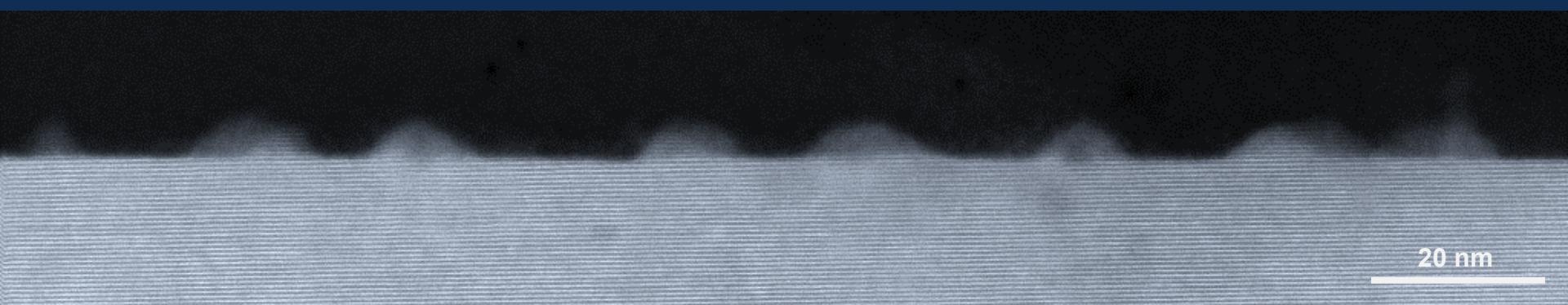


*Exceptional service in the national interest*



## Quantum Size Controlled Etching of InGaN Quantum Dots

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

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<sup>2</sup>*Center of High Technology Materials, University of New Mexico, Albuquerque, NM 87106*

[\\*gtwang@sandia.gov](mailto:gtwang@sandia.gov)

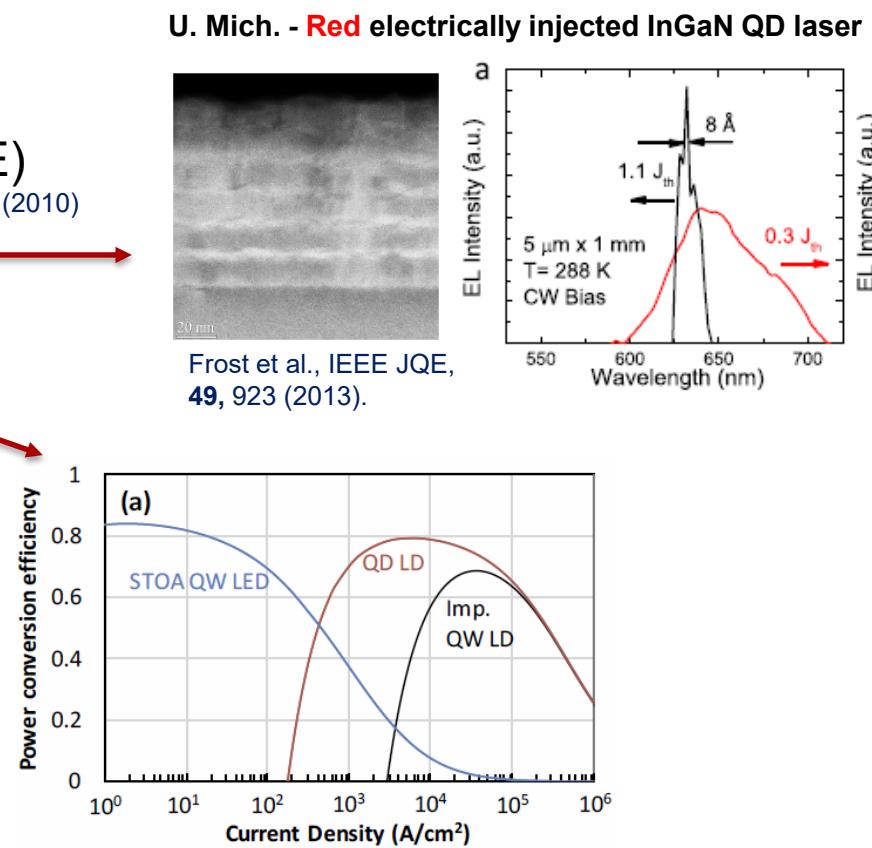
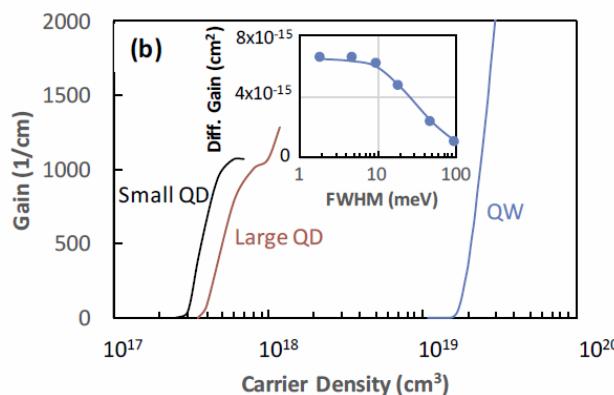


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# Motivation: InGaN Quantum Dots (QDs) as emitters

## 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



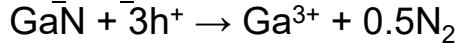
Jonathan J. Wierer, Jr., Nelson Tansu, Arthur J. Fischer, and Jeffrey Tsao, "III-nitride quantum dots for ultra-efficient solid-state lighting," *Laser and Photonics Reviews*, **10**, 612 (2016) / DOI 10.1002/lpor.201500332

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

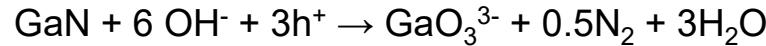
# (In)GaN Photoelectrochemical (PEC) Etching

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

in  $1 \text{ M H}_2\text{SO}_4$

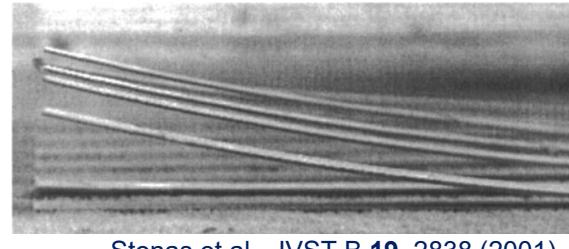
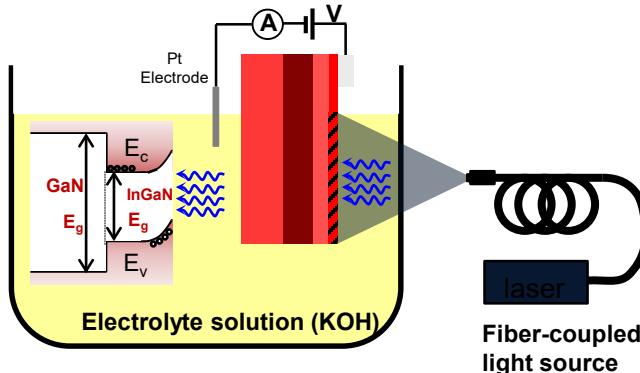


in  $1 \text{ M KOH}$

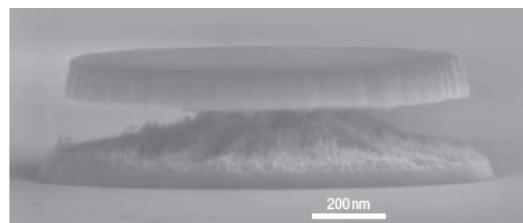


Huygens et al., J. ECS **147**, 1797 (2000)

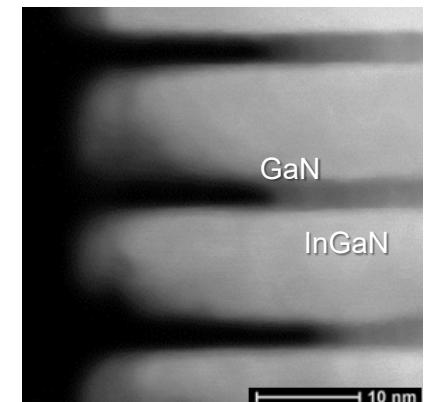
- Laser or lamp excitation (Xe arc lamp, tunable ps Ti:S)
- KOH ( $\sim 0.1\text{M}$ ) typically used as electrolyte for GaN
- Band gap selective (etch InGaN over GaN) based on wavelength used



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



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

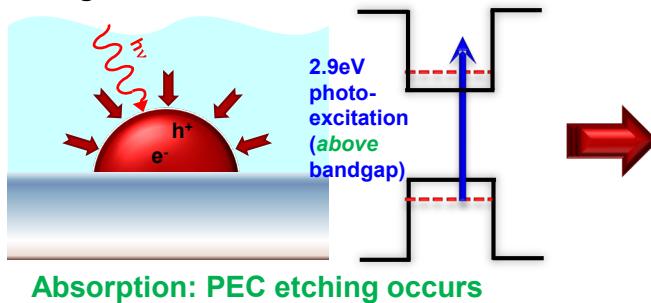


Xiao et al., Elec. Acta **162**, 163 (2015)

# Controlled fabrication of QDs via PEC etching

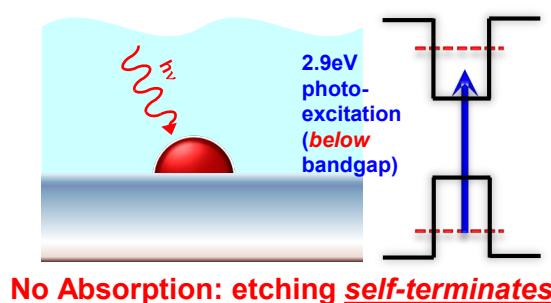
## Quantum Size Control: Use size quantization to control QD size

“Large” nanostructure



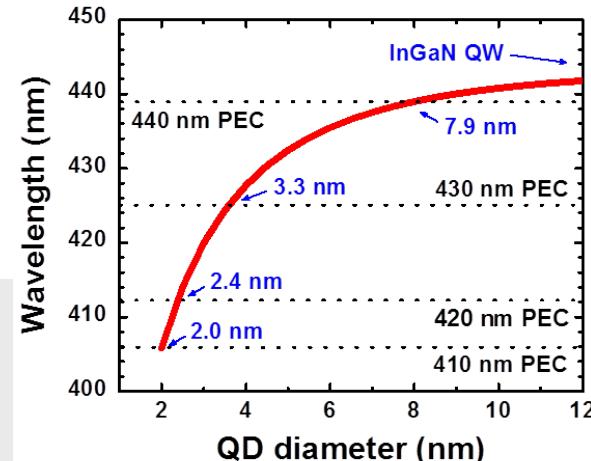
Absorption: PEC etching occurs

Quantum nanostructure



No Absorption: etching self-terminates

Bandgap for idealized spherical  $\text{In}_{0.13}\text{Ga}_{0.87}\text{N}$  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  $E_g > E_{\text{photon}}$  pump (no more carriers needed for etch)
- Self-terminating etch process
- Final QD size (band gap) depends on PEC etch wavelength used
- “Monodisperse” QD distributions ??
- Earlier work on “size selective photocorrosion” to shrink size of colloidal CdS QDs using monochromatic light<sup>1,2</sup>

<sup>1</sup>Matsumoto et al., J. Phys. Chem. **100**, 13781 (1996)

<sup>2</sup>Torimoto et al., J. ECS **145**, 1964 (1998)

# Starting MOCVD-grown InGaN/GaN samples

## Uncapped single InGaN QW



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

---

## Capped single InGaN QW



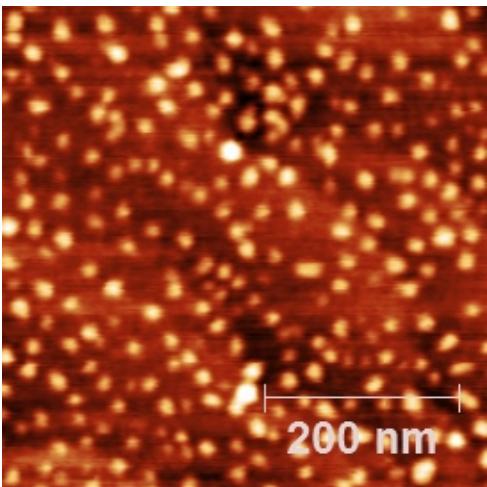
- ~3 nm  $\text{In}_{0.14}\text{Ga}_{0.86}\text{N}$  QW, 10 nm GaN cap
  - AFM is not useful for capped samples
  - Luminescence brighter than uncapped samples
- InGaN underlayer (~2% In) used in this sample
- Etch is thought to proceed through GaN cap via pits, dislocations

# QSC-PEC etched uncapped InGaN layer - AFM Measurements

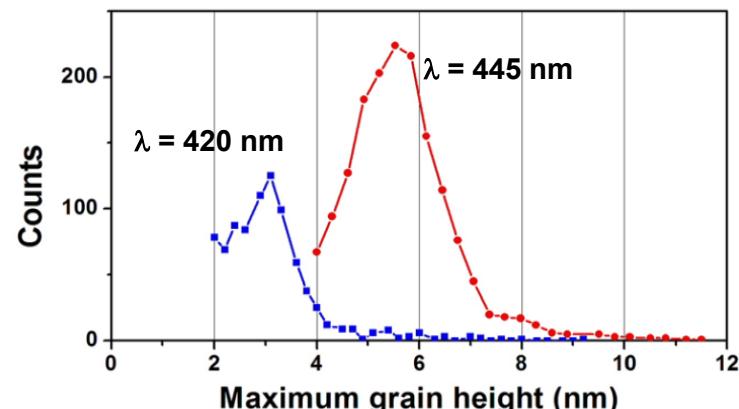
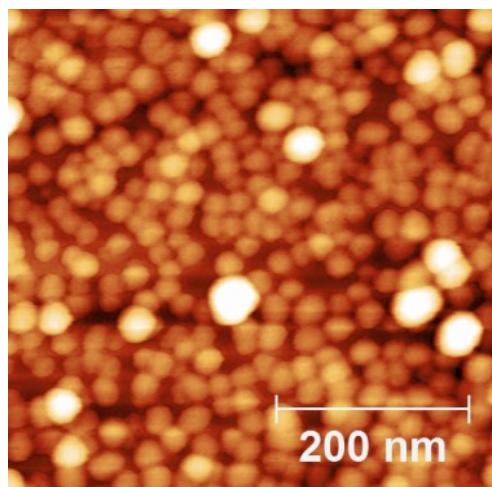
## Uncapped InGaN QW



PEC etch  $\rightarrow \lambda = 420$  nm



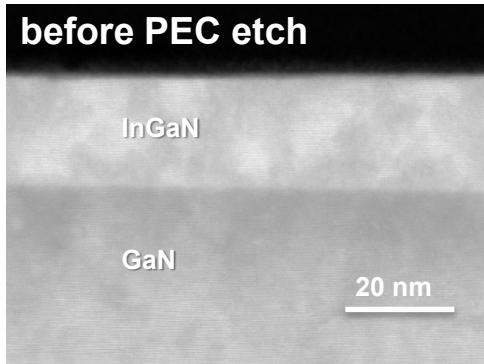
PEC etch  $\rightarrow \lambda = 445$  nm



# QSC-PEC etched uncapped InGaN layer – Scanning TEM measurements

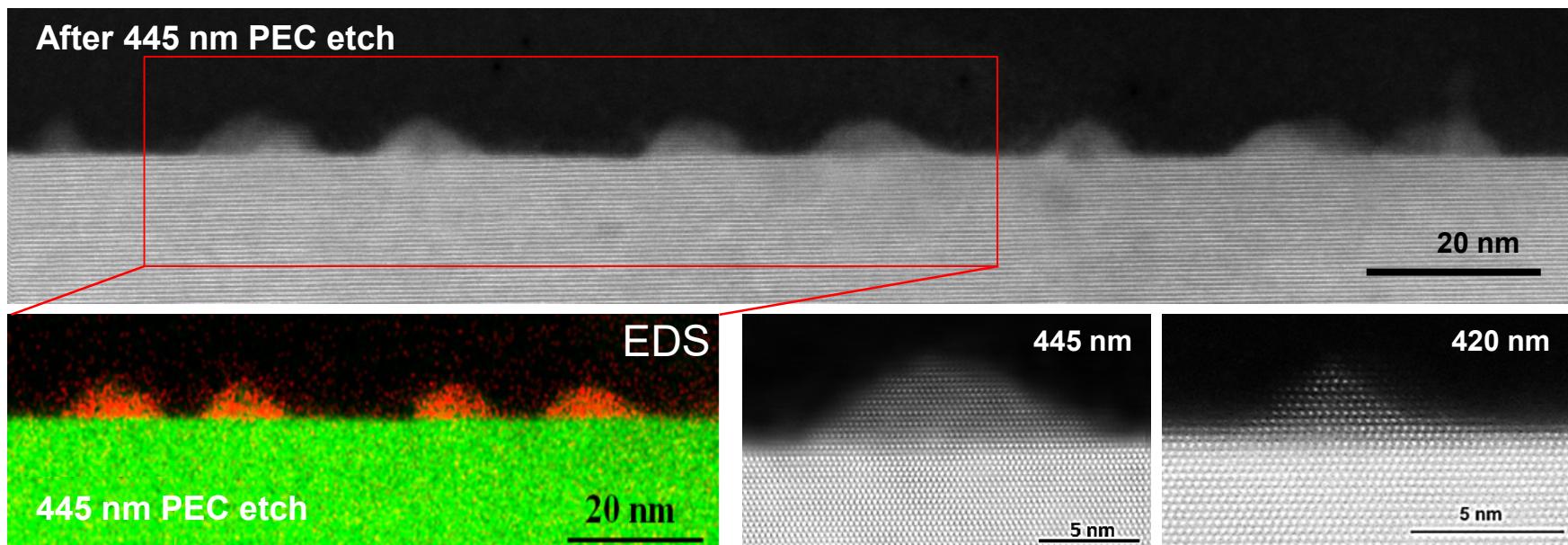
## Uncapped InGaN QW

### before PEC etch



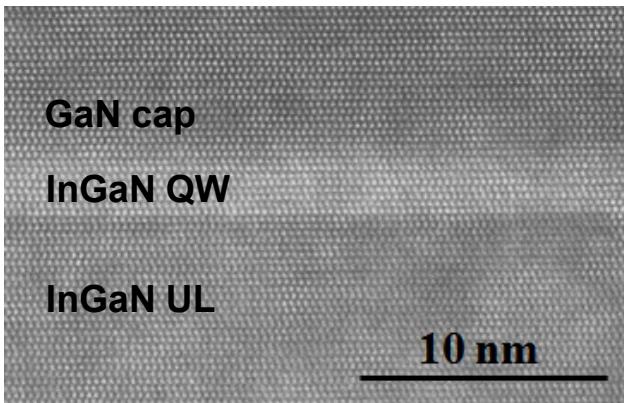
- Cross-sectional high-angle annular dark-field (HAADF) scanning TEM images
- Samples etched at **420 nm** and **445 nm**
- Energy dispersive (EDS) x-ray mapping
  - QDs on surface are InGaN (**Red** = In, **Green** = Ga)
- InGaN QDs are epitaxial to the underlying GaN
- No underlayer, no cap → PL is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

### After 445 nm PEC etch



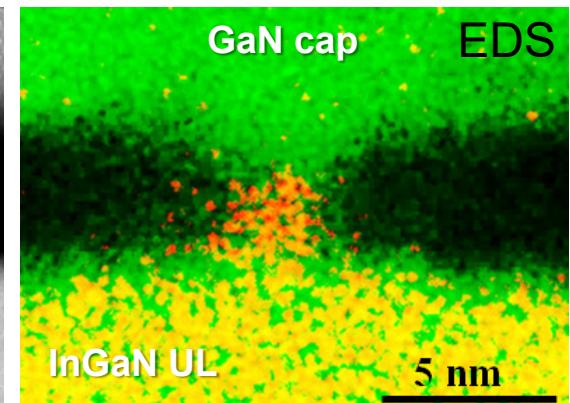
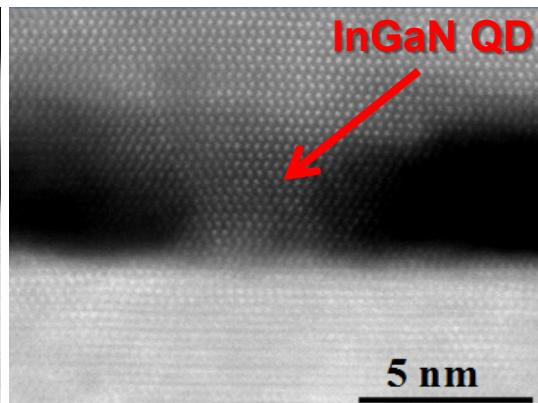
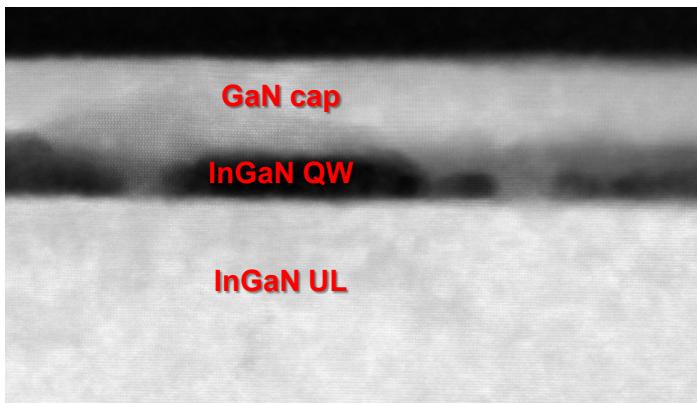
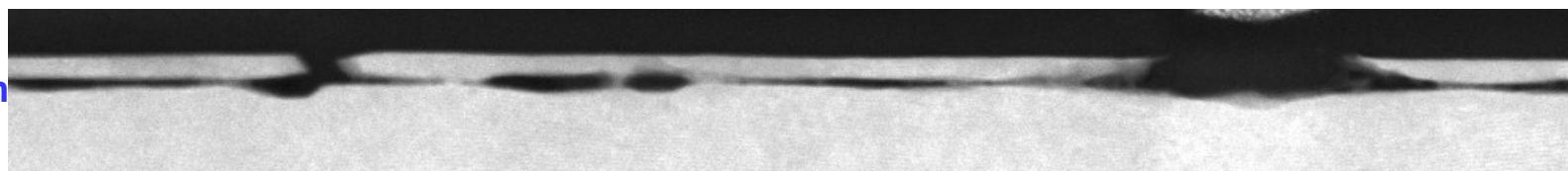
# QSC-PEC capped InGaN layer w/InGaN underlayer – scanning TEM measurements

before PEC etch



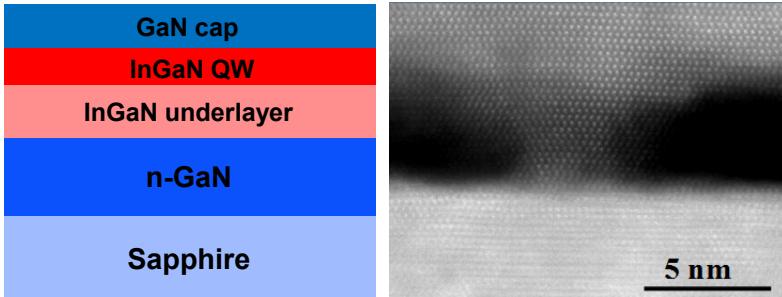
- Sample PEC etched at 420 nm
- Etch appears to break through GaN cap – defects?
- EDS mapping: dots are InGaN
- **2% InGaN UL + GaN cap  $\rightarrow$  QD PL is  $\sim 100x$  brighter**
- GaN cap provides (partial) passivation

after PEC etch



# LT Photoluminescence from QSC-PEC etched InGaN QDs

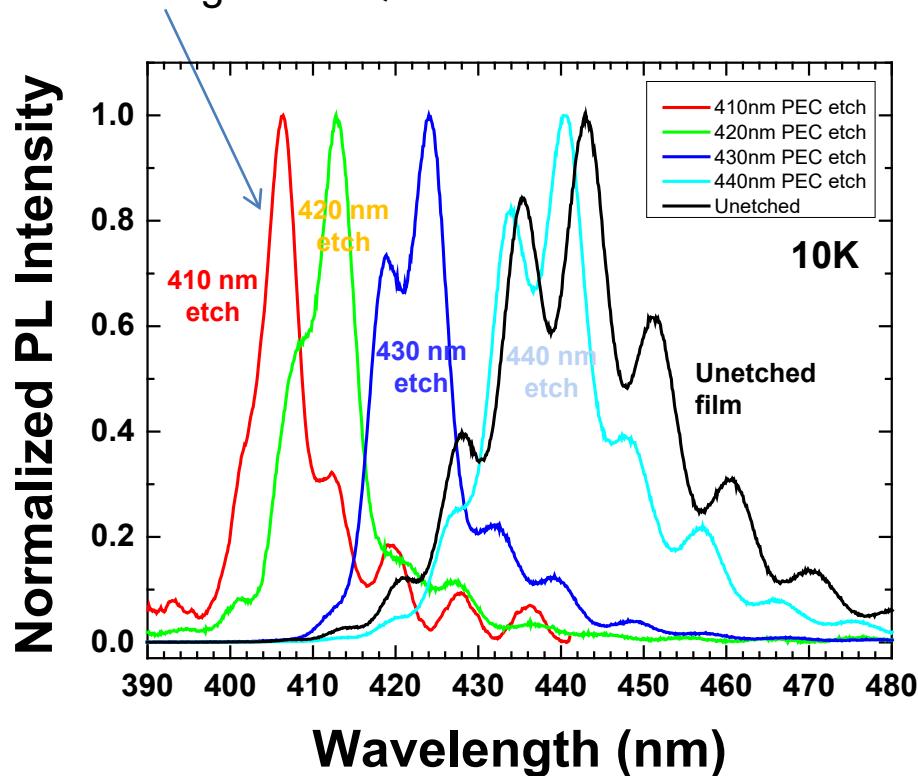
## Capped InGaN QDs



## Photoluminescence (PL) data:

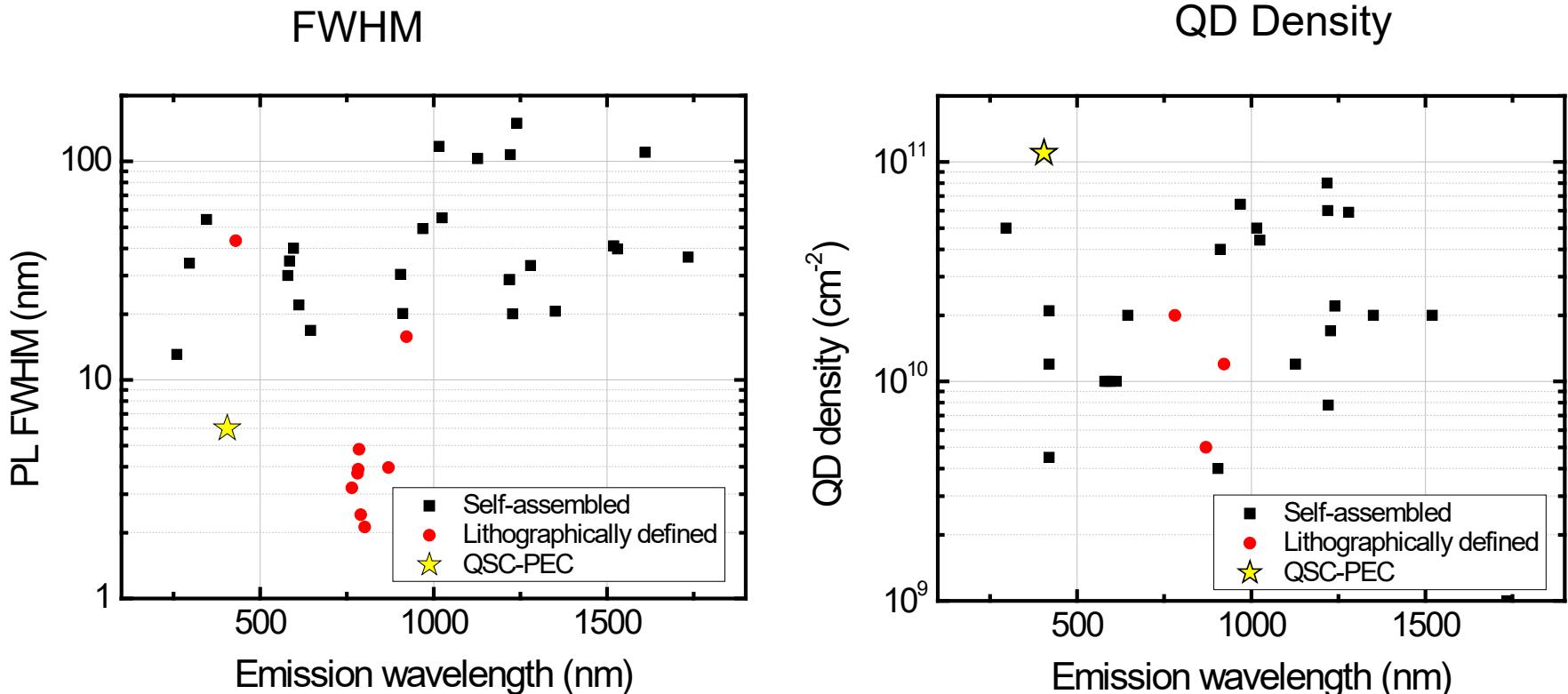
- 375 nm pump (ps pulsed), 10K
- Etched QD PL **wavelength correlates** (but doesn't exactly coincide) with **PEC etch wavelength**
- PL linewidth **decreases with decreasing etch wavelength**: 24 nm (film)  $\rightarrow$  6 nm (QDs etched at 410 nm)
- **Quantum size-controlled PEC etching works!**

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)

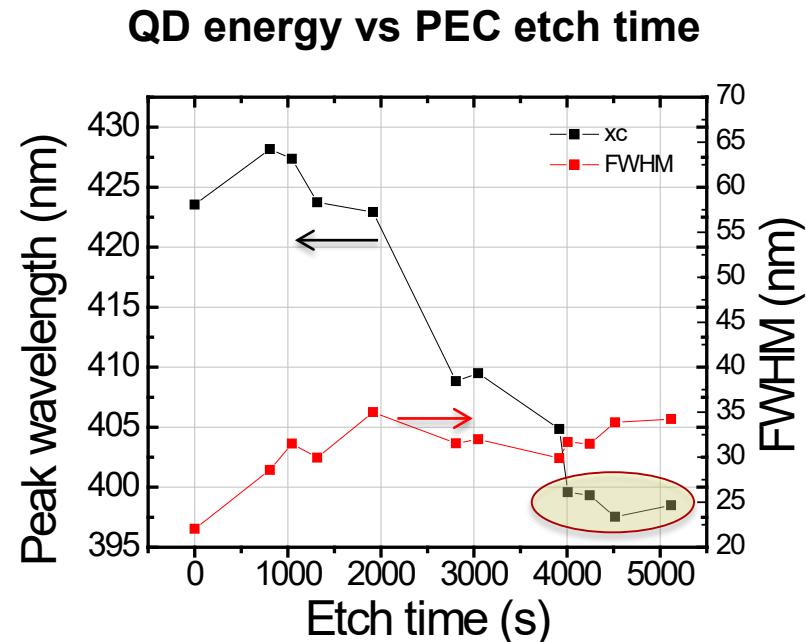
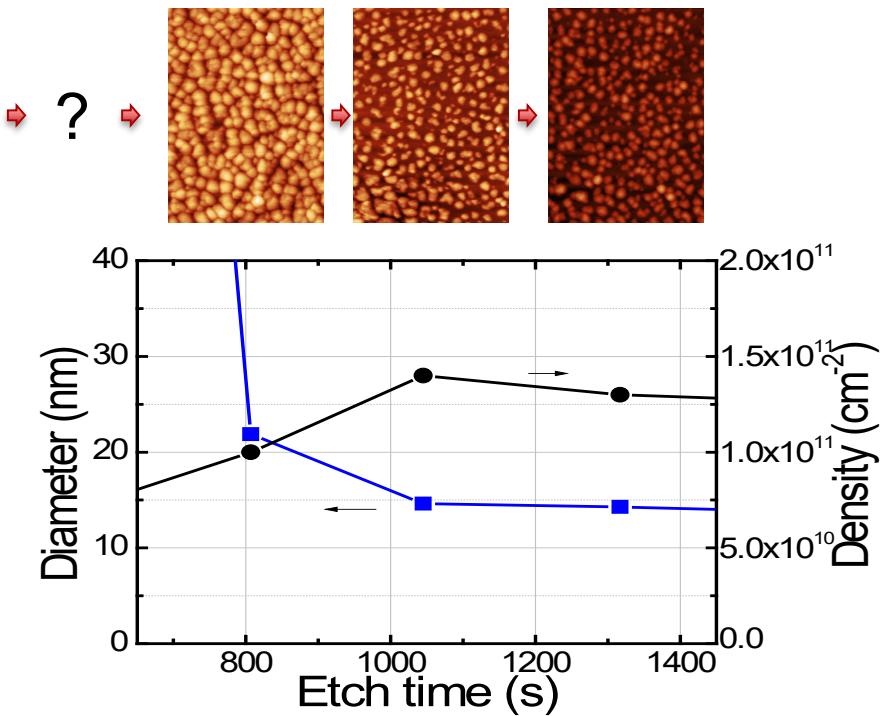
# (Partial) Survey of III-V/N QD literature



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

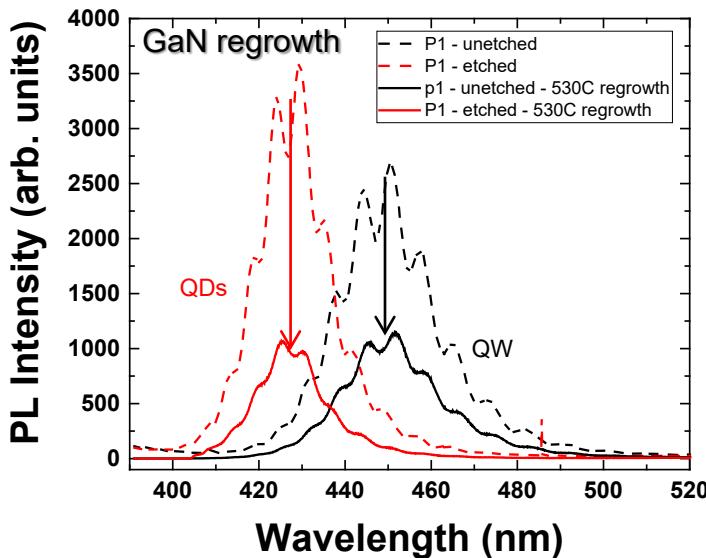
# QSC-PEC Etch Time Evolution of InGaN QDs

- 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



# 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 unetched InGaN QWs and PEC etched InGaN QDs.



Relative integ. InGaN PL intensity after GaN regrowth

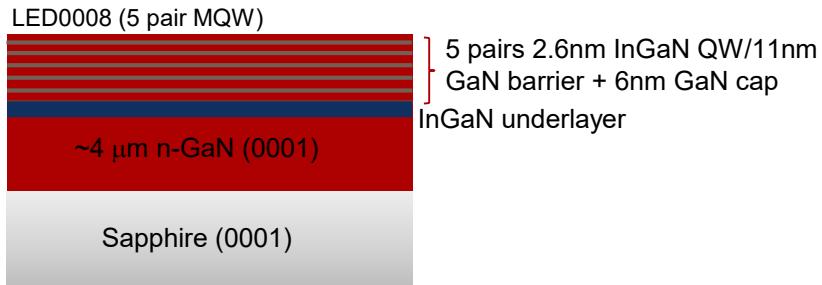
	530°C	600°C	600 ramp to 750°C	750°C
QW (unetched)	0.43	0.8	0.35	0.72
QD (etched)	0.29	0.26	0.1	0.05

- Regrowth of GaN decreases both QW and QD PL intensity; 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

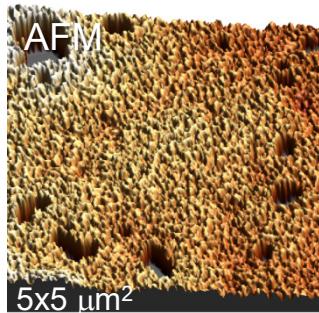
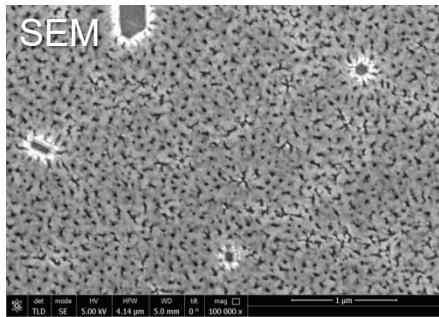
**Preliminary results: Regrowth of GaN capping layer decreases PL intensity of QWs and QDs. Regrowth of AlGaN/GaN seems more promising, although further study needed.**

# QSC-PEC Etching of InGaN/GaN Multiple Quantum Wells

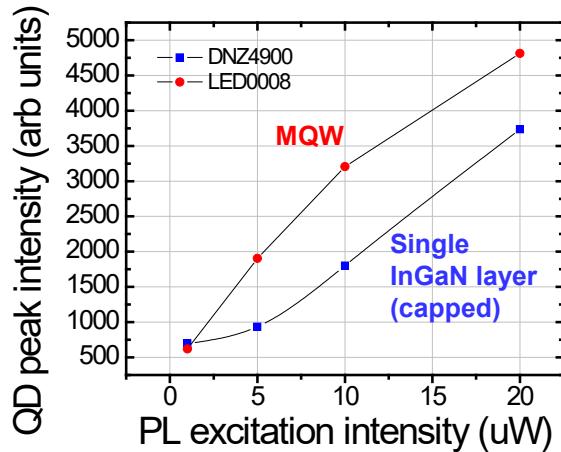
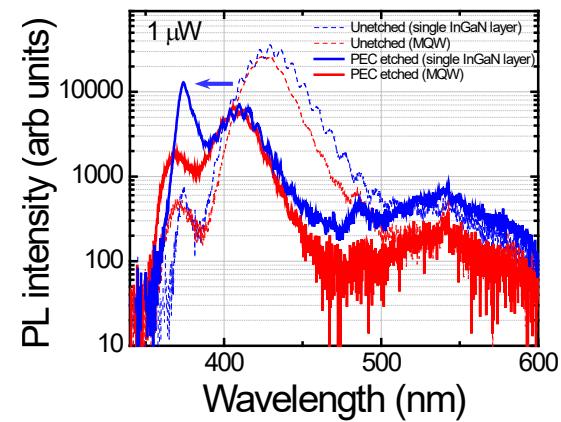
- QD lasers need multiple layers of QDs to provide sufficient gain
- Etch InGaN/GaN **MQWs** to provide **multiple layers of capped/passivated QDs?**



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

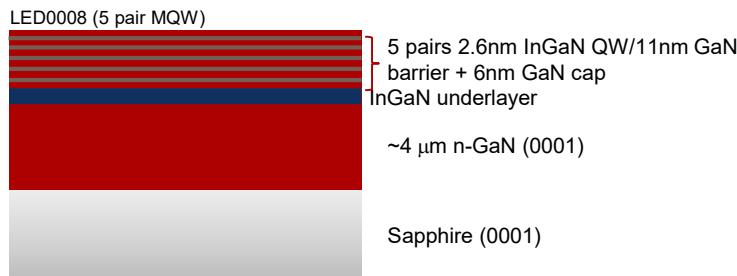


PL **blue-shift** indicates etching of MQWs into QDs, but PL intensity only slightly higher than single layer capped InGaN QDs (not 5x higher)

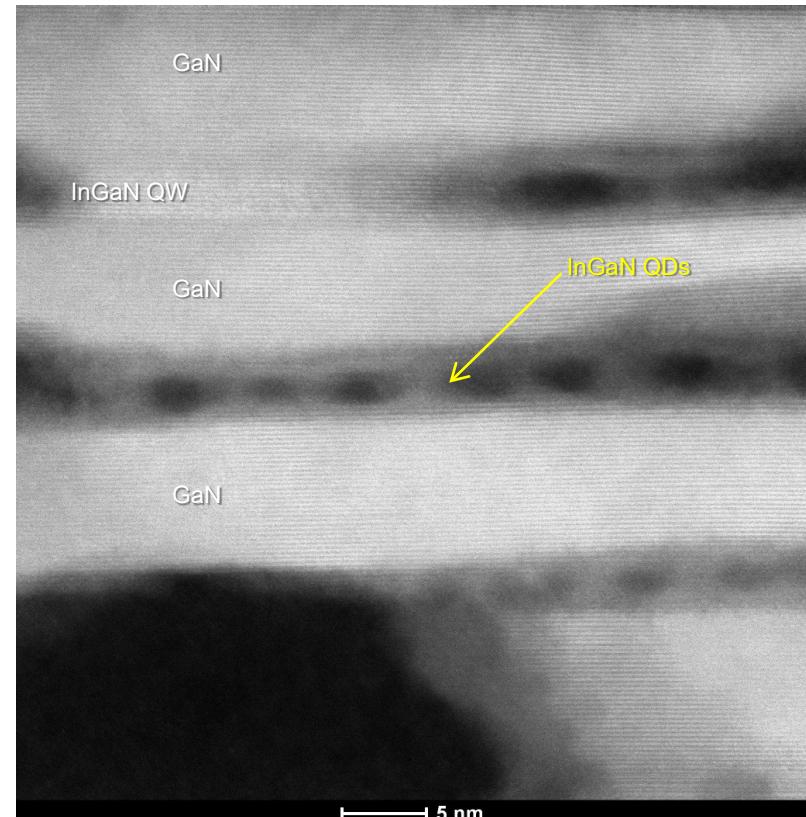
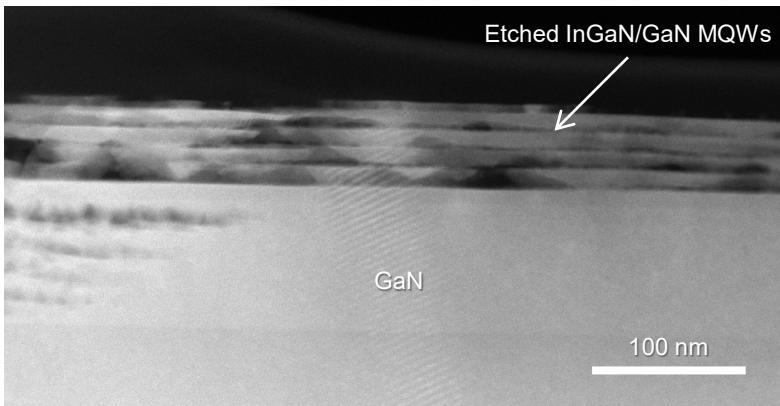


# QSC-PEC Etching of InGaN/GaN Multiple Quantum Wells

- 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  $\text{H}_2\text{SO}_4$ , 45min



STEM by Ping Lu

# Summary

Scanning electron micrograph (SEM) showing a dense array of InGaN quantum dots (QDs) on a substrate. The image is in grayscale with a white scale bar in the bottom right corner labeled "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  $\text{cm}^2$ )
  - PL linewidth reduced from 24 nm to less than  $\sim 6$  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



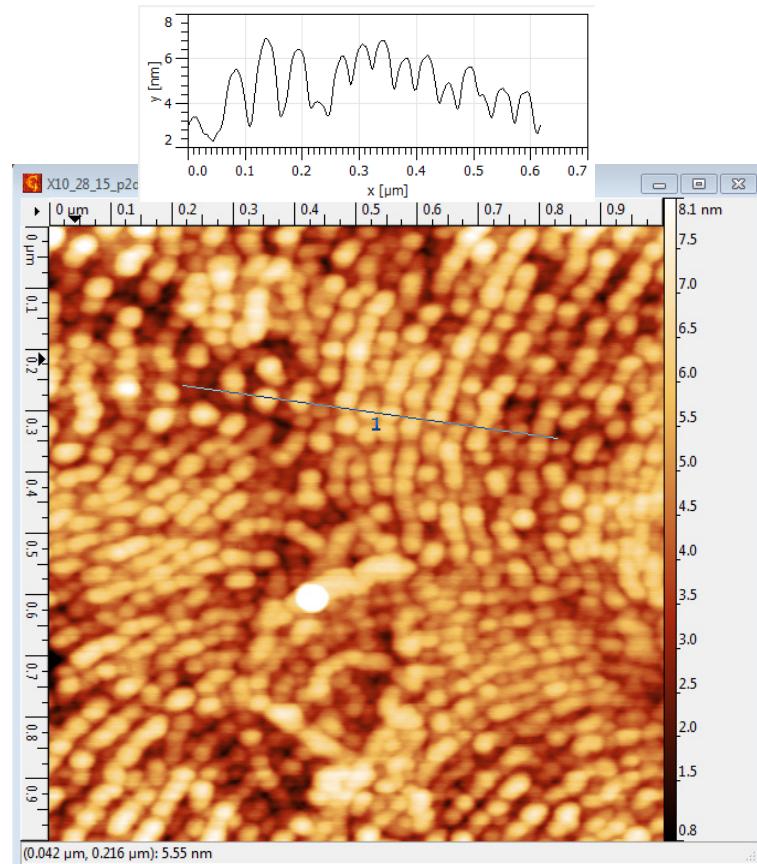
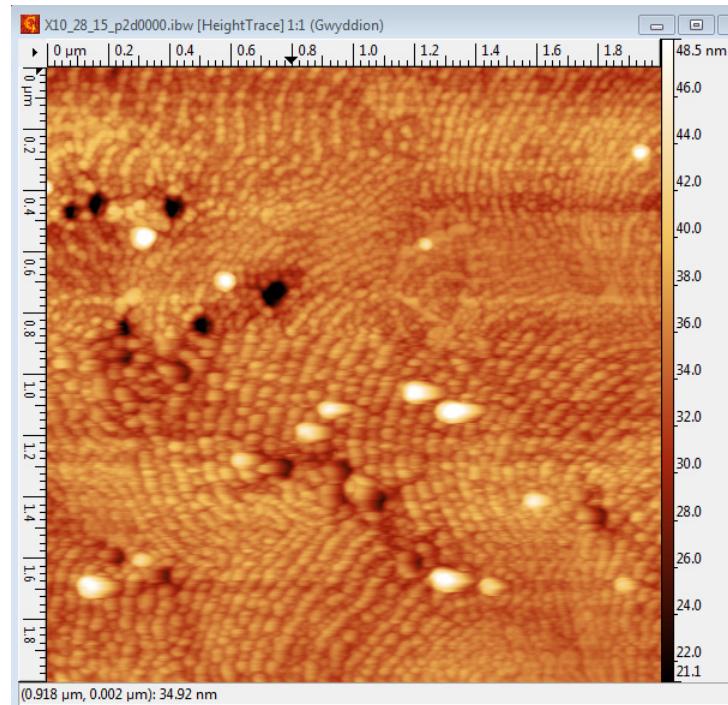
# Backup Slides



# QSC-PEC Etch Evolution of InGaN QDs

Milestone: Identify and investigate mechanism of film transition to dots

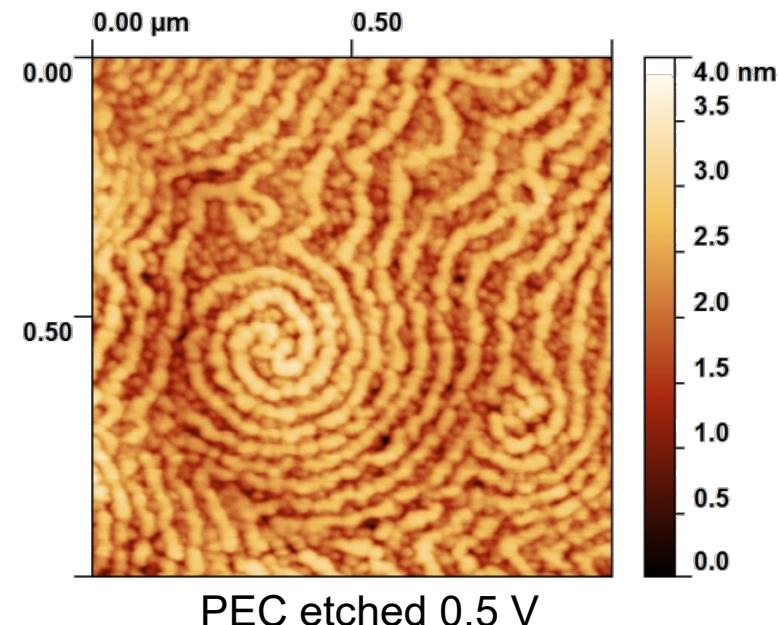
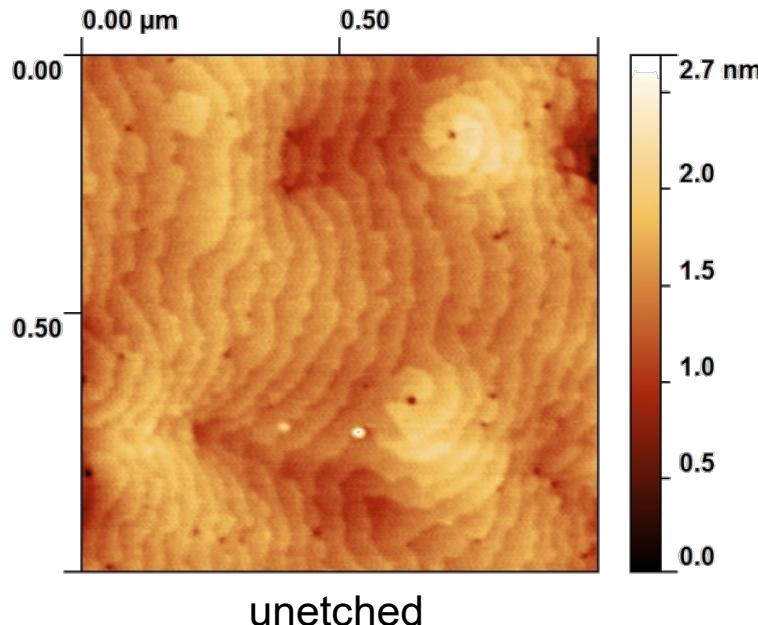
- Analysis of AFM images indicates initial dot distribution is not random, as originally assumed
- Dot/island “nucleation” along step edges?



# QSC-PEC Etch Evolution of InGaN QDs

Milestone: Identify and investigate mechanism of film transition to dots

- QD distribution and density may be controllable by initial surface morphology
- Vicinal (offcut) substrates – changes step spacing by offcut angle
- Next: track and compare same region pre- and post-PEC etched surface morphology. Modeling to investigate transition of smooth film into rough film and discrete islands



# 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

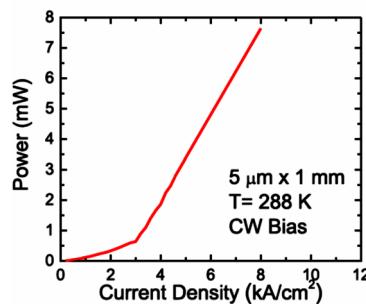
- **Visible QD diode lasers:**

- 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
- $T_o = 236K$

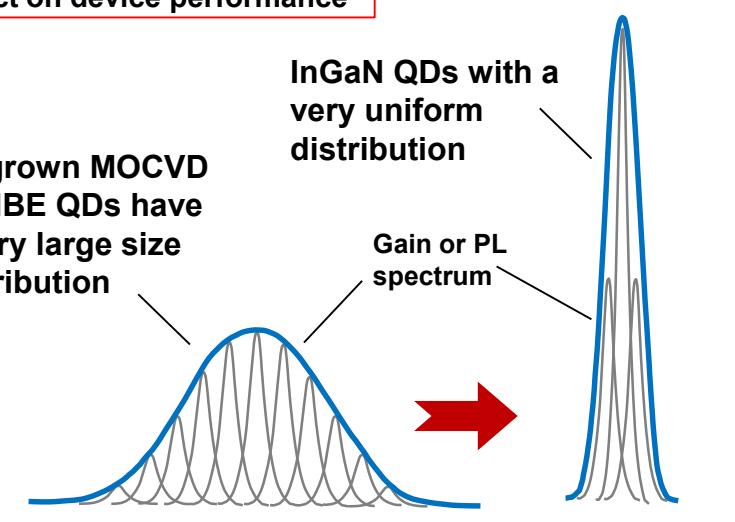
Frost et al., IEEE JQE, 49, 923 (2013).



## Monodisperse QD Distributions

### Impact on device performance

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

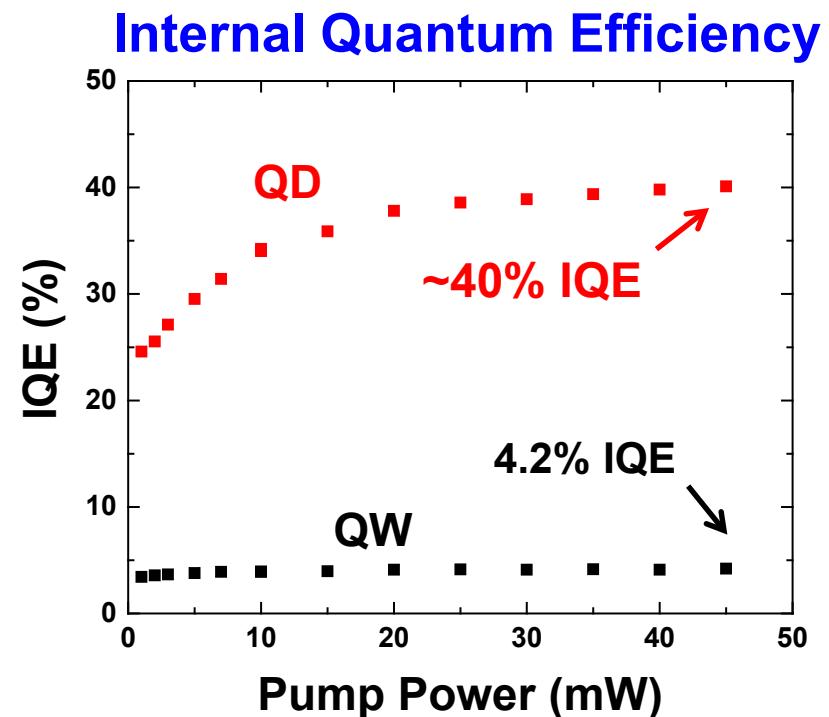
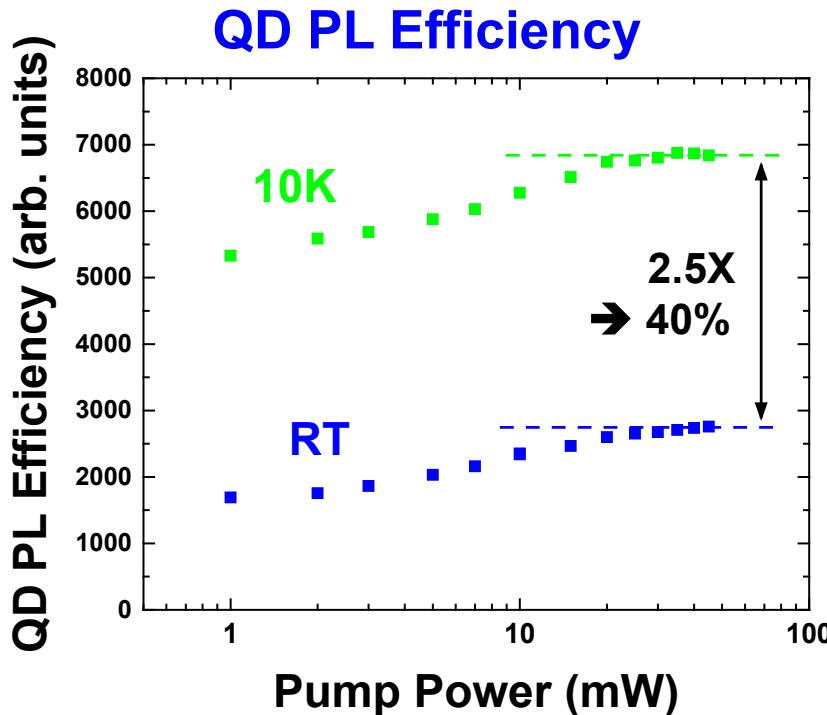


# InGaN QD internal quantum efficiency

## Capped InGaN QW

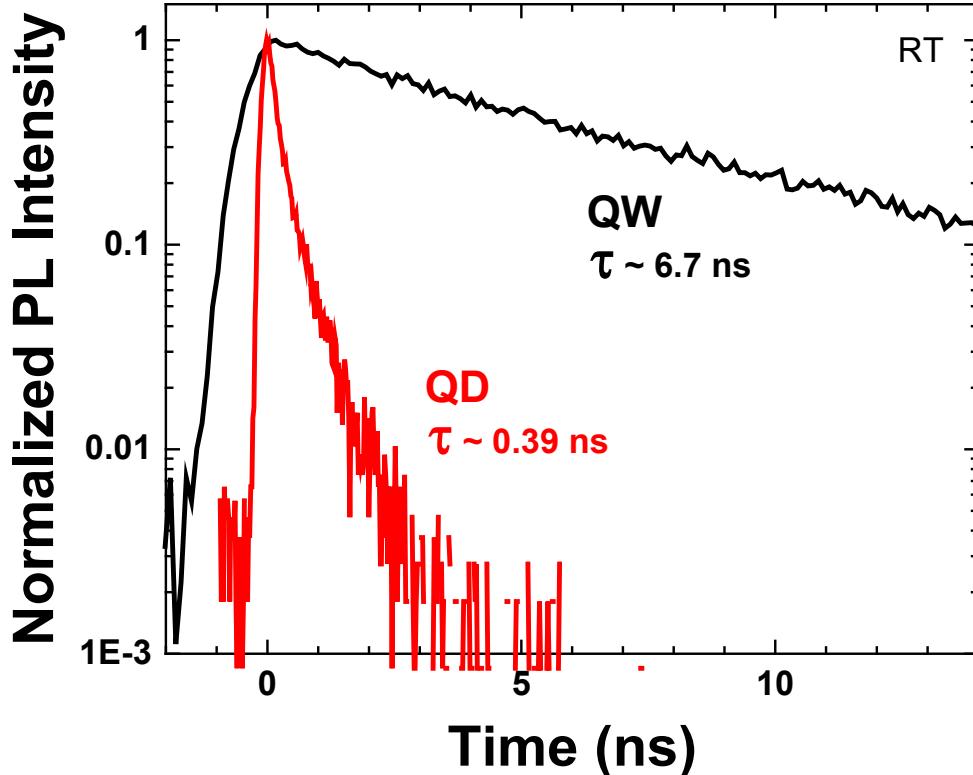


- Compare 10K and RT PL efficiency
- Assumes 10K PL is 100% efficient
- PL Intensity drops by >100X after QD etching
- IQE goes up by almost 10X after QD etching
- QDs are expected to have better IQE



# Time-resolved PL data from InGaN

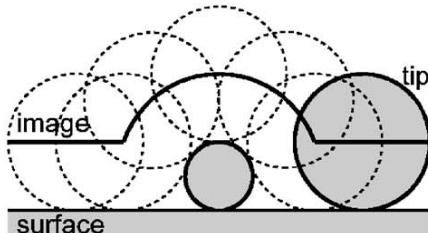
QDs  
Capped InGaN QW



## TRPL data:

- 405 nm pump ( $\sim 2$  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  $\rightarrow$  QDs**

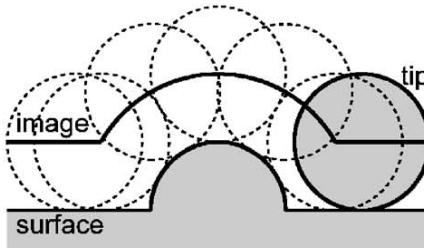
# AFM of QDs



Spherical feature

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

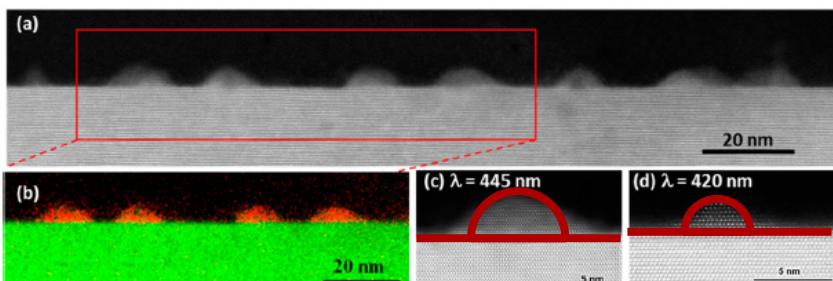
Convolution, 3 quantities  $\rightarrow$  image (w),  
tip (R), real surface (r),  
If know 2, can determine the third



Hemispherical feature

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

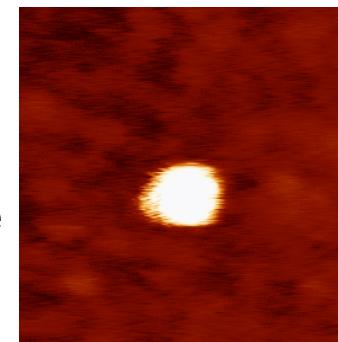
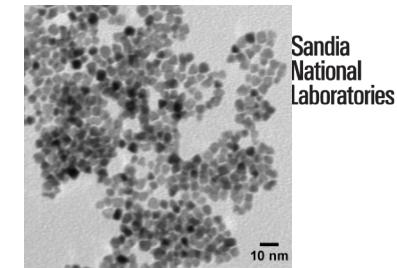
For our QDs



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

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

AFM image of 5 nm Pt nanoparticle dispersed on silicon



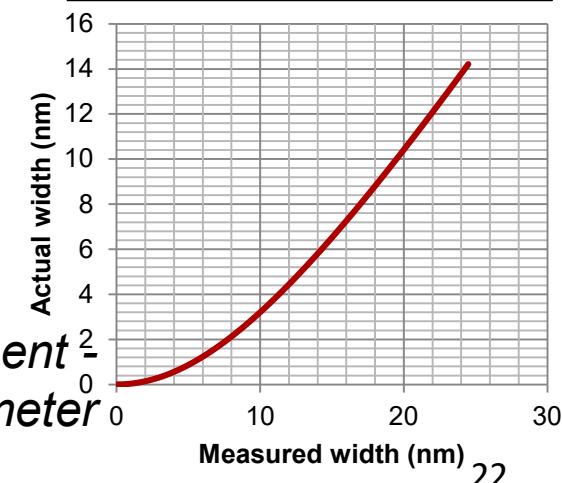
100nm x 100nm  
512x512 pixels

Assuming spherical particle

Modeling QDs as hemispheres,  
(height =  $\frac{1}{2}$  width)

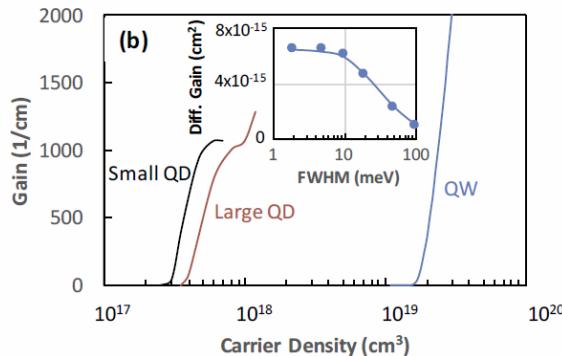
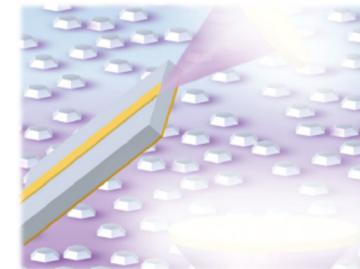
For 7 nm tip size,

Tip radius = 7.3nm

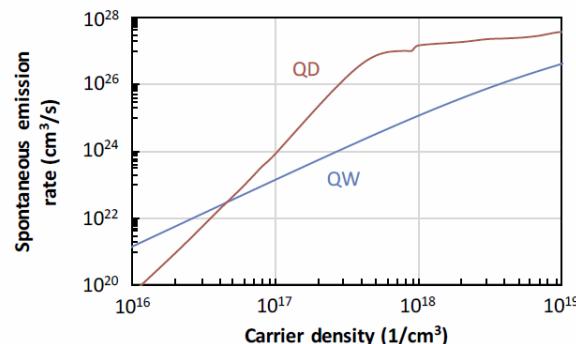


# Quantum Dots as the active region in LDs and LEDs?

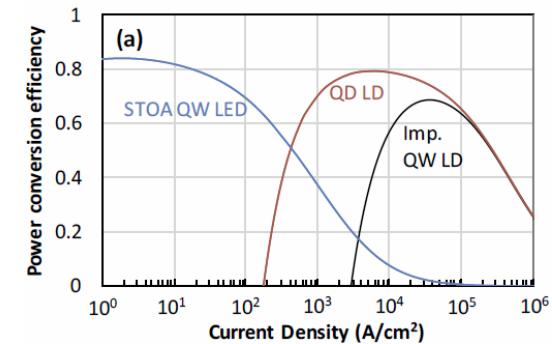
- Compared to current InGaN quantum well (QW) active regions, **QD active regions could significantly improve efficiencies of both laser diodes and LEDs**



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



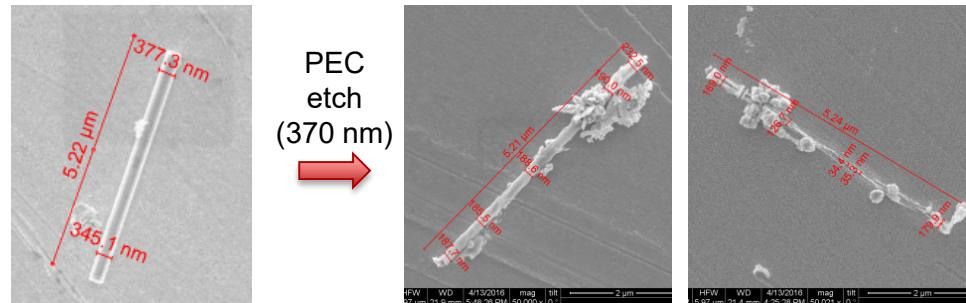
Plot of (a) power conversion efficiency vs. current density of a state-of-the-art (SOTA), QW-based LED (blue line), an improved QW-based LD (black line), and a QD-based LD (red line). The QD LD has extremely low threshold currents and peak efficiencies that rival the QW-based LED.

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**

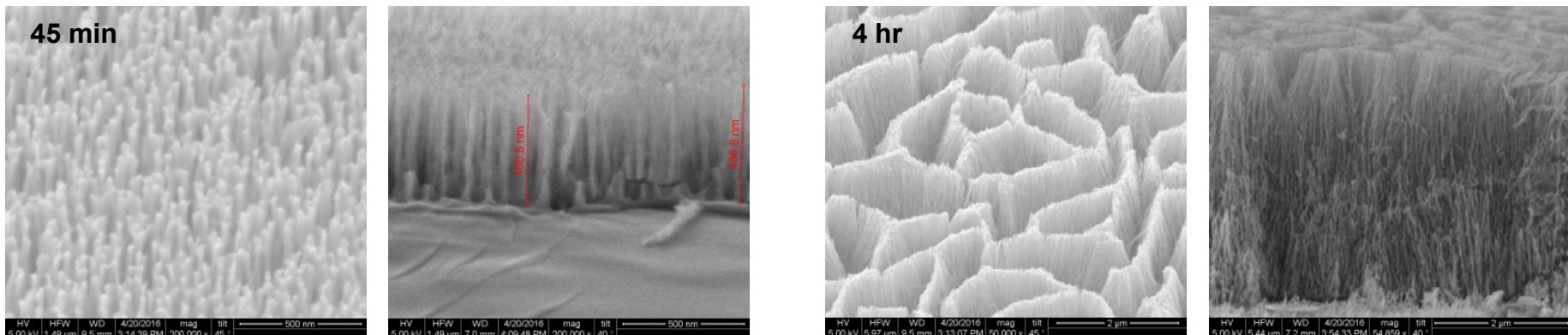
# PEC etching of GaN nanowire arrays

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



- 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 H<sub>2</sub>SO<sub>4</sub>



- 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)*

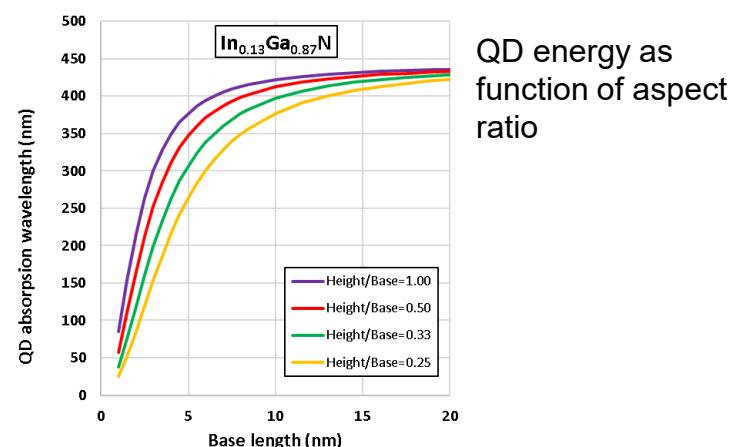
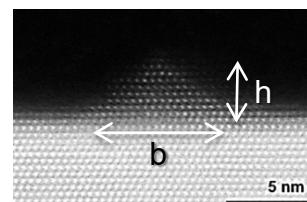
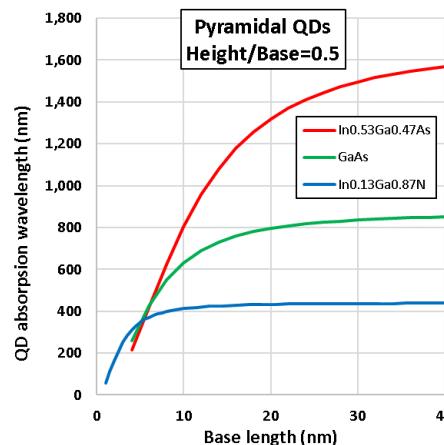
# Technical Accomplishment: QSC-PEC etching model

- 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

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

- 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



- 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.