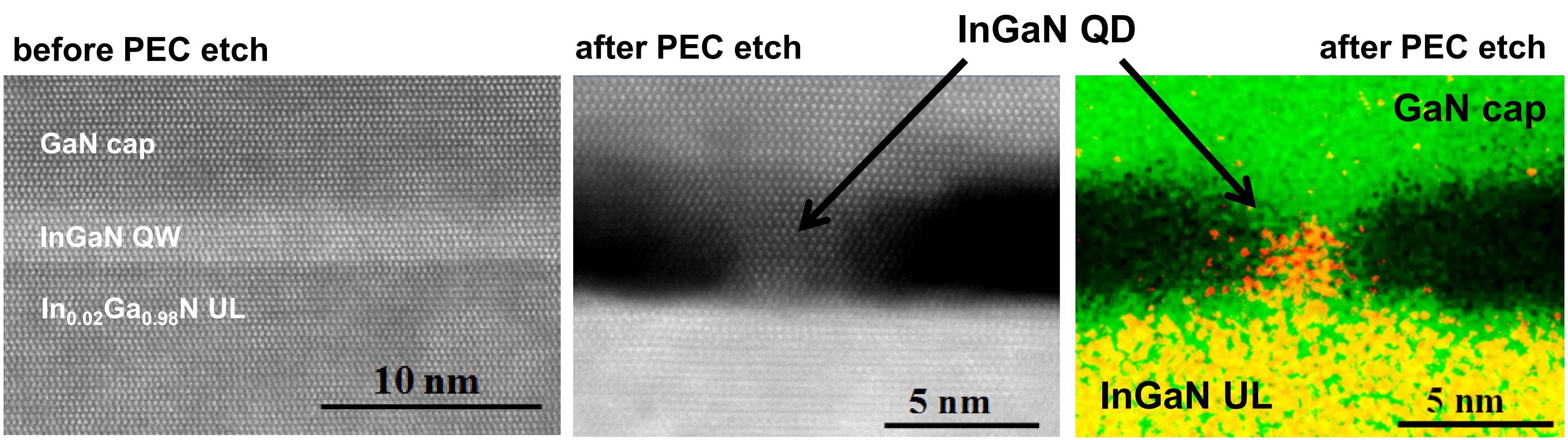
The challenge going forward is to find methods to synthesize QDs to meet the required sizes, inhomogeneous broadening, and densities

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

Capped InGaN QW

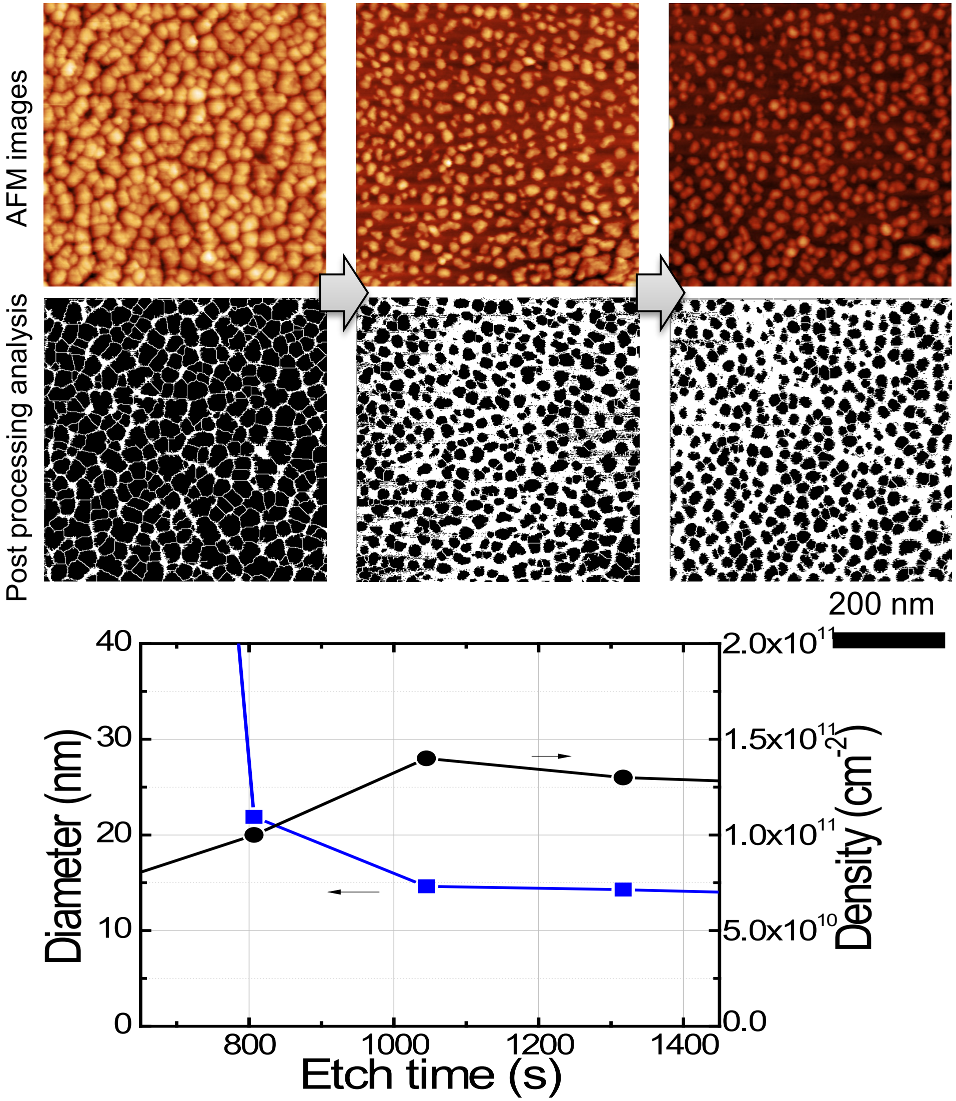


- High-angle annular dark-field (HAADF) TEM images
- Sample PEC etched at 420 nm
- EDS mapping shows that dots are InGaN
- InGaN QDs are epitaxial to the underlying GaN
- 2% InGaN underlayer + GaN cap → PL is ~100x brighter
- GaN cap provides partial passivation



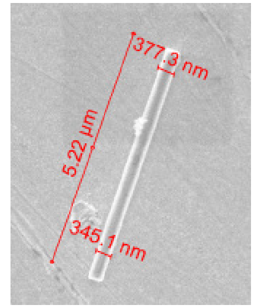
X. Xiao et al., Nano Lett. **14**, 5616−5620 (2014)

QSC-PEC Etch Evolution of InGaN QDs

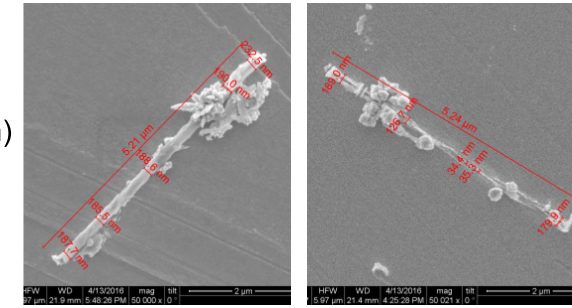


PEC etching of GaN nanowire arrays

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

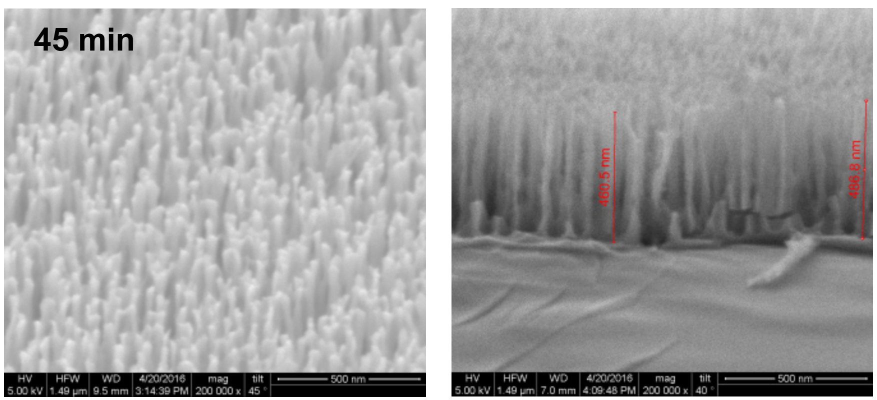


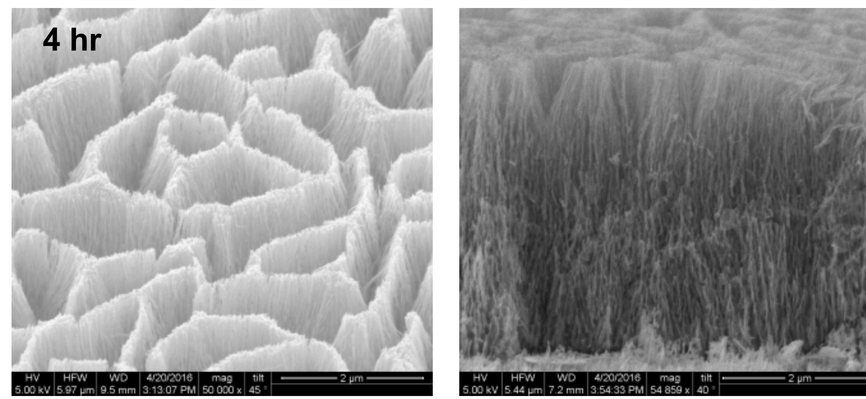
PEC etch (370 nm)



- 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





- 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)*

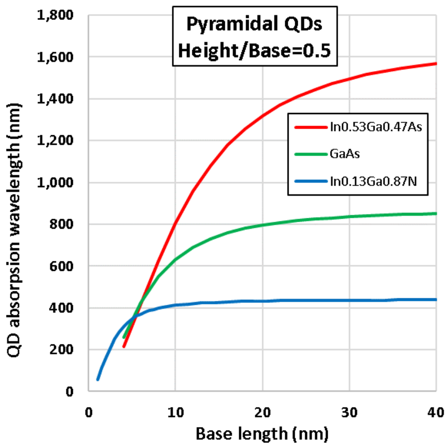
Technical Accomplishment: QSC-PEC etching model

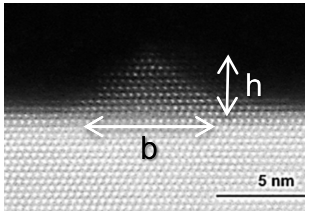
- **Fortran code written to model (1) QD size evolution; due to (2) laser absorption / carrier creation; parasitic-loss terms due to (3) radiative recombination and (4) surface defect recombination; and (5) PEC etching oxidation reaction at the QD surface**

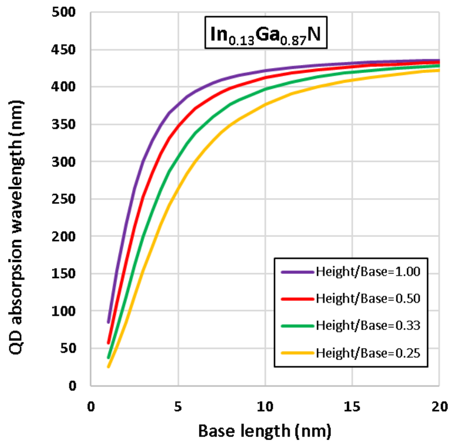
$$\underbrace{\dot{N}_{atoms}}_{1} = \underbrace{\alpha_{abs}(E_g, N) I_{laser} V(N)}_{2} - \underbrace{\rho B_{rad} V(N)}_{3} - \underbrace{\rho v_{surf} A(N)}_{4} - \underbrace{\rho v_{etch} A(N)}_{5}$$

- **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

- **Future model developments: (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.**