SAND2014-16995PE

Precision Laser Assisted Photoelectrochemical Fabrication of III-V Semiconductor Quantum Structures

Xiaoyin Xiao
e-mail: xnxiao@sandia.gov

Arthur J. Fischer, Ping Lu, Daniel D. Koleske, Michael E. Coltrin, George T. Wang, Ganapathi S. Subramania, and Jeffrey Y. Tsao

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000..

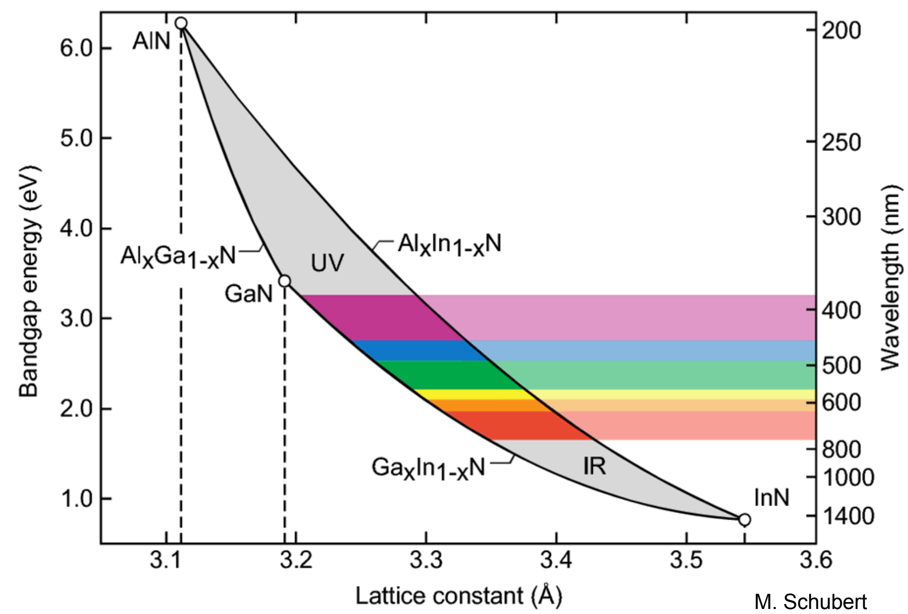
65th ISE Meeting in Lausanne, Switzerland, August, 2014

About Solid State Lighting (SSL)

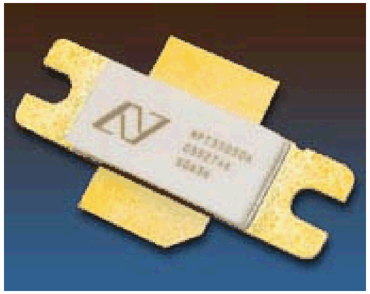
Basis: III-Nitride (Al, Ga, In, N) Semiconductors

III-Nitride (AlGaInN) Properties

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



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



Nitronex GaN power transistor

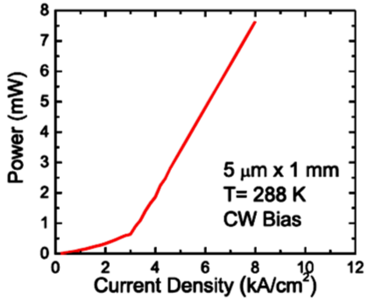
InGaN Quantum Dot (QD) Emitters

- 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:
  - Laser for lighting is gaining momentum
  - Low threshold, high efficiency, better temperature performance
  - Monodisperse QDs

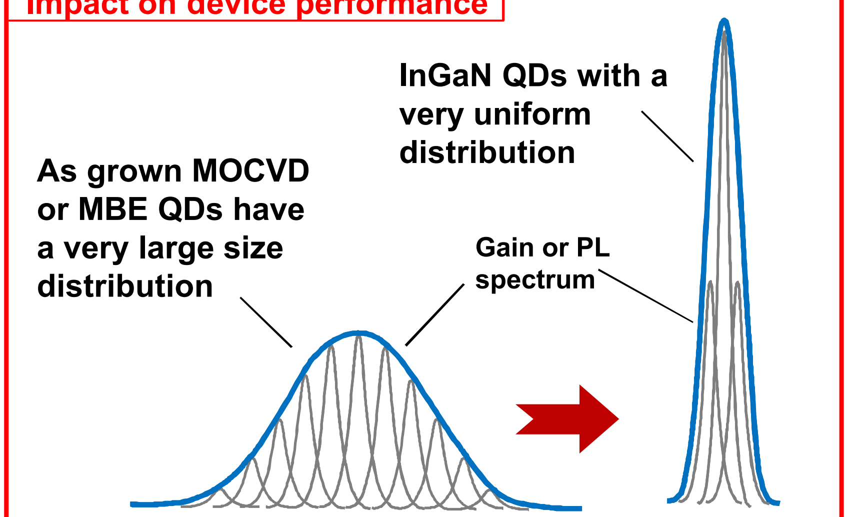
InGaN QD laser:
- **University of Michigan**
- **Electrically injected**
- **630 nm**
- **T_o = 236K**

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



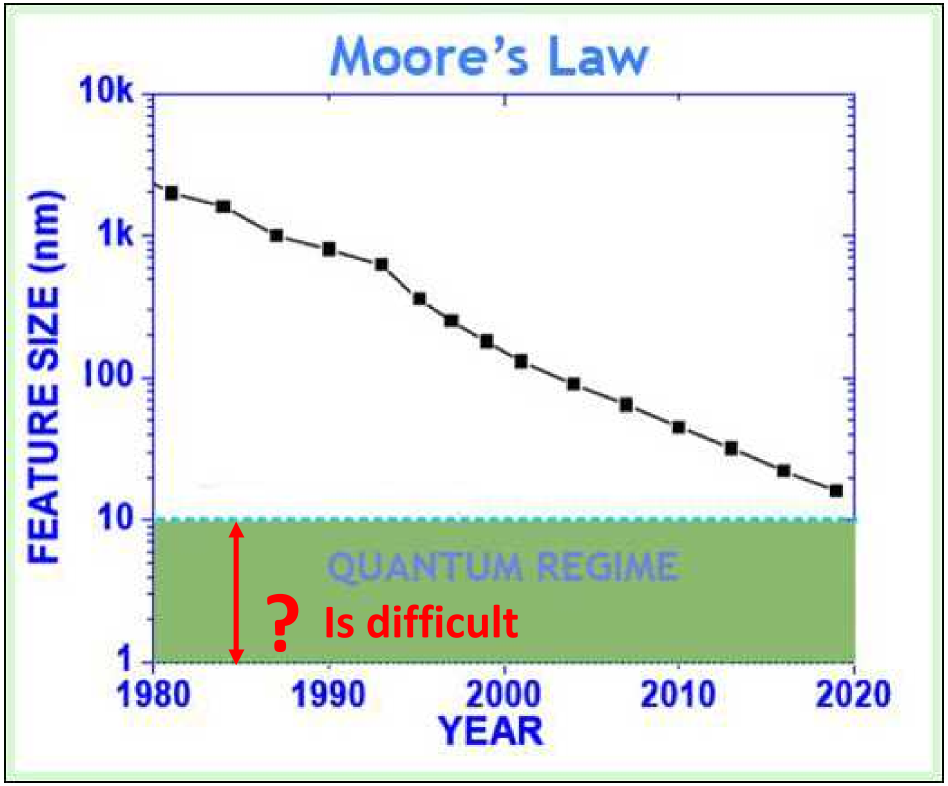
Monodisperse QD Distributions

Impact on device performance



Quantum confined structures: fabrication

1. Lithographical methods



2. S-K quantum dots

Strain-induced Stranski–Krastanov growth

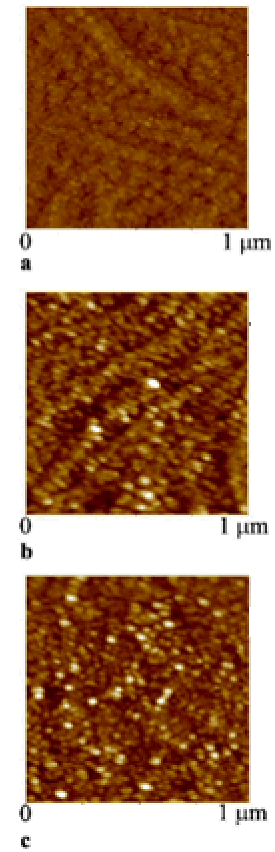


Fig. 2 AFM (1 μm × 1 μm) images of a 2.9 ML, b 4.4 ML, and c 5.8 ML InGaN grown at $T = 633°C$

Random location

Broad size distribution

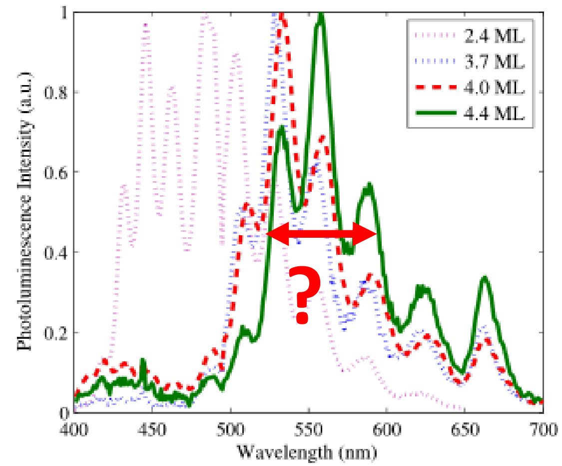
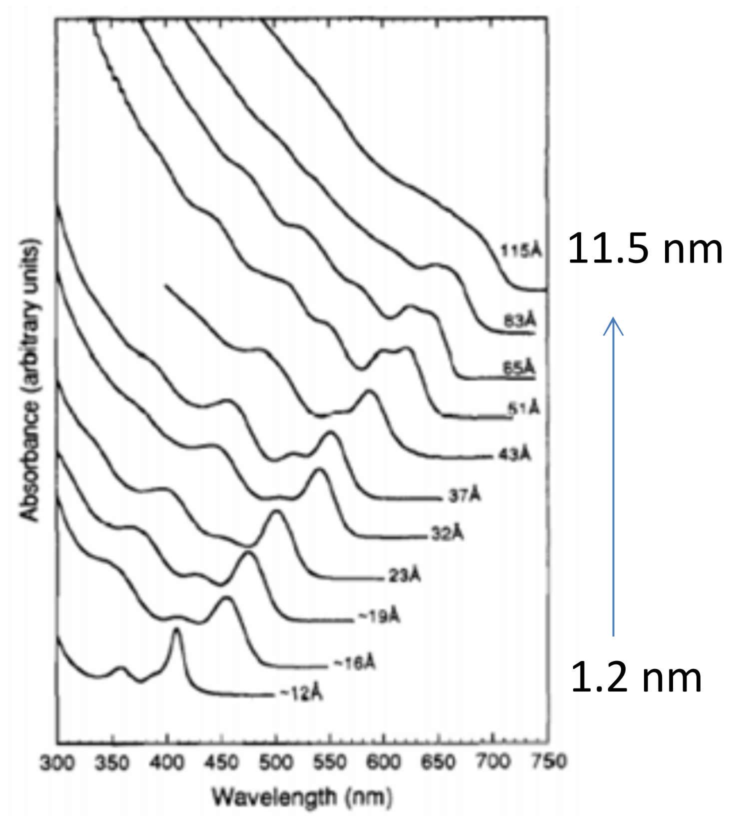


Fig. 5 Normalized photoluminescence intensity versus wavelength at room temperature for 2.4-, 3.7-, 4.0-, and 4.4-ML-thick InGaN

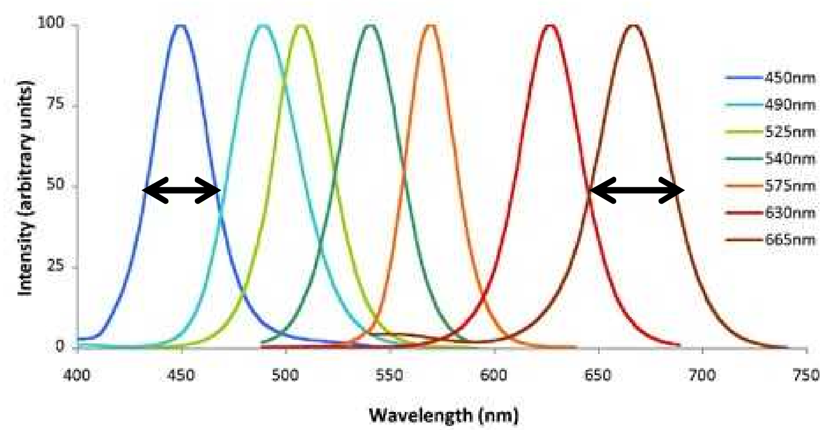
Appl Phys A (2009) 96: 403–408

Quantum confined structures: fabrication

3. Colloidal chemistries: simple and size-tunable



CdSe NPs in hexane

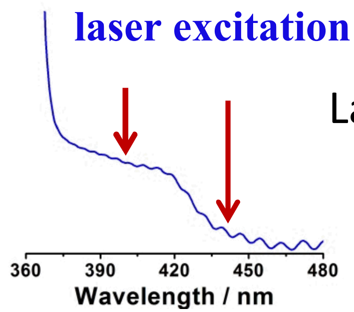


Cd/Se-ZnS core shell quantum dots

- Narrow size distribution
- Narrow PL peaks, ~50 nm above
- Passivation plays role

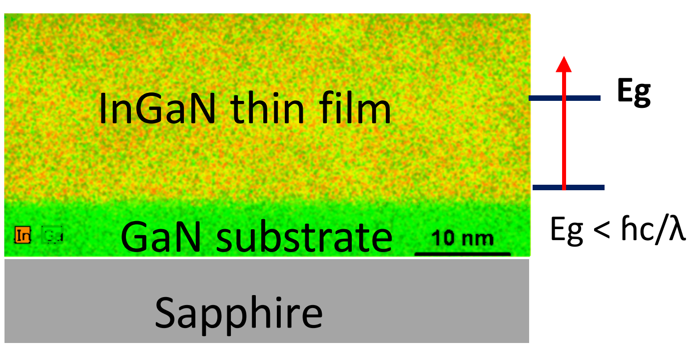
? Always dependent on organic/inorganic coatings
? No easy ways to integrate the dots into devices
? No colloidal chemistry for InGaN dots

Contents



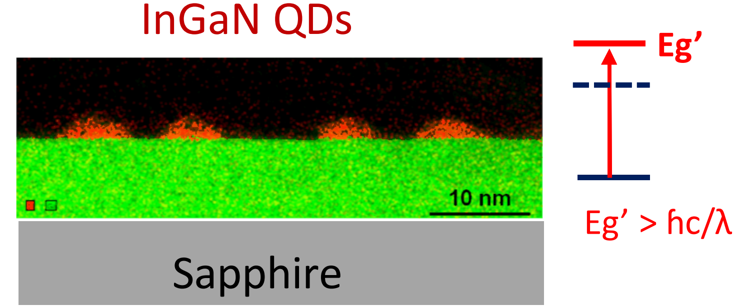
Laser linewidth ~ **1 nm**

$In_{0.13}Ga_{0.87}N$



PEC etching

InGaN QDs



Light absorption
PEC etching continues

metal-organic vapor-phase epitaxy (MOVPE)

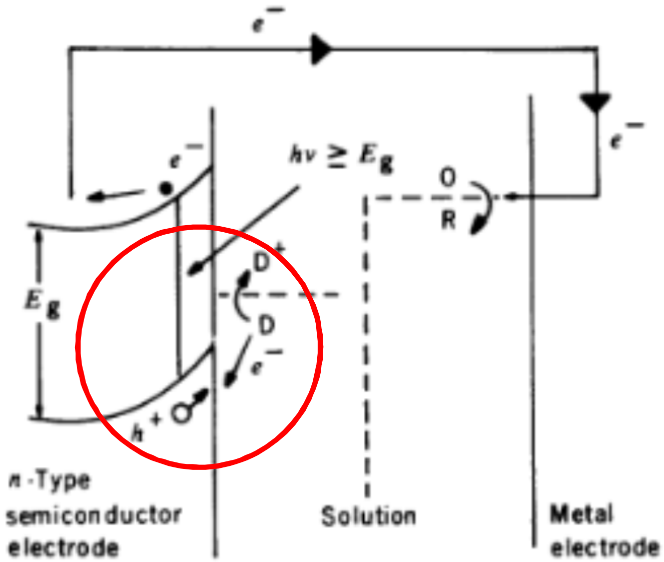
Less light absorption
PEC etching self-limiting

Photoelectrochemistry: a wide range of applications

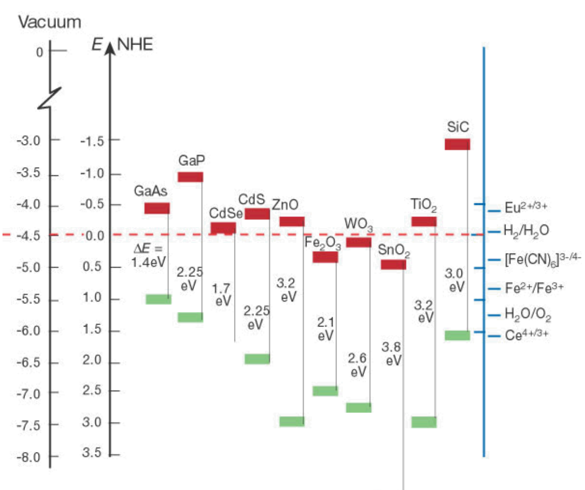
Chemical fuels ⟷ Light ⟷ Electricity

↓

Semiconductor process



N-type semiconductor oxidation



11 January 1980, Volume 207, Number 4427

SCIENCE

Photoelectrochemistry

Allen J. Bard

Summary. The electron-hole pair formation that occurs at the interface between a semiconductor and a solution upon absorption of light leads to oxidation or reduction reactions of solution species. The principles of such photodriven processes are described as well as applications of semiconductors in electrochemical cells and as particulate systems for carrying out heterogeneous photocatalysis and photoelectrosynthesis.

The interconversion of different forms of energy has been of central importance in science and technology. Just as the practical application of heat engines, electric generators and motors, and storage batteries led to the development of the fields of thermodynamics and electrochemistry in the 19th and 20th centuries, so the problem of utilizing solar energy for the direct production of electrical fuels, with overall field efficiencies of about 1 percent (*1*). The fabrication of artificial photosynthetic systems for the conversion of abundant materials (for example, H_2O and CO_2) to fuels (for example, H_2 and CH_3OH), directly or by electrolysis or the production of electricity, is clearly an important goal (*2*, *3*). Moreover, photochemical reactions could be employed to replace other ener-

one (Fig. 1A). The wavelength of light that causes such a transition is that with an energy equal to or greater than the difference in energies of the two orbitals, E_g. The result is an electron-hole (e^-h^+) pair formed by this intramolecular pumping in species, S. This produces an excited state, denoted S* (see Fig. 1A). If the e^-h^+ pair can be separated so that the e^- flows to a suitable acceptor species, A,

$$S^* + A \rightarrow S^+ + A^- \quad (1)$$

or an electron from a suitable donor, D, fills h^+

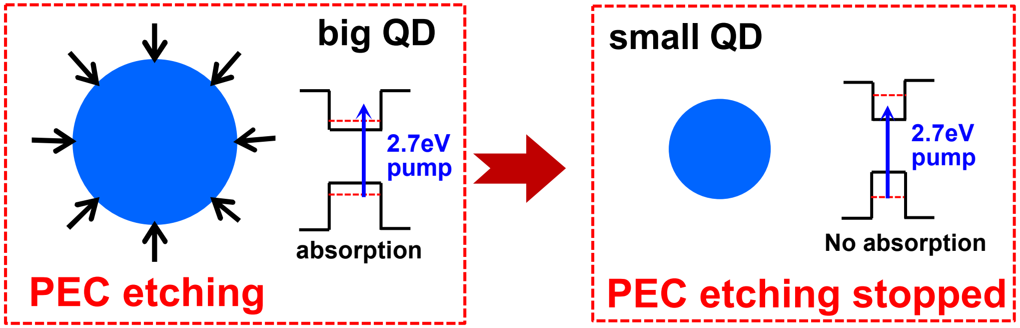
$$S^* + D \rightarrow S^- + D^+ \quad (2)$$

then the light energy has been stored, at least for a short time, as redox chemical energy. The reaction of S^+ and A^- or S^- and D^+ is spontaneous (or "downhill") and capable of liberating energy (that is, is exoergic). If e^- is pumped through a wire, it has been converted to an electrical current flow. However, excited states are very short-lived (typically lasting from nanoseconds to milliseconds in liquids) and the e^-h^+ pairs frequently recombine very quickly with the captured light energy degraded to heat or, sometimes with the emission of a photon, as in

Fabrication of InGaN QDs via PEC etching

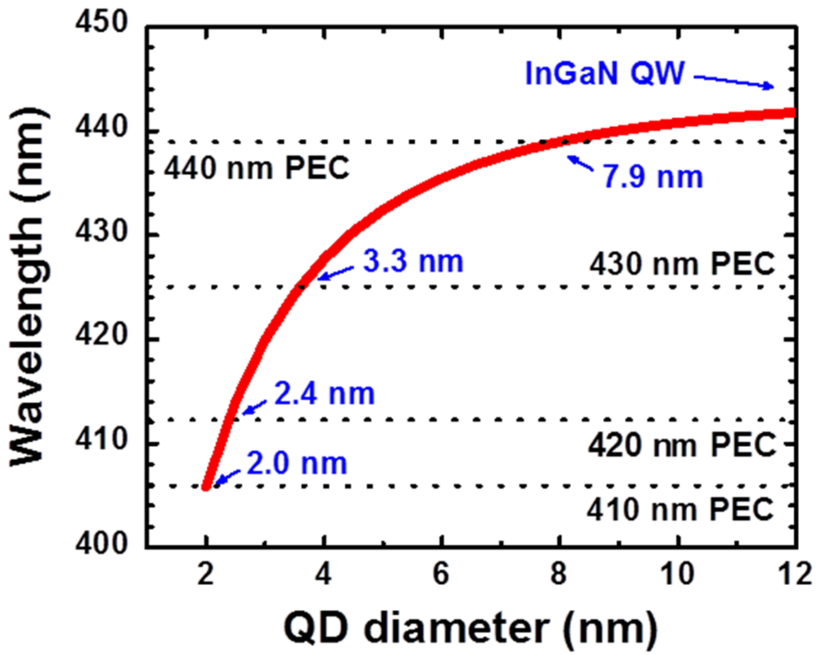
Quantum Size Control: Use size quantization to control QD size

Self-limiting PEC etch process:



- For QDs, band gap depends on size
- As etch proceeds,
  - QD size gets smaller, band gap goes up
  - Etch terminated for $E_g > E_{photon}$ pump
- Self-terminating etch process
- QD size depends on PEC wavelength
- Extremely monodisperse QDs ?

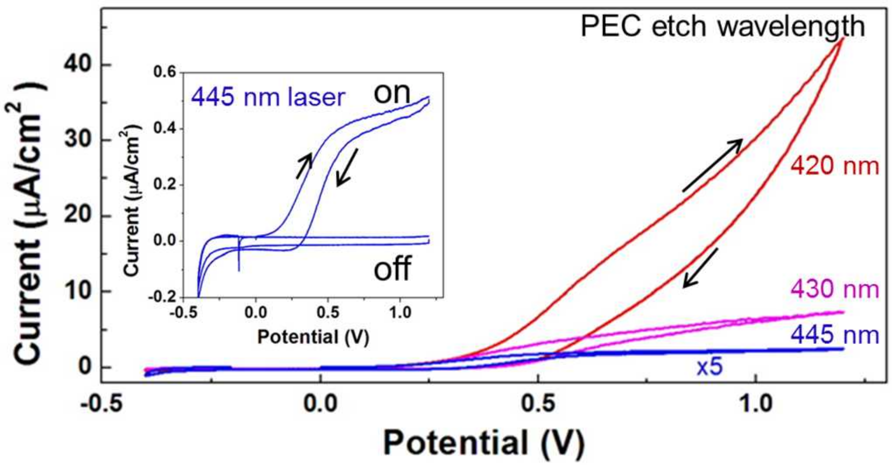
Towards precision size control

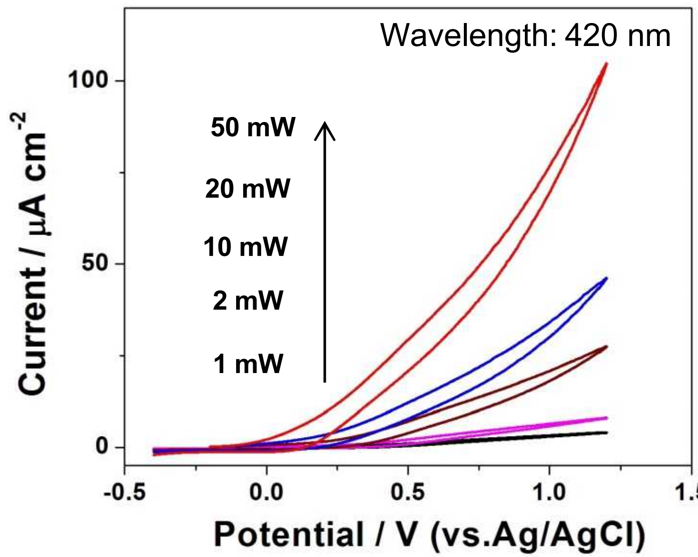


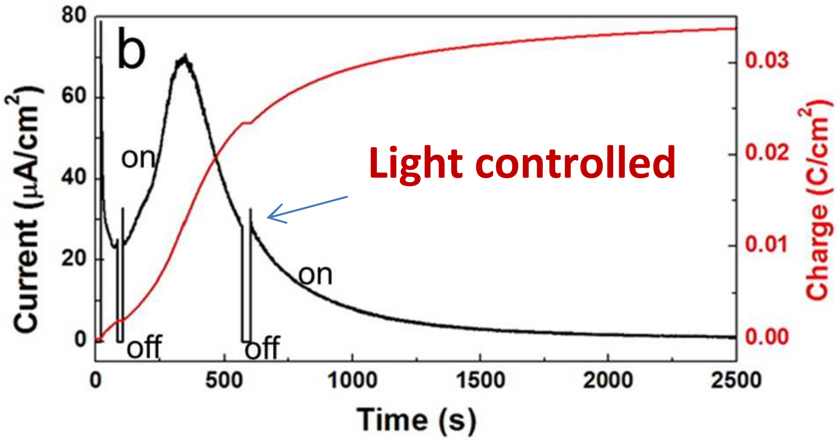
G. Pellegrini, et al., Journal of Applied Physics 97, 073706 (2005).

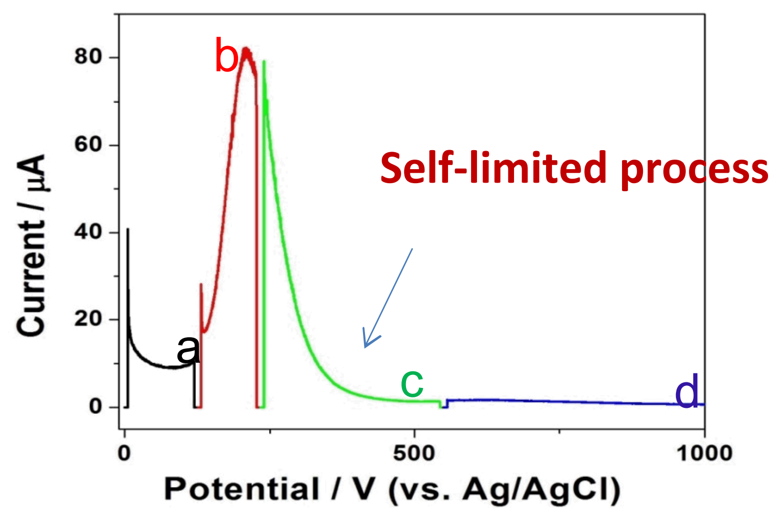
Self-terminated photoelectrochemical etching

0.2 M H_2SO_4



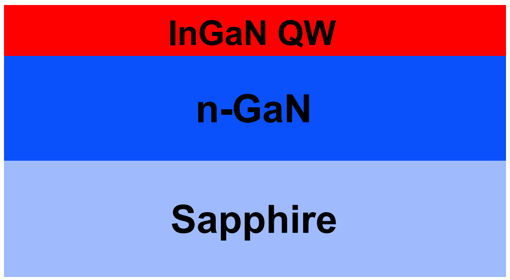






MOCVD-grown InGaN QW samples

Uncapped singe InGaN QW

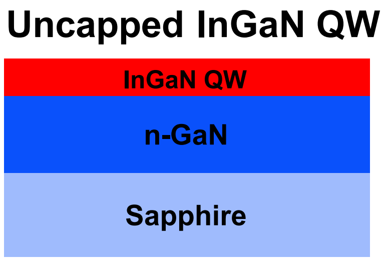


- Grown by MOCVD on sapphire substrates
  - 3 to 20 nm InGaN quantum well (QW)
- No InGaN underlayer is used in this sample
- Uncapped single QW sample (14% In):
  - Amenable to surface characterization of QDs
  - TEM, AFM characterization
  - Luminescence weaker than capped sample

Capped singe InGaN QW

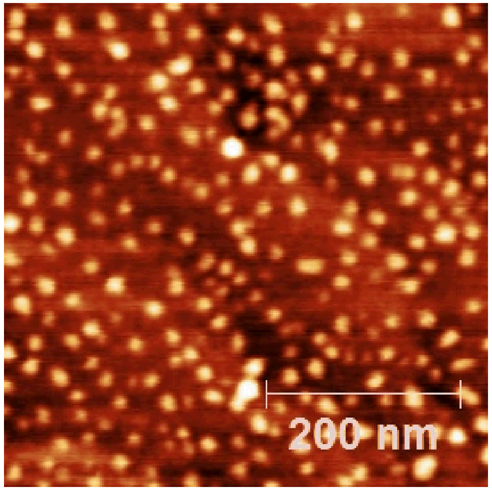
- Grown by MOCVD on sapphire substrates
  - 3 nm InGaN QW, 10 nm GaN cap
- InGaN underlayer (~2% In) used in this sample
- Capped single QW sample (14% In):
  - AFM is not useful for capped samples
  - Luminescence brighter than uncapped samples
- Etch is thought to proceed via pits, dislocations

Atomic Force Microscope (AFM) Measurements

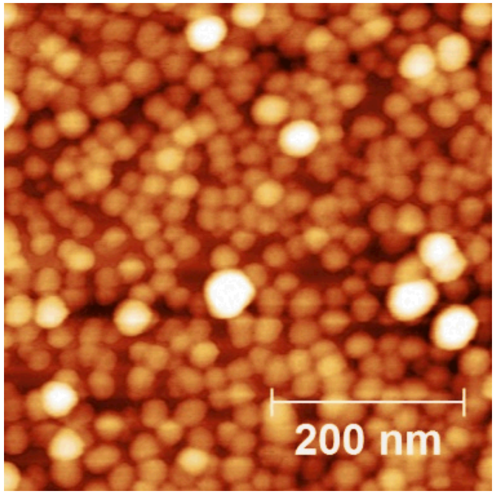


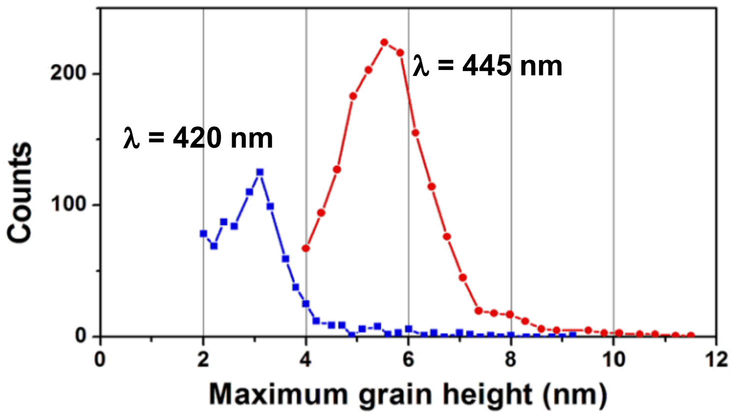
- Samples etched for two hours at 420 nm and 445 nm
  - Laser power density: ~ 3 mW/cm^2
- High dot density: 10^{11}/cm^2
- Some big dots (10-20 nm) remain: due to dislocations?
- QD size depends on PEC etch wavelength

PEC etch→ λ = 420 nm



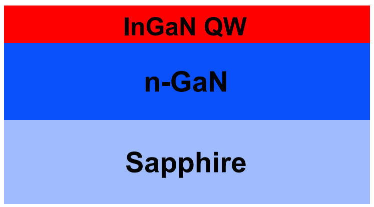
PEC etch → λ = 445 nm



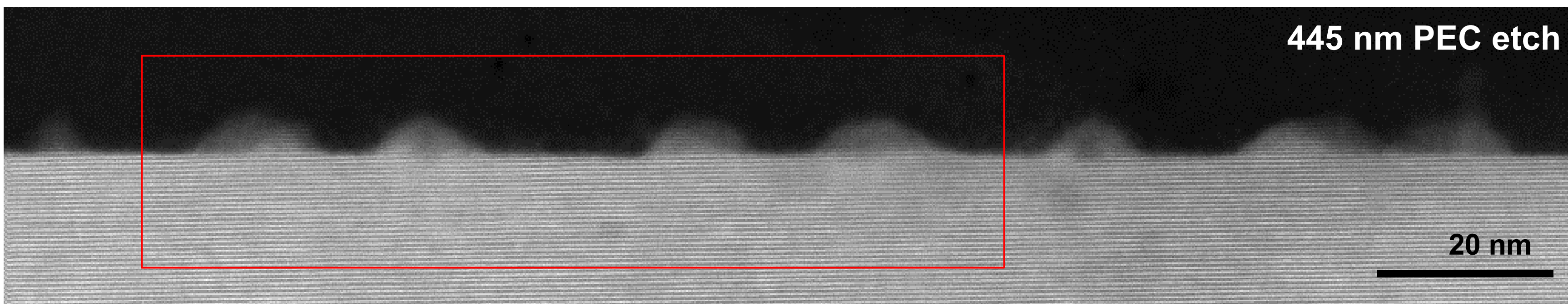


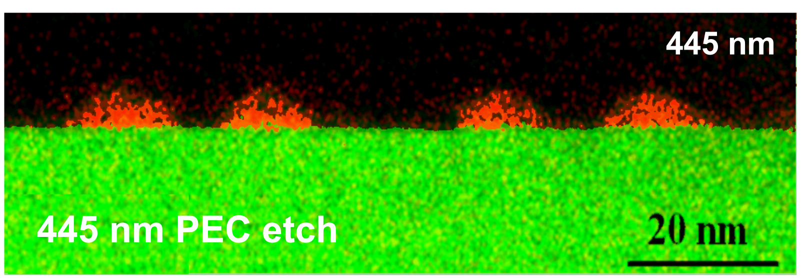
Transmission Electron Microscope (TEM) Images

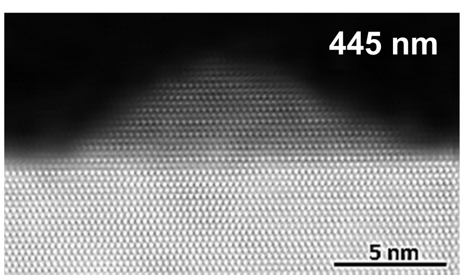
Uncapped InGaN QW

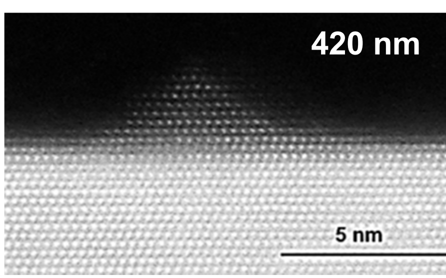


- High-angle annular dark-field (HAADF) TEM images
- Samples etched at 420 nm and 445 nm
- Energy dispersive x-ray mapping
  - QDs on surface are InGaN
  - Red = indium, green=gallium
- InGaN QDs are epitaxial to the underlying GaN
- No underlayer, no cap → PL is not very bright



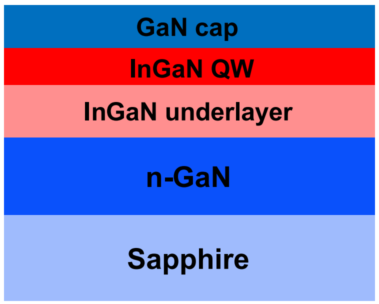






Transmission Electron Microscope Images

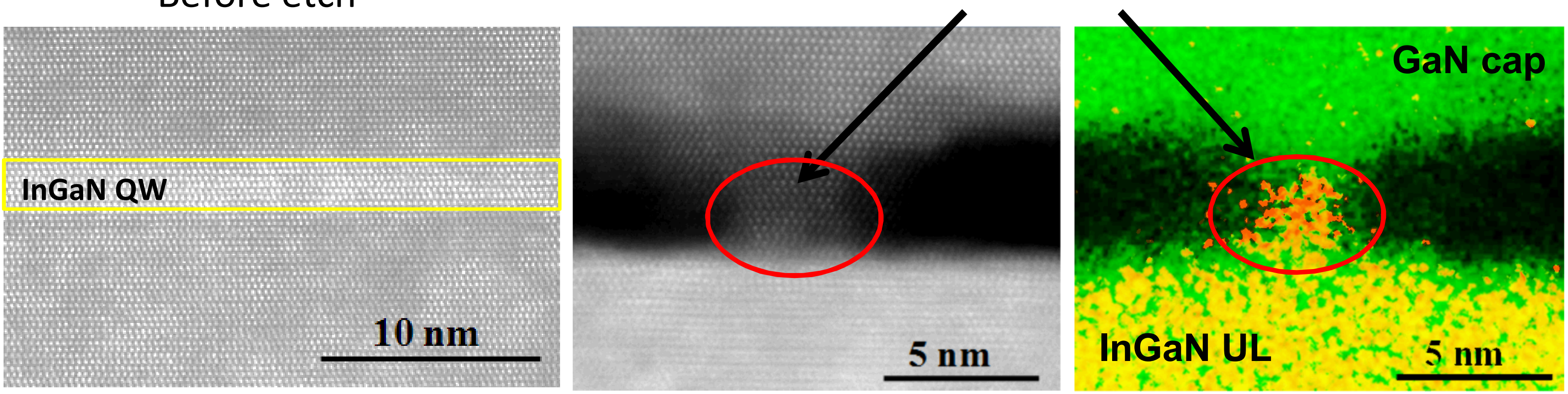
Capped InGaN QW



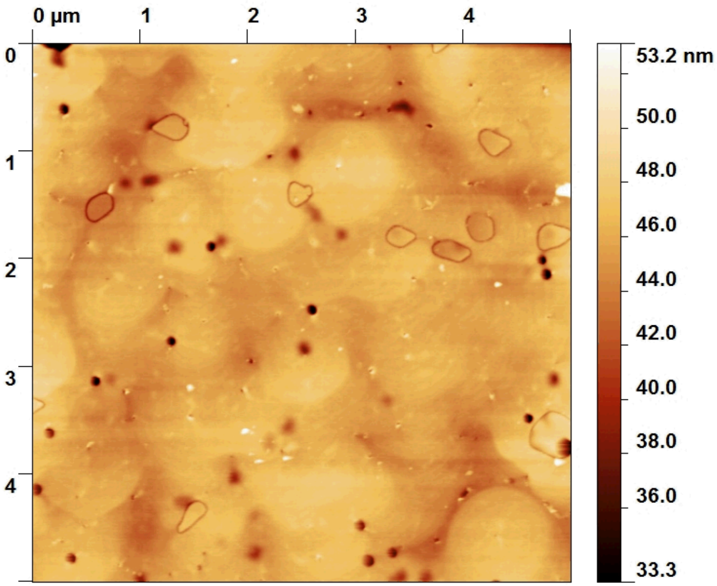
- High-angle annular dark-field (HAADF) TEM images
- Sample etched at 420 nm
- EDX mapping shows that dots are InGaN
- InGaN QDs are epitaxial to the underlying GaN
- 2% InGaN underlayer + GaN cap → PL is much brighter
- GaN cap provides partial passivation

Before etch

InGaN QD

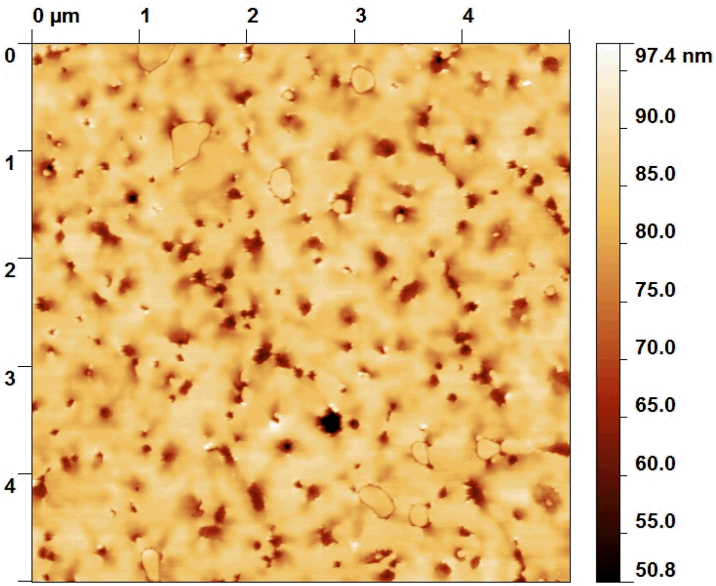


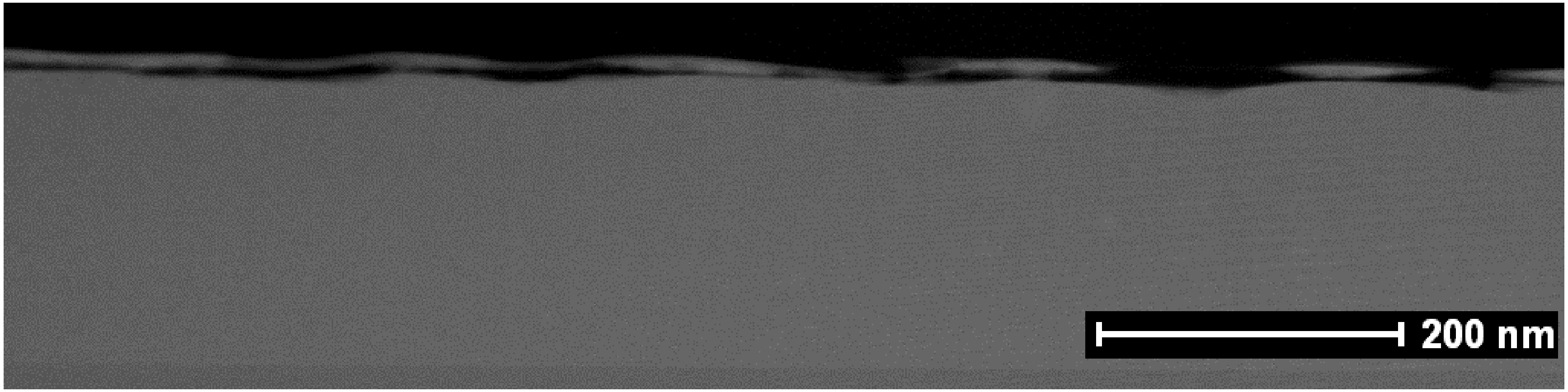
PEC etch of capped InGaN quantum wells



PEC etch

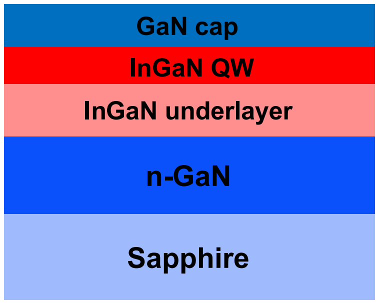
420 nm laser





Photoluminescence from fabricated InGaN QDs

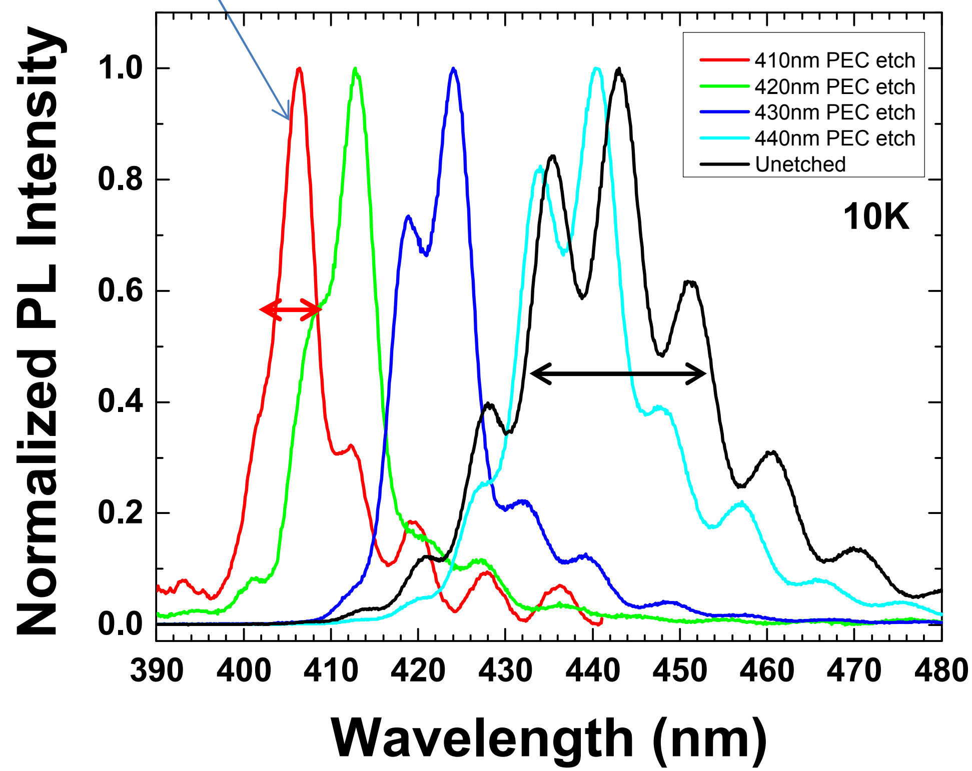
Capped InGaN QW



Photoluminescence (PL) data:

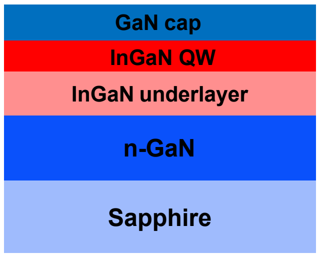
- 375 nm pump (ps pulsed)
- 10K PL data
- PL wavelength determined by PEC etch wavelength
- PL linewidth: 24 nm → 6 nm
- Quantum size-controlled PEC etching works!

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

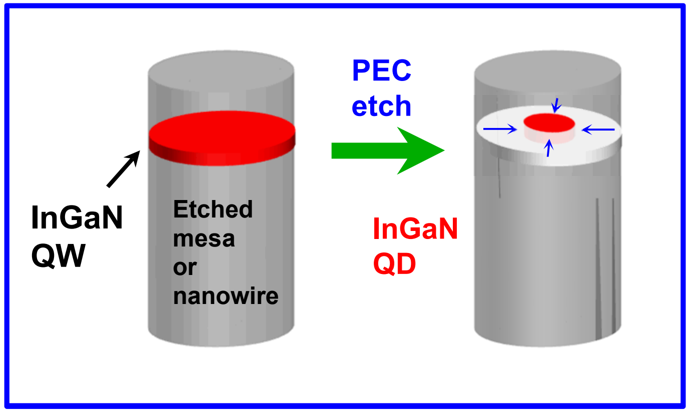


Emission from single InGaN QDs

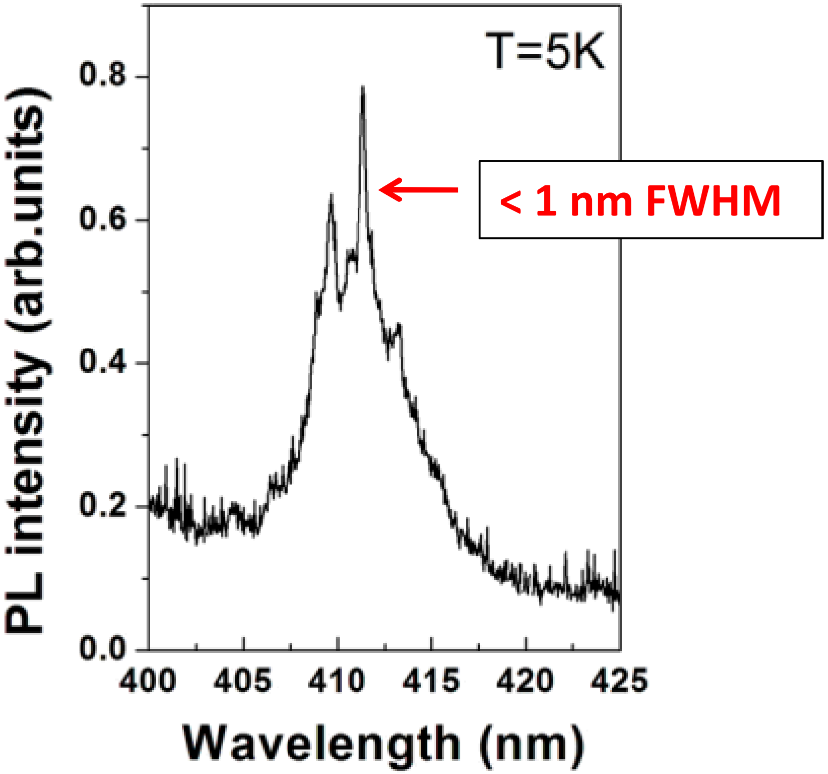
Capped InGaN QW



- Posts (150 – 200 nm) patterned with e-beam lithography
- Narrow PL emission (<1 nm FWHM) observed
- Fabricate InGaN QDs at deterministic locations
- InGaN QD single photon source

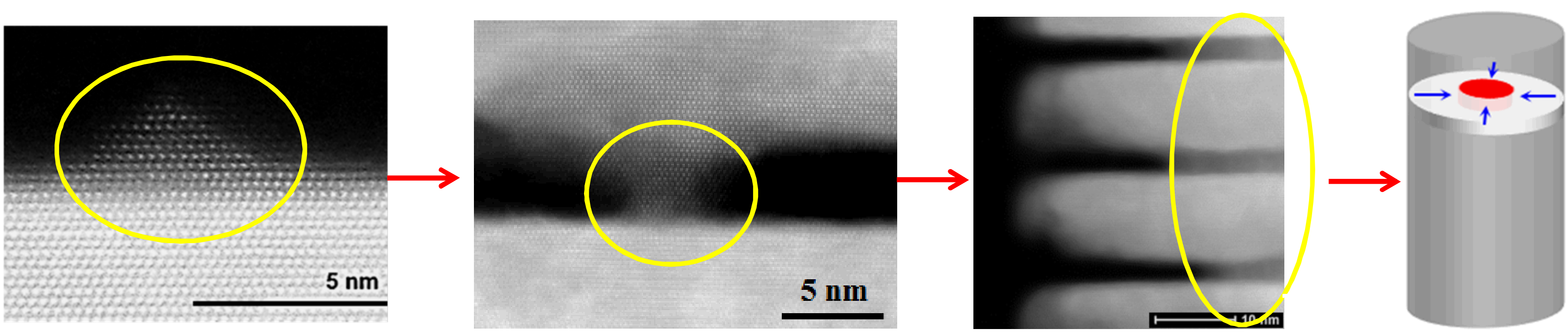


Deterministic locations



Summary/Conclusions

- Demonstrated fabricated InGaN QDs using PEC etching
  - AFM data indicates **10^{11}** QDs per cm^2
  - TEM EDX mapping shows we have **epitaxial** InGaN QDs
- Quantum size-controlled etching of InGaN QDs
  - **QD size and emission λ determined by PEC wavelength**
- PL linewidth reduced from 35 nm to less than **6** nm
  - Shows an improved QD size distribution
- Demonstrated emission from single InGaN QDs
  - Working towards **deterministic placement** of InGaN QDs



About Sandia National Laboratories

- ✓ On-site workforce: ~12,000
- ✓ FY13 budget: $2.3 billion