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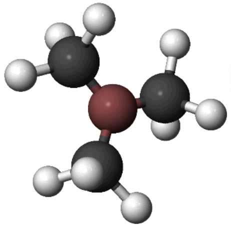
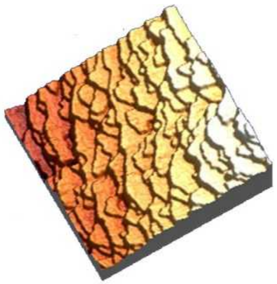
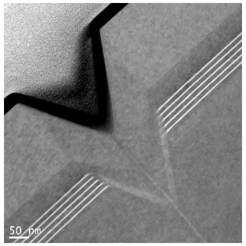
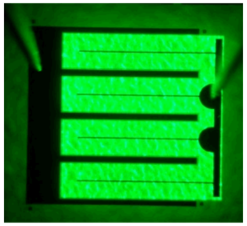




MOVPE of Group III Nitrides for Optical and Power Electronics Applications





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University of Nevada, Las Vegas
September 30, 2014

Exceptional service in the national interest

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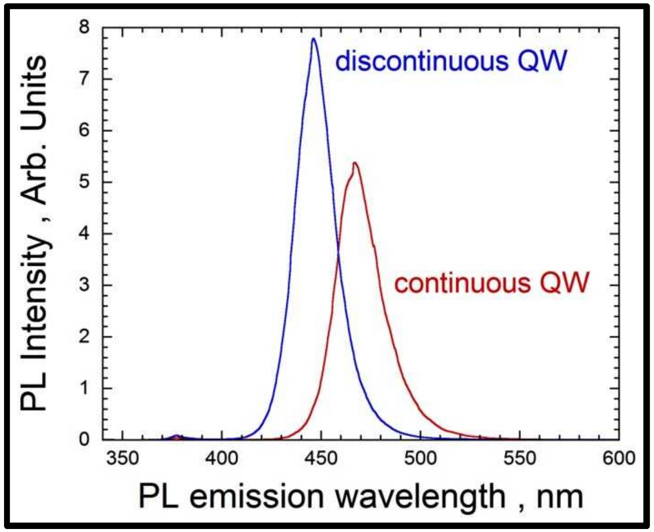
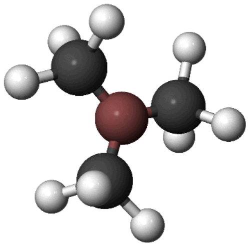
Outline

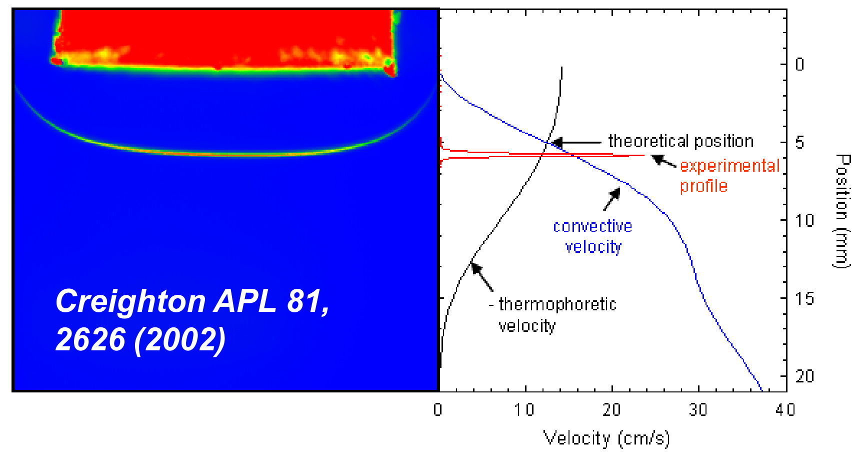
- GaN MOVPE essential tools.
- Making your own substrate – GaN on sapphire.
- Tricks for brighter InGaN quantum wells (QWs)
  - Underlayers and GaN barrier temperature.
- Advanced Stuff
  - AlGaN capping InGaN quantum wells.
  - Using hydrogen to etch InGaN.
- What's next?

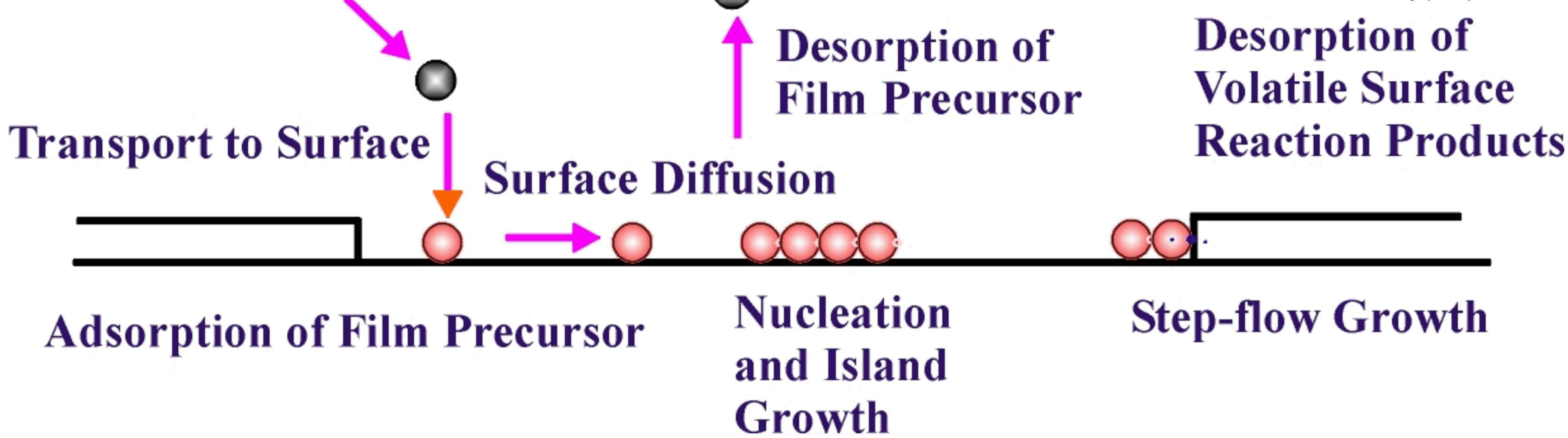


Metalorganic Vapor Phase Epitaxy (MOVPE)



$$Ga(CH_3)_3 + NH_3 \rightarrow GaN + 3\ CH_4$$

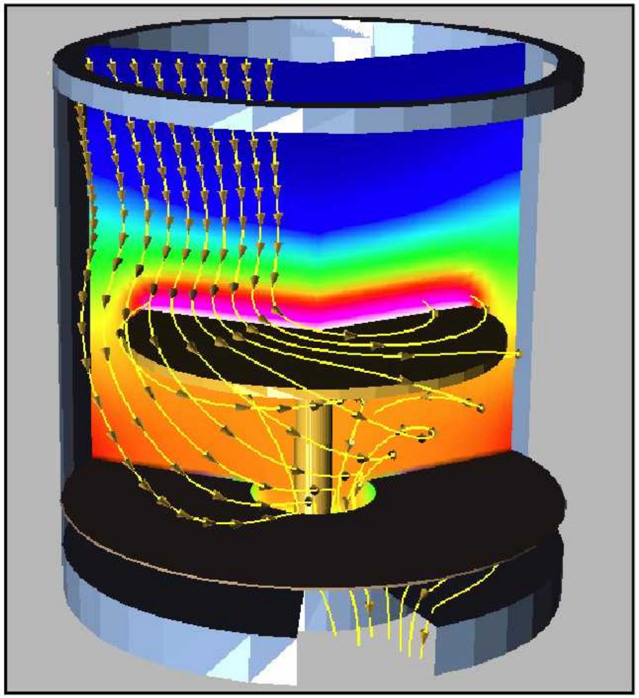




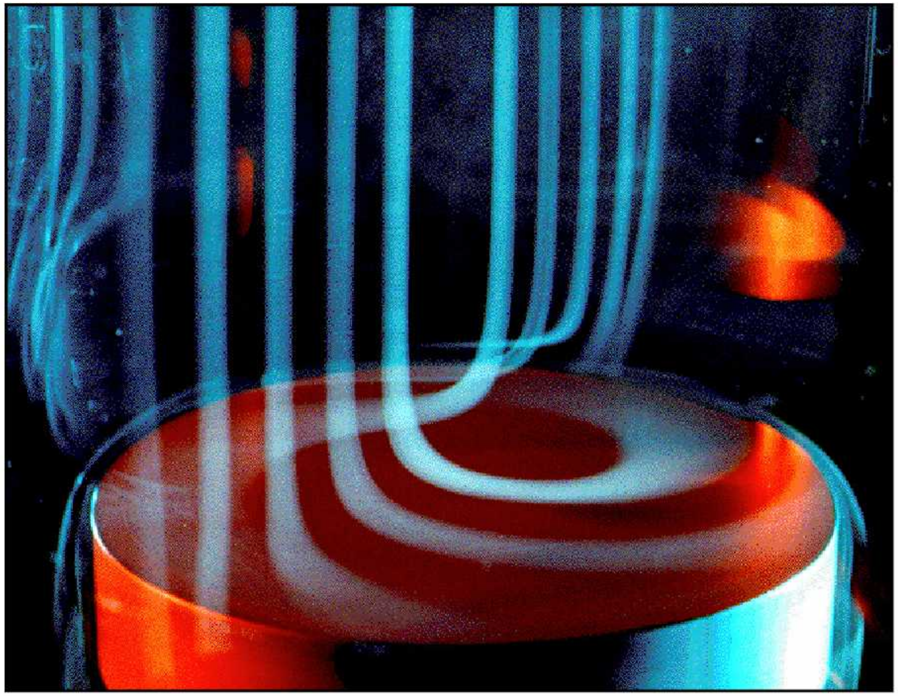
Metalorganic Vapor Phase Epitaxy (MOVPE)

Also need to consider the fluid flow dynamics at temperature

Computer Generated Flow Patterns in Rotating Disc System

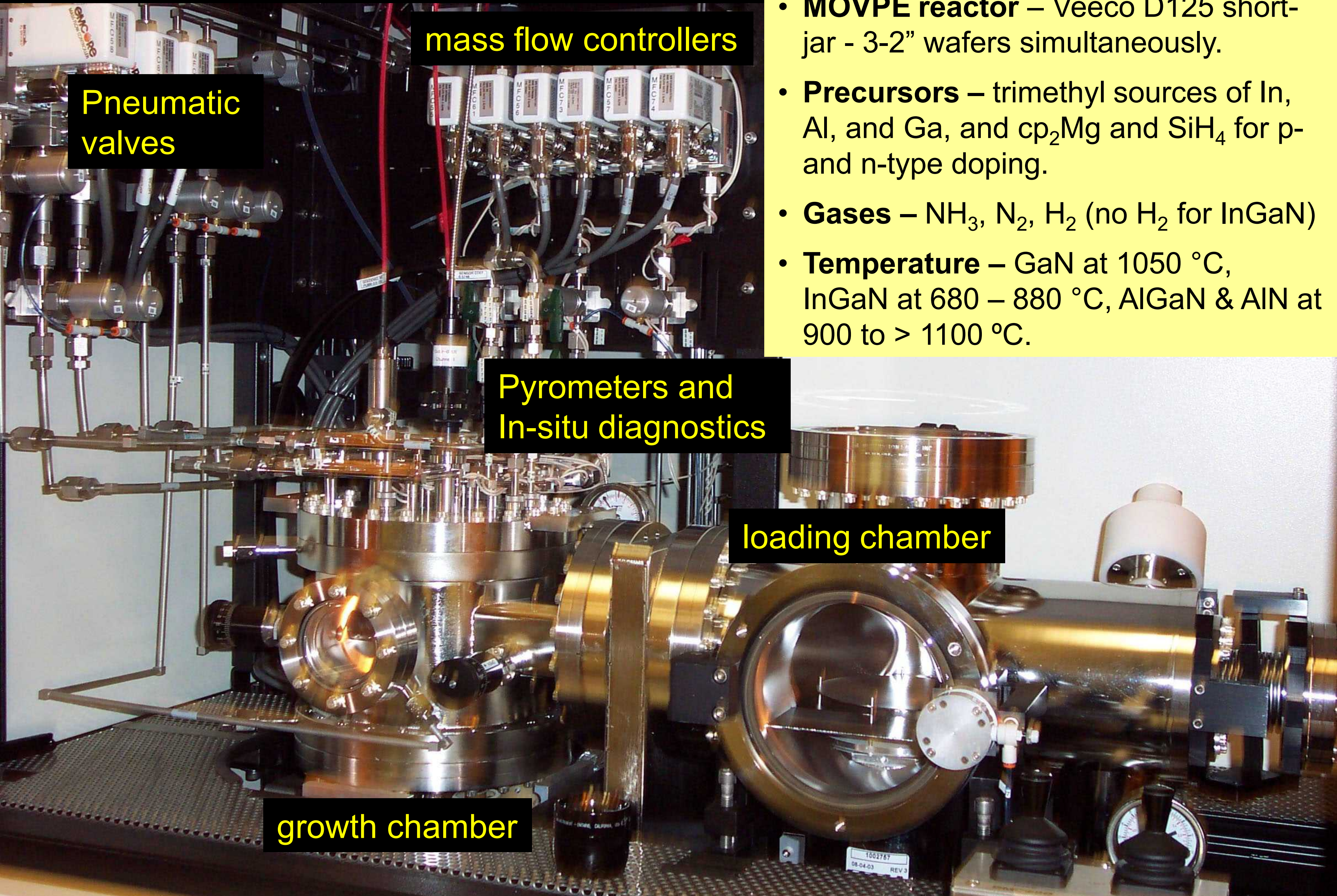


Smoke Flow Patterns in Rotating Disc System



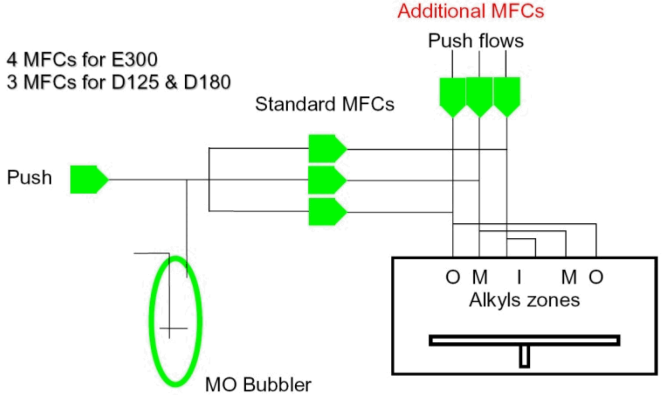
Data Courtesy of Sandia National Laboratories

- **MOVPE reactor** – Veeco D125 short-jar - 3-2” wafers simultaneously.
- **Precursors –** trimethyl sources of In, Al, and Ga, and cp_2Mg and SiH_4 for p- and n-type doping.
- **Gases –** NH_3, N_2, H_2 (no H_2 for InGaN)
- **Temperature –** GaN at 1050 °C, InGaN at 680 – 880 °C, AlGaN & AlN at 900 to > 1100 ºC.

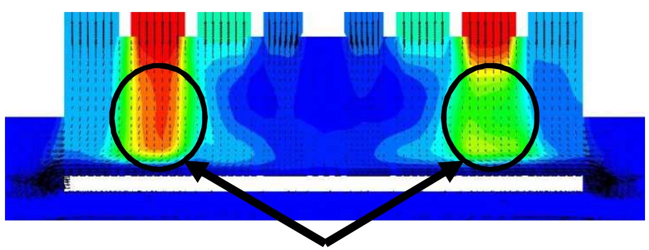


System designed to minimize chemical pre-reaction

Use additional push flows for velocity matching
(L. Kadinski, J. Cryst. Growth 261 (2004) 175)

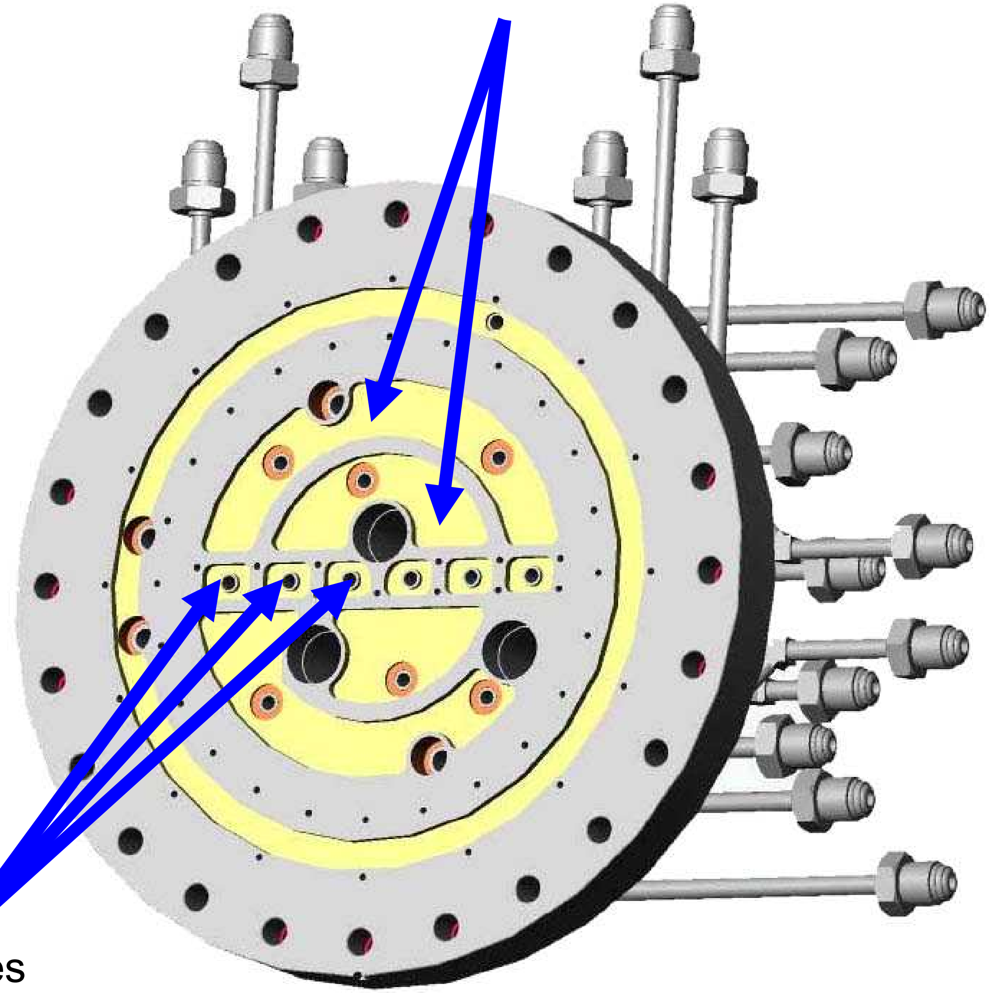


Simulated Flow in GaNzilla Reactor with
Addition of Alkyl Push Flow.



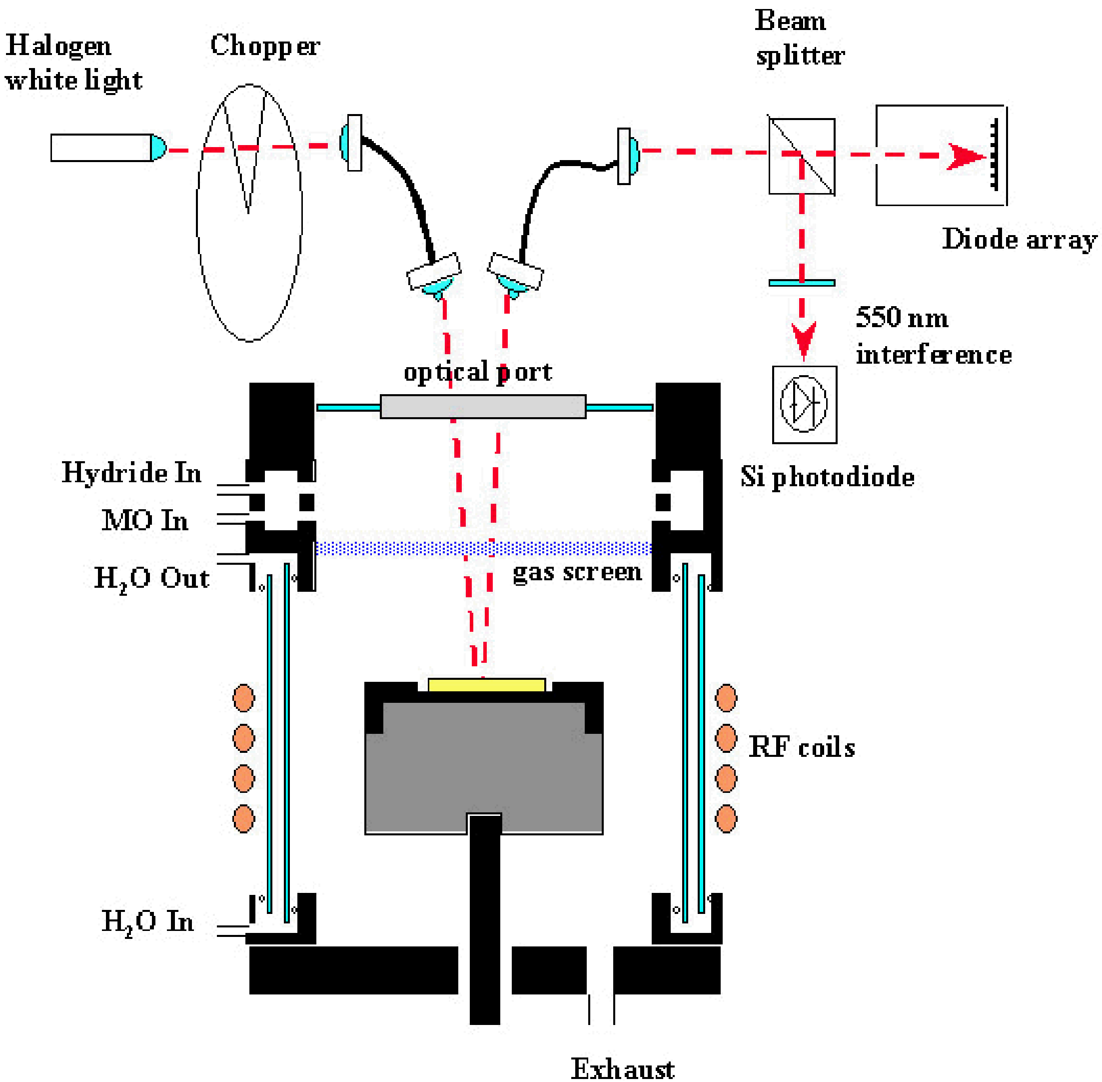
No recirculation observed in flow simulation.

Two hydride (NH_3) zones



Three alkyl (MO) zones
Inner, middle, and outer tied together

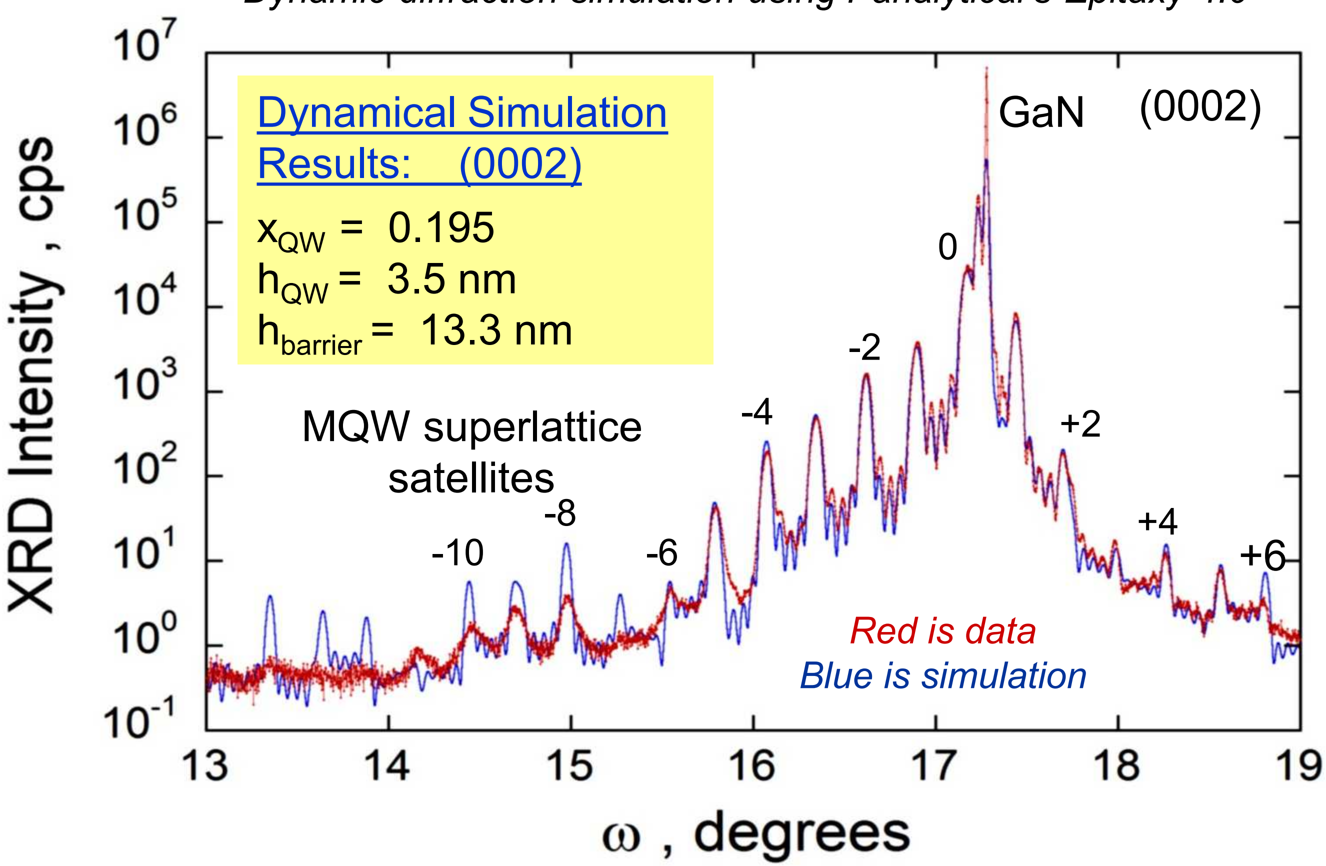
In-Situ Reflectance Monitoring During Growth

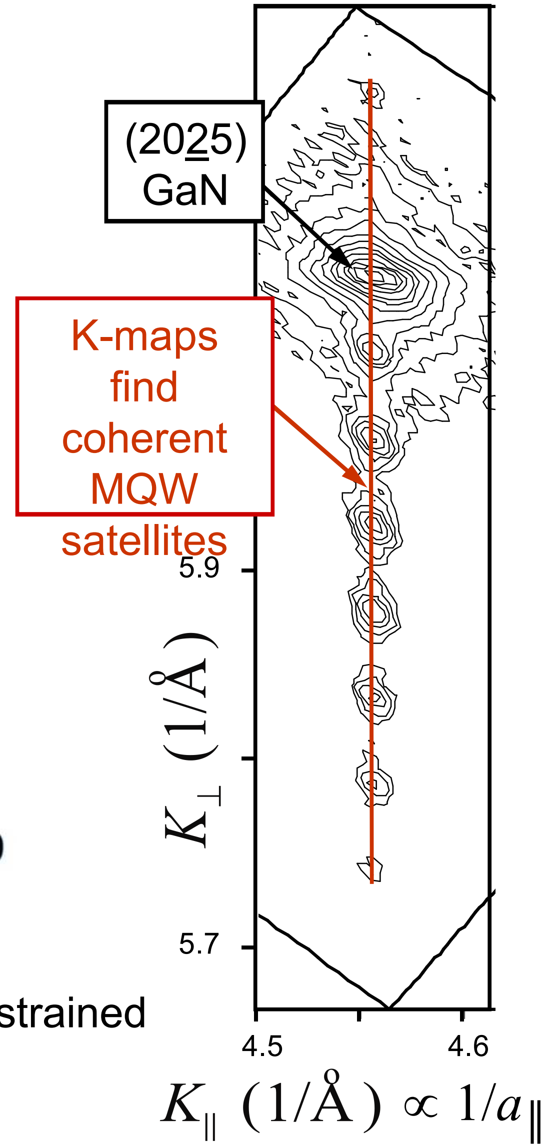


- Use light – can't use electrons because of growth pressure.
- With chopper have emissivity correcting pyrometry (400 nm – surface temperature)
- Reflectance contains data on growth rate, alloy concentrations, surface roughness, etc.
- Other systems can measure wafer curvature, can relate to layer strain - essential for GaN on Si.

X-ray diffraction (XRD) for structural information

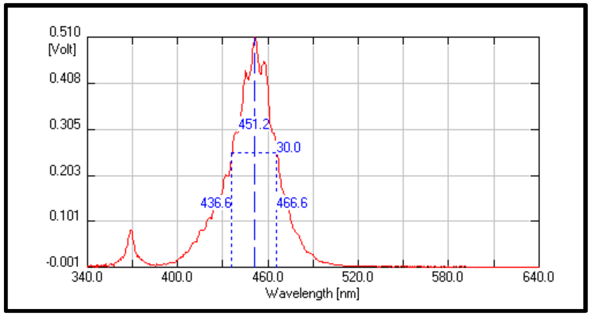
Dynamic diffraction simulation using Panalytical's Epitaxy 4.0



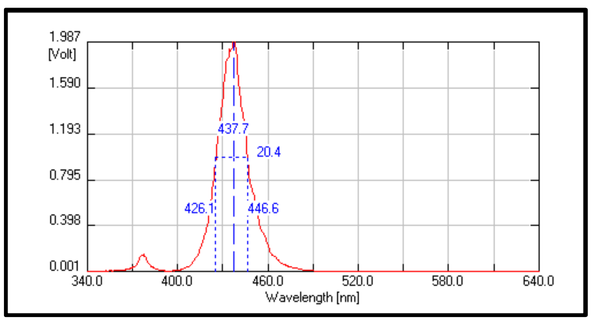


Dynamic diffraction fit assumes that the InGaN QWs are coherently strained to the GaN lattice. Coherency strain is confirmed by k-space map.

Photoluminescence for optical information



1) Measure lab standard on same scale as new sample (estimated IQE ~15%)

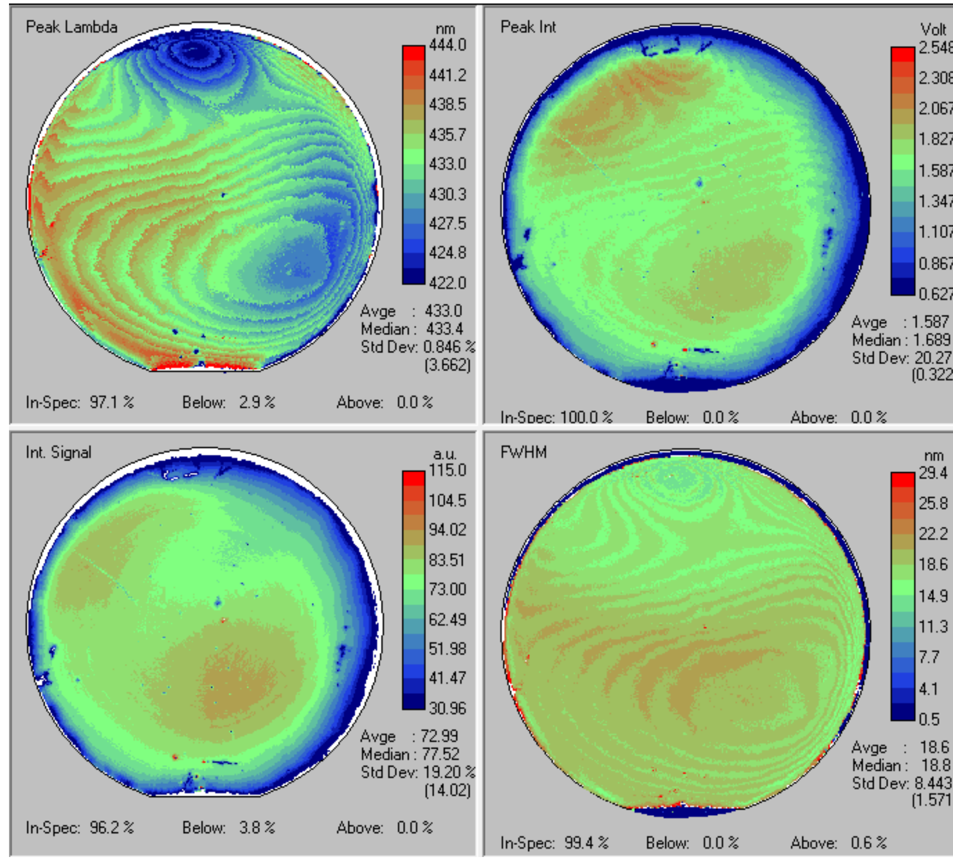


2) Normalize all PL signal to standard sample to account for variations in laser intensity. This sample is ~4x brighter.

3) Map wafer

Wavelength

Peak intensity

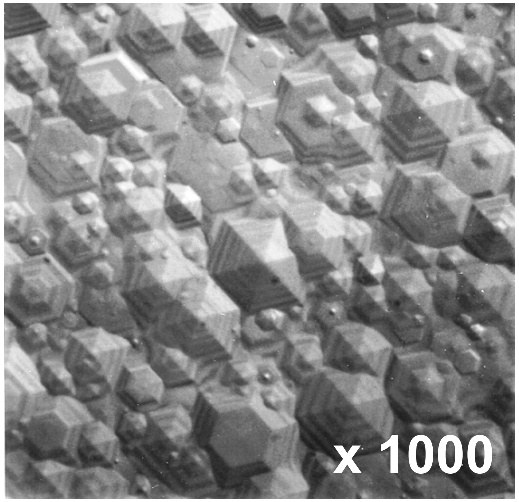


Integrated intensity

Peak FWHM

Making your own substrate

GaN on sapphire



GaN without nucleation layer
Before 1986
Few devices

GaN with nucleation layer
After 1986
Lots of devices

Invention of nucleation layer essential for GaN

- Why sapphire? Sapphire compatible with MOVPE growth environment, however yields GaN with high dislocation density.
- 1986, Amano and Akasaki[1] used thin **AlN "buffer layers"** to improve optical & electrical properties of GaN on sapphire.
- 1991, Nakamura[2] developed **GaN nucleation layers**.
- 1991, Nakamura reports blue LEDs, x10 brighter than SiC LEDs.
- 1992, Nakamura reports a GaN electron mobility ~ 900 cm^2/Vs
- 1993, Nakamura reports a 125 µW LED at 20 mA current
- 2006, Cree reports a 131 lumens/watt white LED.
- 2013, Cree XLamp - CCT= 4400K, 0.35 A, 276 lm/W.

*1) Amano et al. Appl. Phys. Lett. **48**, 353 (1986);*
*2) S. Nakamura, Jpn. J. Appl. Phys., Part 2 **30**, L1705 (1991).*

Hiroshi Amano

Isamu Akasaki

Shuji Nakamura

Today

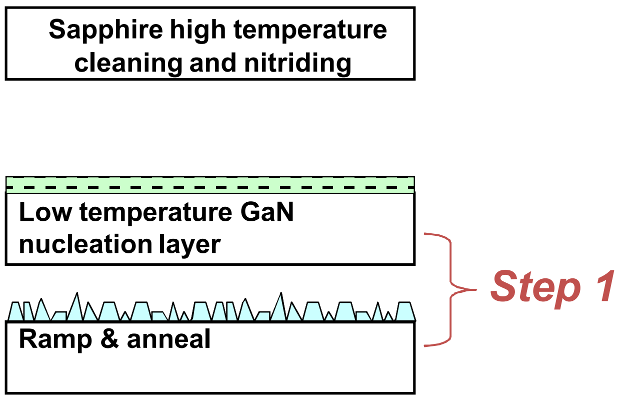
Nakamura's two-step GaN process

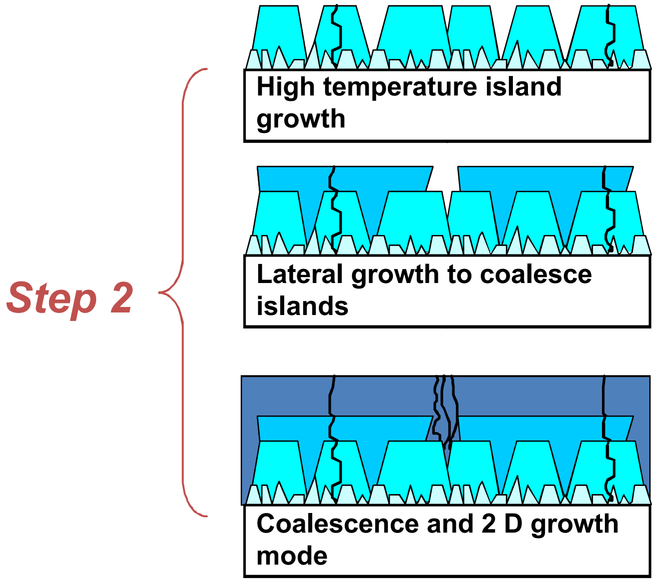
S. Nakamura, Jpn. J. Appl. Phys., Part 2 ***30****, L1705 (1991)*
Grain evolution from K. Hiramatsu, et al., Journal of Crystal Growth 115, 628 (1991).

1) Sapphire heated to high temperature (1050 – 1100 ºC) in H_2 to "clean" the surface; surface sometimes exposed to NH_3 at high temperature.

2) Grow 20 – 30 nm GaN NL at 500 – 600 ºC; as grown NL contains "cubic" material with stacking faults.

3) Heat GaN NL to 1000 – 1080 ºC in flowing H_2, N_2, and NH_3. Wurtzite GaN nuclei form.





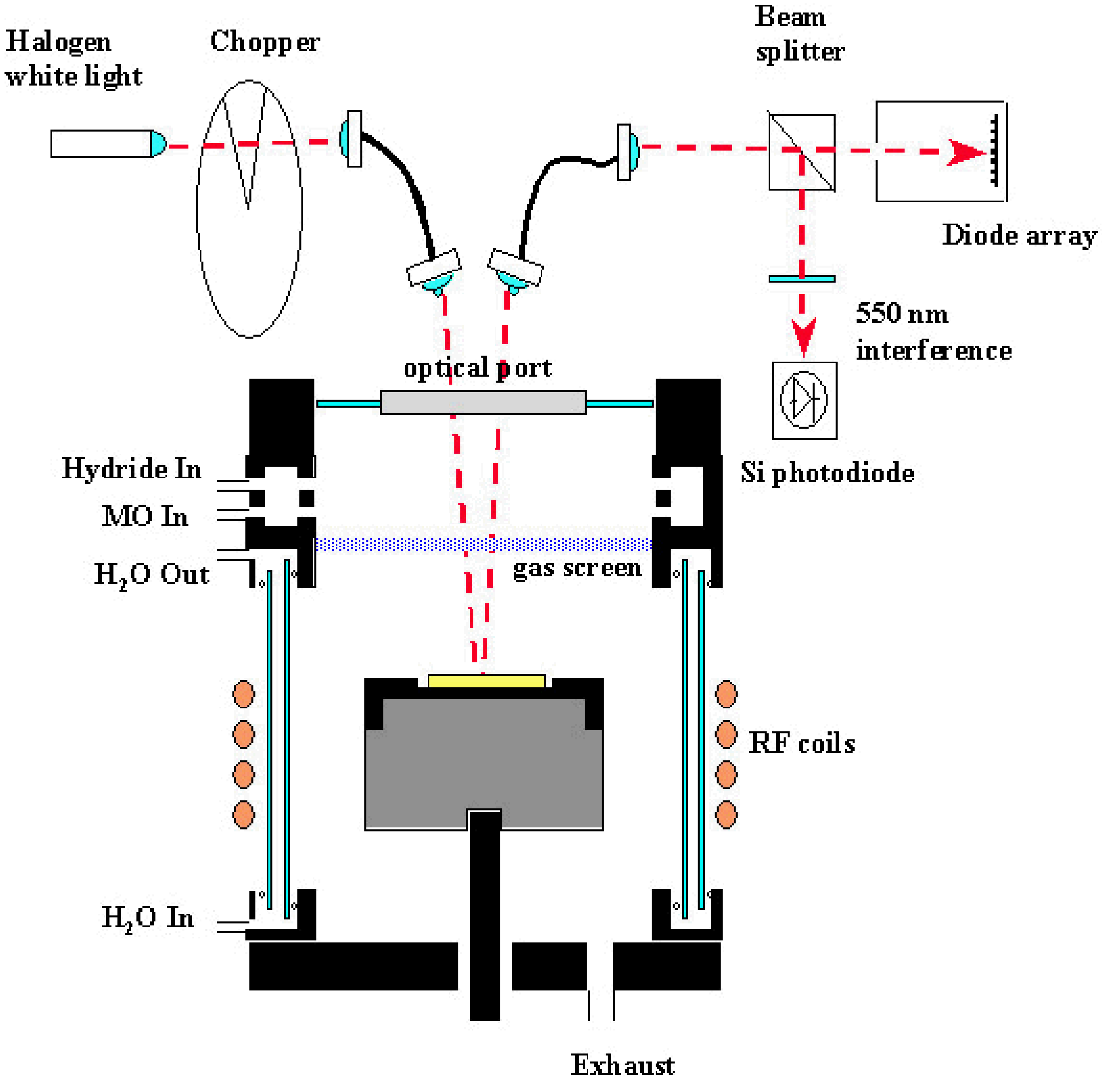
4) At high temperature, Ga source is turned on. Isolated GaN grains grow on the GaN nuclei. Some dislocations propagate up from the GaN grains.

5) Islands grow laterally / vertically; grains begin to coalesce. Growth conditions can be tuned to increase / decrease lateral growth rate.

6) When grains have coalesced, growth becomes 2-D. Dislocations are formed as GaN grains coalesce to accommodate grain twist / tilt.

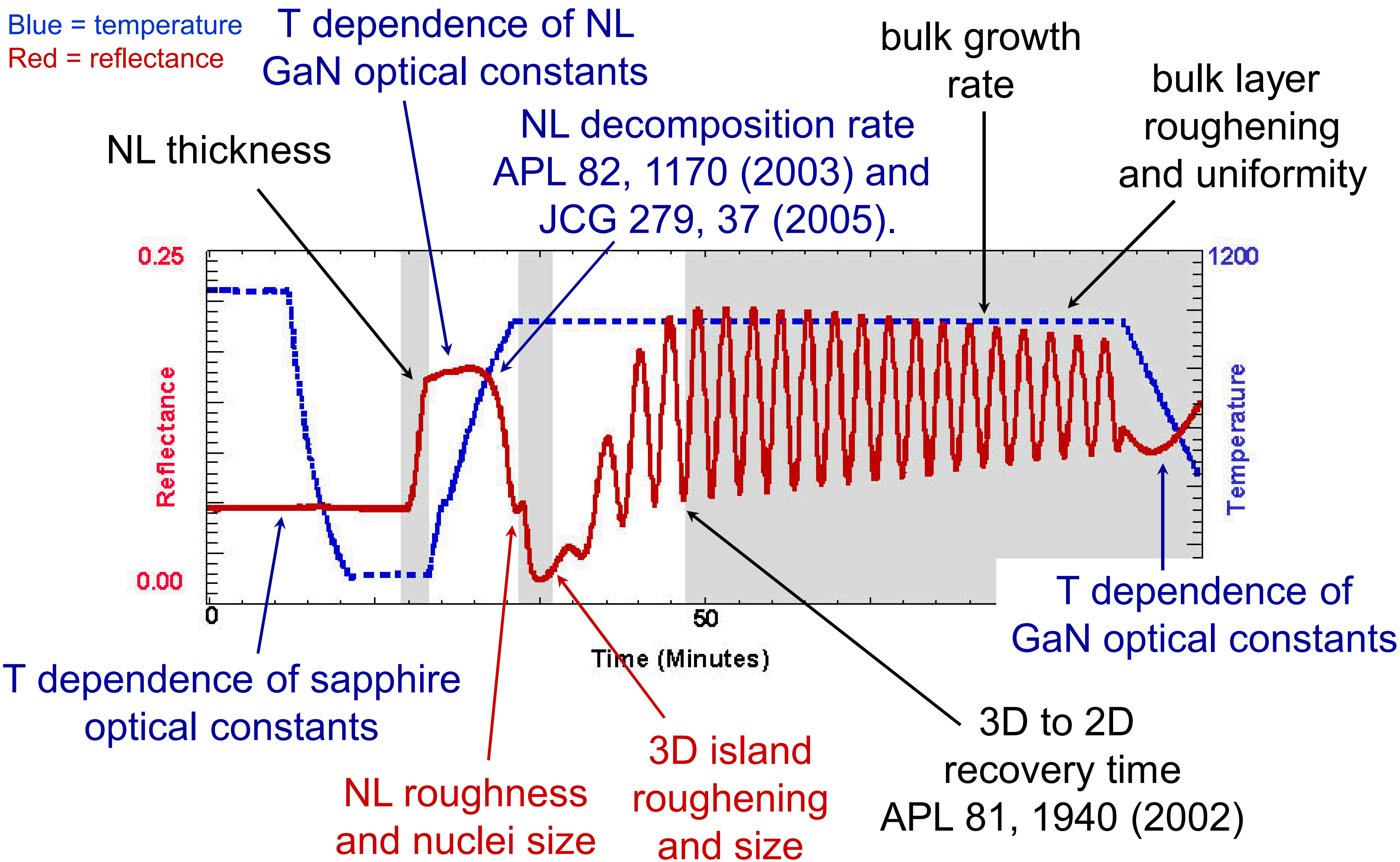
How do the wurtzite GaN nuclei form?

In-Situ Reflectance Monitoring During Growth



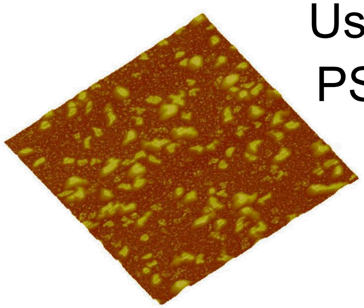
- Use light – can't use electrons because of growth pressure.
- With chopper have emissivity correcting pyrometry (400 nm – surface temperature)
- Reflectance contains data on growth rate, alloy concentrations, surface roughness, etc.
- Other systems can measure wafer curvature, stress - essential for GaN on Si.

What can be learned from optical reflectance



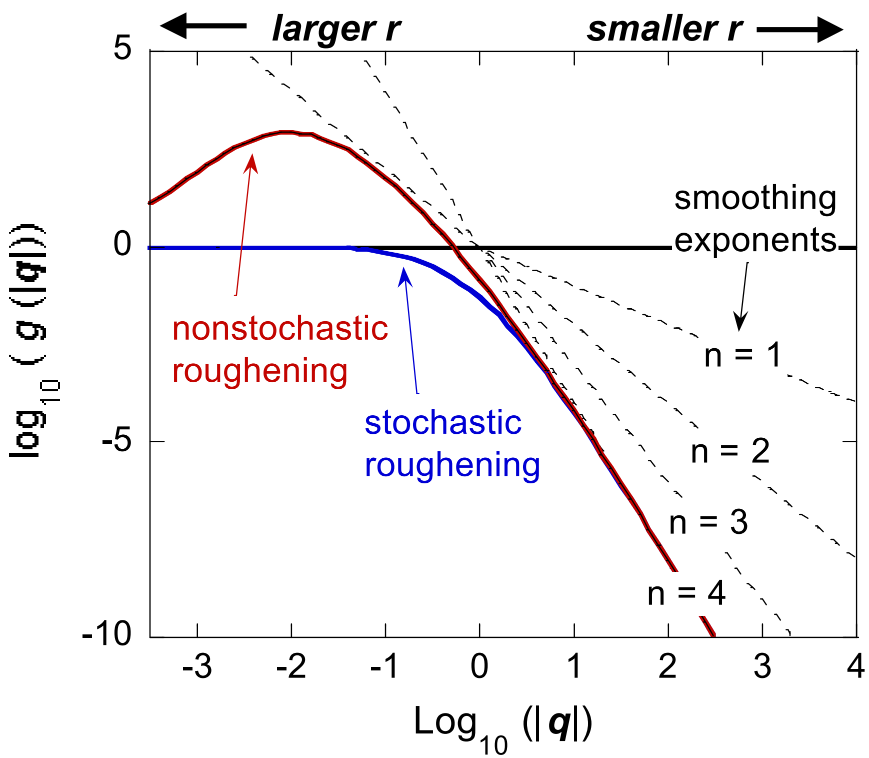
Power Spectral Density Analysis

Discussed by Tong and Williams in Ann. Rev. Phys. Chem. 45, 401 (1994).



Use AFM image to calculate the height-height correlation function = PSD
PSD or g can be calculated from h(x,y) as a function of q, *where* $q = 1/r$.

$$\sigma_{RMS} = \left(\Sigma\, g\,(\,q\,)\right)^{1/2}$$



Smoothing mechanisms

$$g(|\mathbf{q}|, t) \propto \frac{\Omega}{c_n |\mathbf{q}|^n}$$

n = 1 - plastic flow driven by surface tension

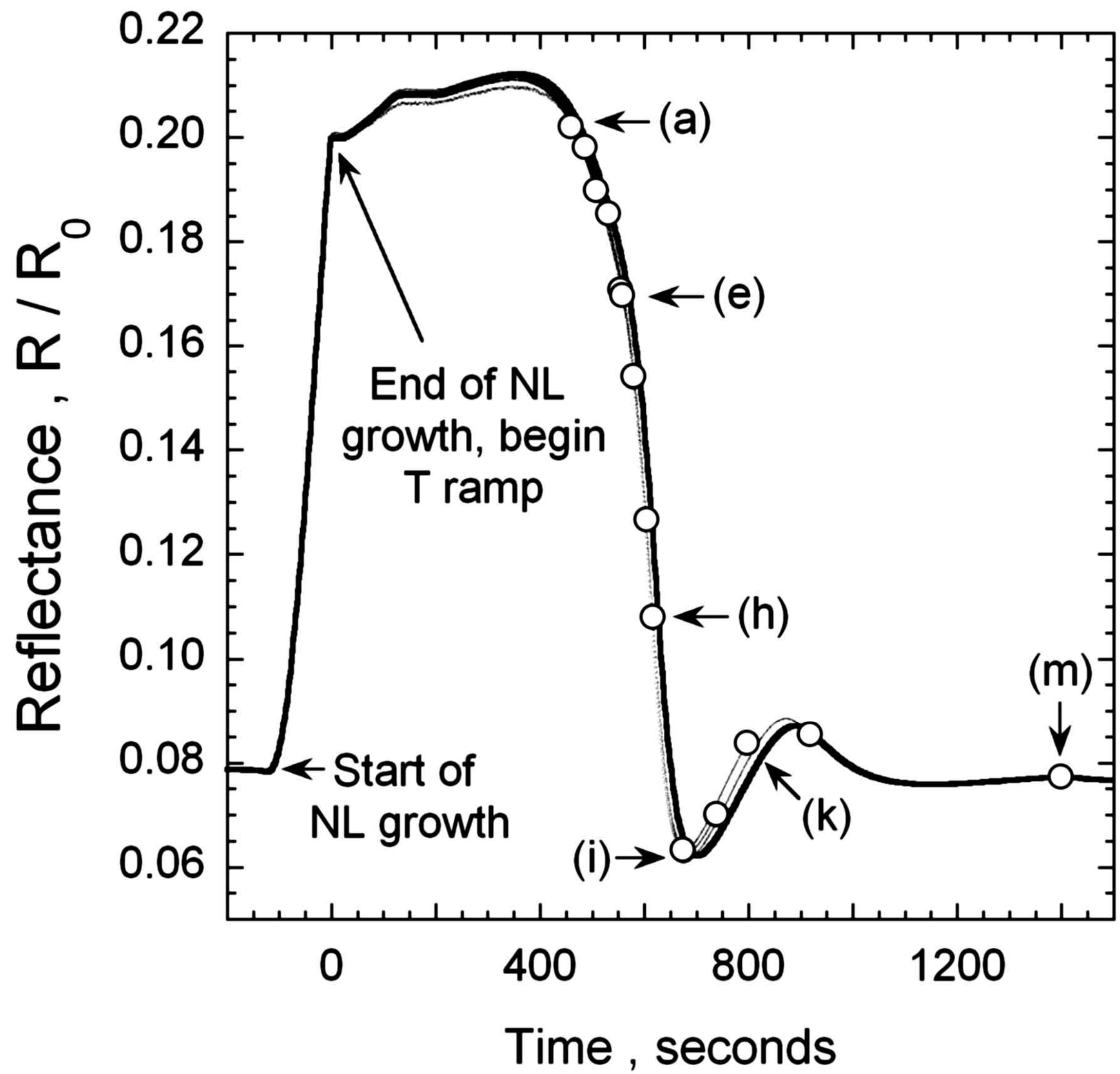
n = 2 - evaporation and recondensation

n = 3 - volume diffusion

n = 4 - surface diffusion

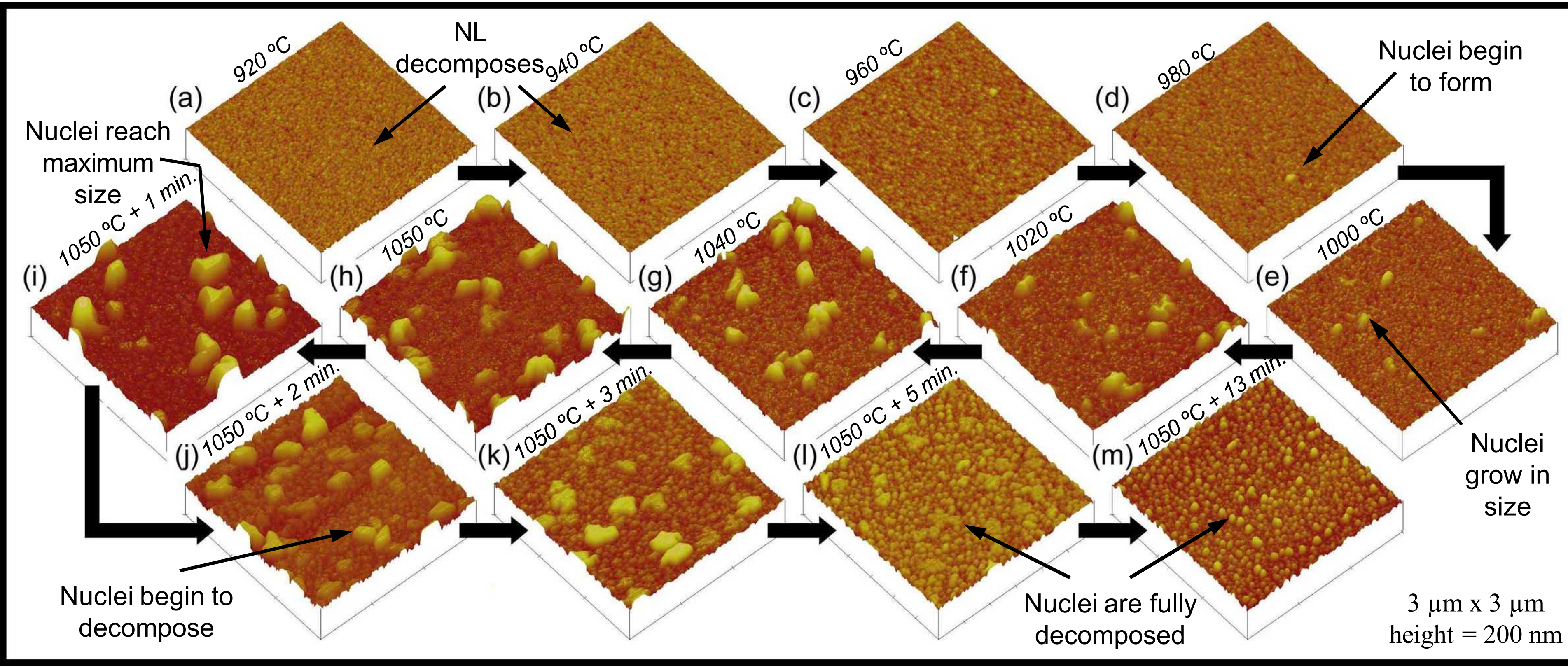
Exponents by C. Herring, J. Appl. Phys. 21, 301 (1950).
Used in Koleske - JCG 273, 86 (2004) and
JCG 391, 85 (2014)

NL growth and anneal reflectance waveform



NL evolution, wurtzite grain development

Arrows indicate increasing annealing temperature + time in H_2, N_2, and NH_3.

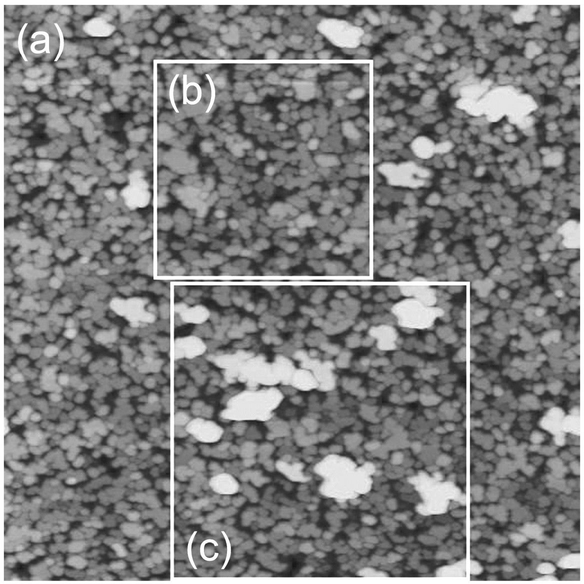


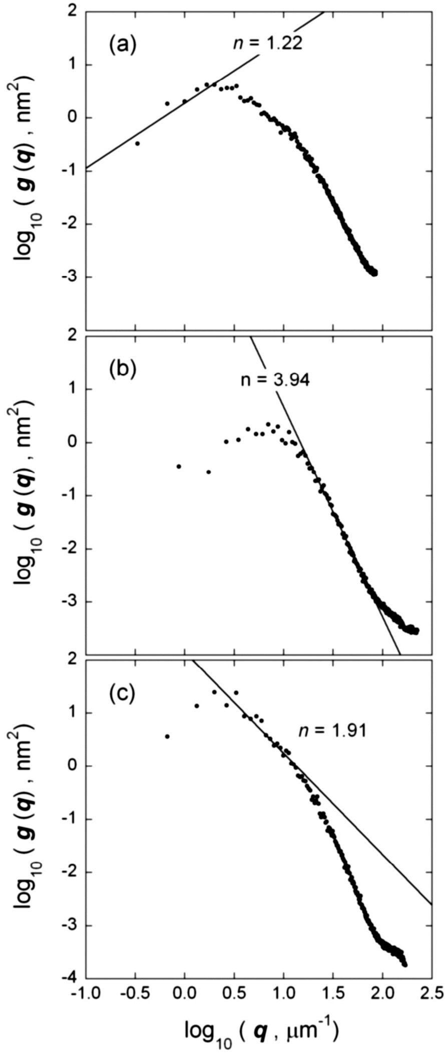
Details in Koleske et al., J. Crystal Growth 273, 86 (2004).

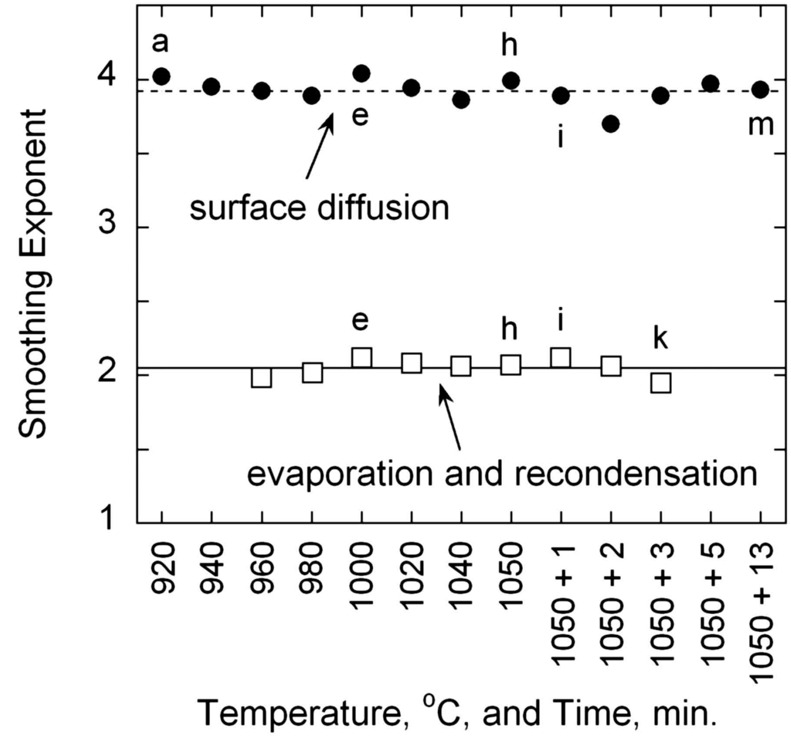
PSD analysis to determine growth mechanism

Koleske et al., J. Crystal Growth 273, 86 (2004).

Calculate height-height correlation function = $g\,(r\,)$ or $g\,(|q\,|\,)$ from $h\,(x\,,y\,)$







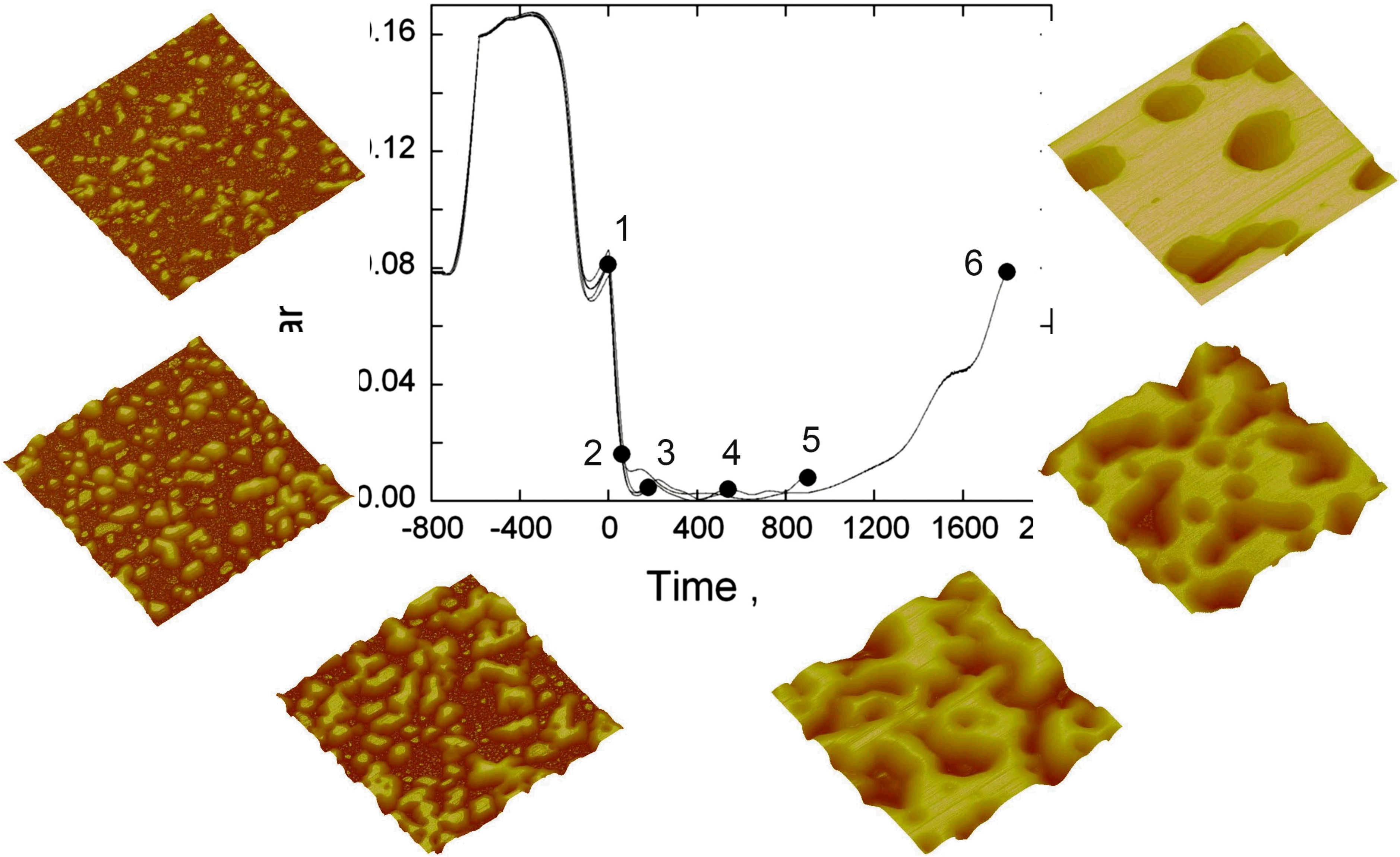
The g (r) is related to the RMS roughness σ_{RMS} by

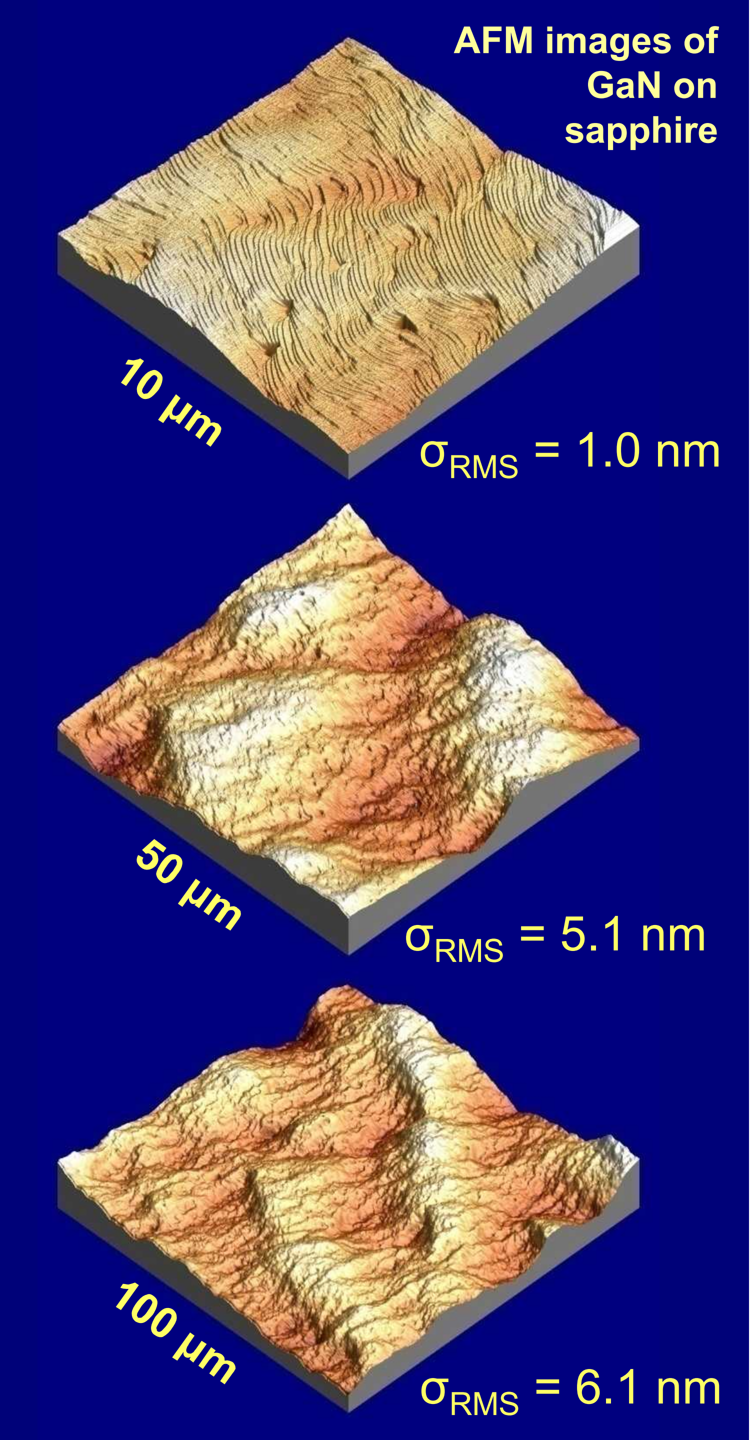
$$\sigma_{RMS} = (\Sigma\, g\,(\,r\,))^{1/2}$$

Low temperature GaN NL is smoothed by surface diffusion (n = 4).

GaN nuclei are formed by evaporation of Ga atoms which migrate through the gas phase then re-adsorb on the surface + NH_3 to form GaN (n = 2).

GaN morphology along reflectance waveform

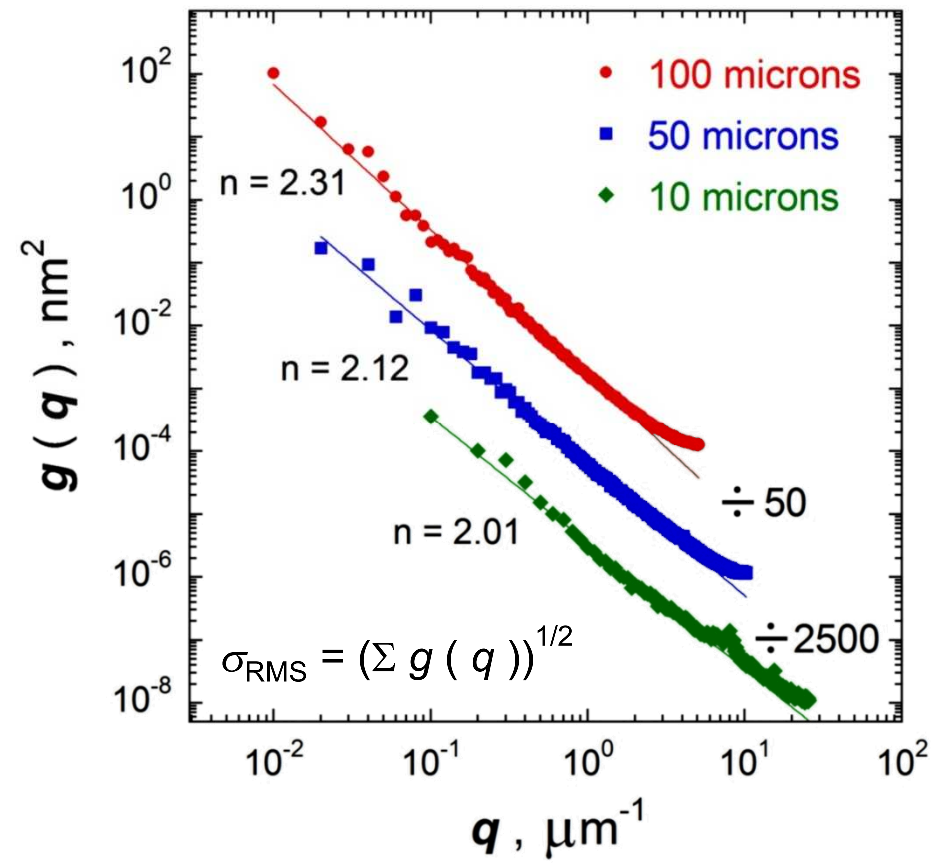




PSD shows how the roughness changes vs. distance, *d* or *q* = 1/*d*

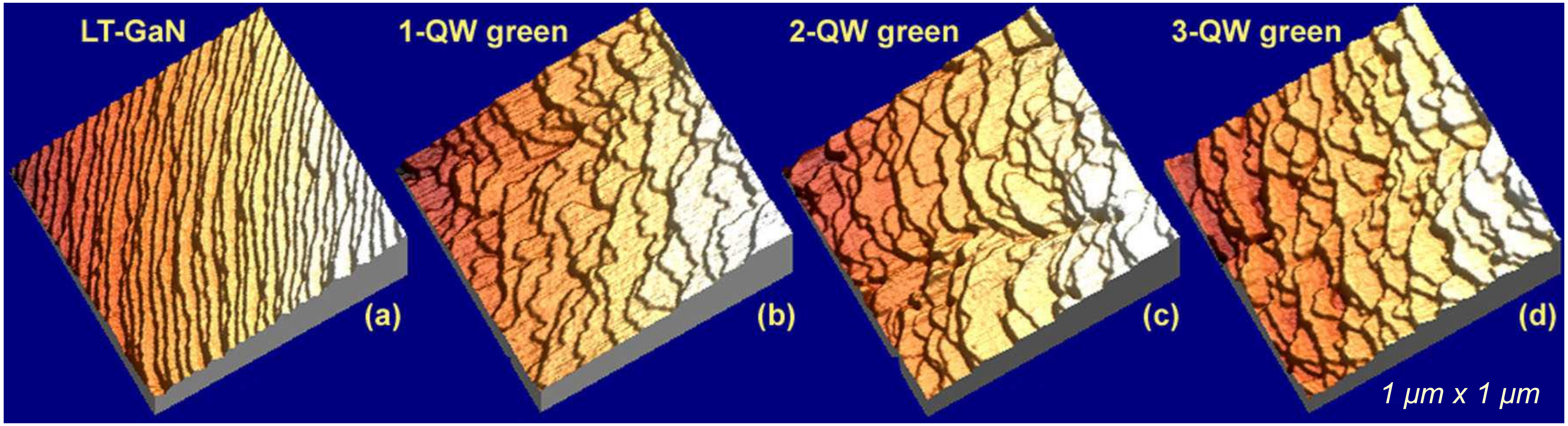
example high T GaN on sapphire

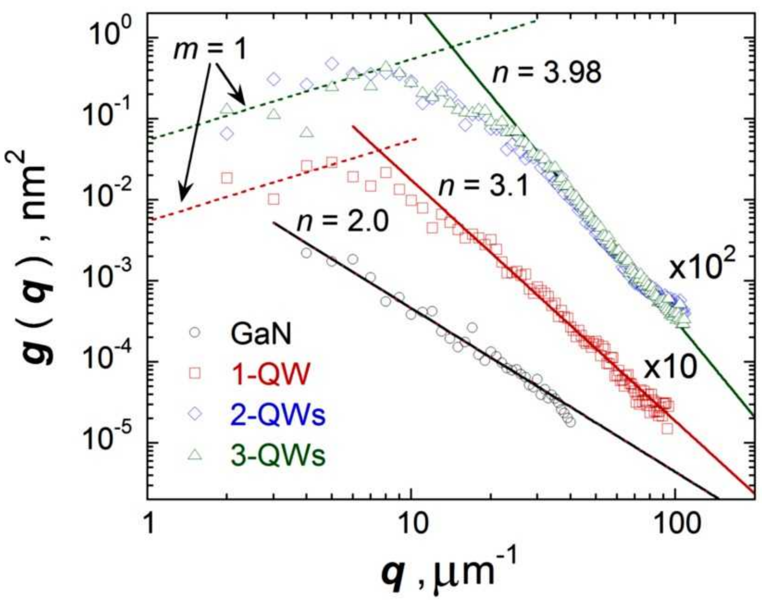
σ_{RMS} typically depends on scan size



n ~ 2 - implies the smoothing mechanism is evaporation and recondensation of Ga atoms

How InGaN MQW increase roughness





PSD analysis shows the change from evaporation/recondensation (n = 2) to surface diffusion (n = 4) as the number of QWs increases.

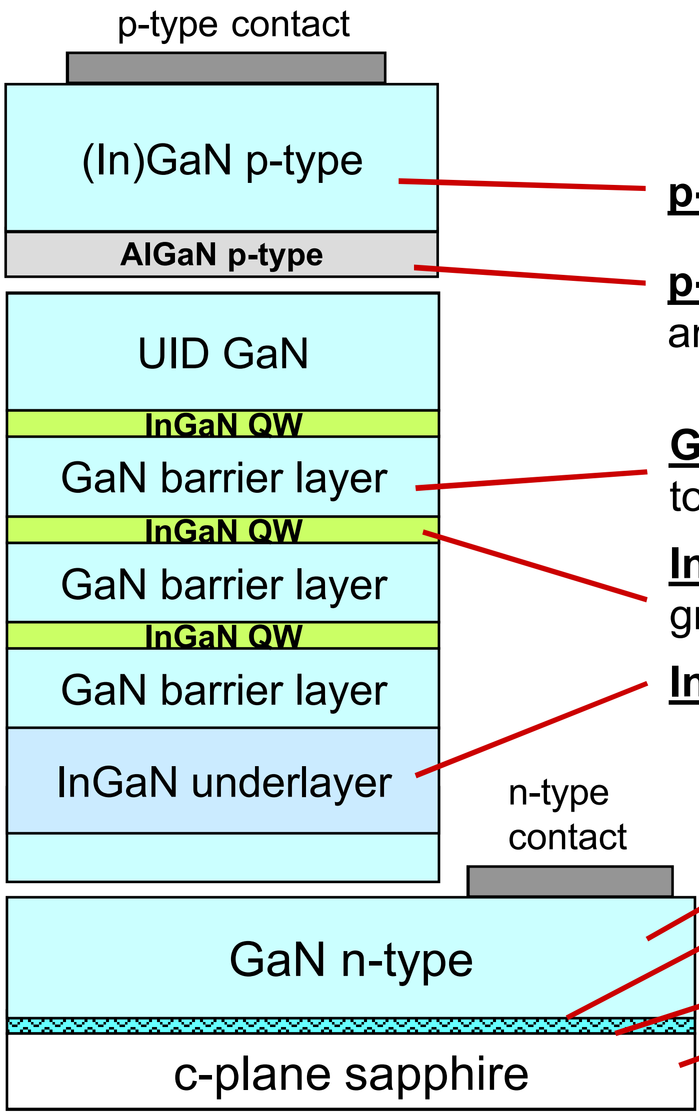
Increased roughness occurs because atoms can only migrate so far across the surface.

Might also provide a small degree of strain relaxation for the InGaN.

Tricks for brighter InGaN quantum wells (QWs)

InGaN underlayers
GaN barrier temperature

Typical LED structure and growth procedure



During growth changes in temperature, gas flows, molar flow rates, and pressure

p-type GaN grown at same temperature as electron block.

p-type AlGaN electron block grown at ~ 970 °C for blue and 930 °C for green – add H_2, 200 torr.

GaN barrier raise temperature to 800 °C then back down to QW growth temperature. (5 QWs + barriers)

InGaN QW growth at 760 °C for blue and 730 °C for green LEDs – use only N_2 and NH_3, 300 torr.

InGaN underlayer (UL) grown at 850 – 870 ºC, 300 torr.

GaN bulk on top of annealed NL.

Heat NL to 1050 °C in NH_3, H_2, and N_2.

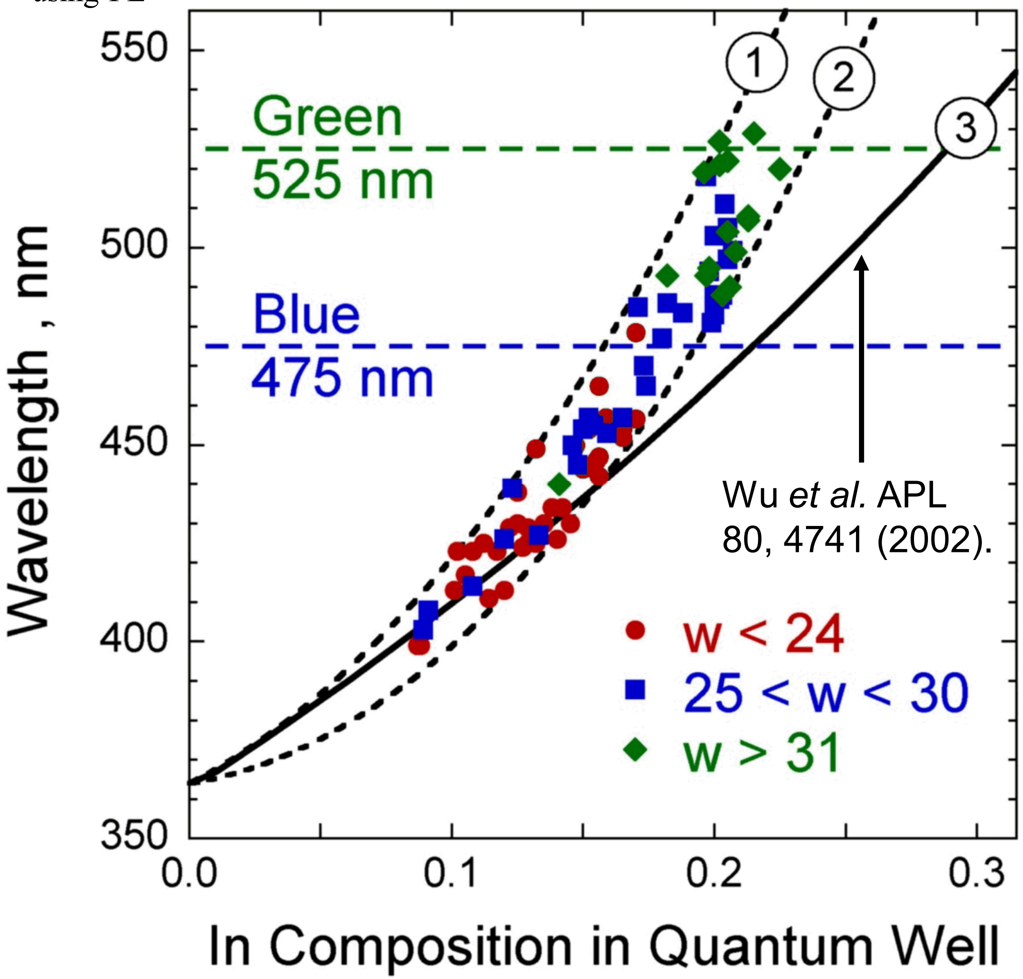
GaN nucleation layer at 530 °C, 500 torr.

Anneal sapphire in H_2 to 1050 °C.

Growth conditions are established to optimize QW intensity and hole concentrations

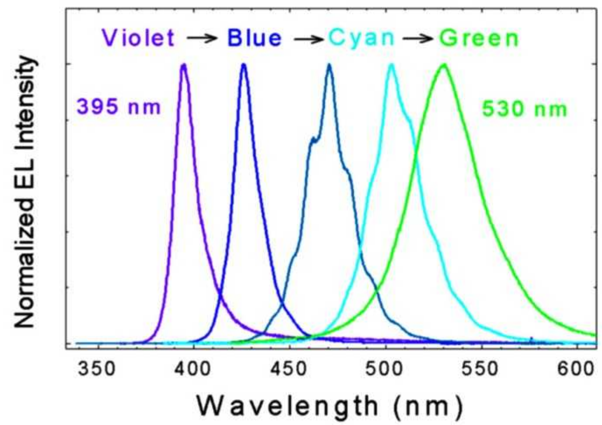
Need $In_{0.20}Ga_{0.80}N$ to achieve green wavelengths

Measured using PL

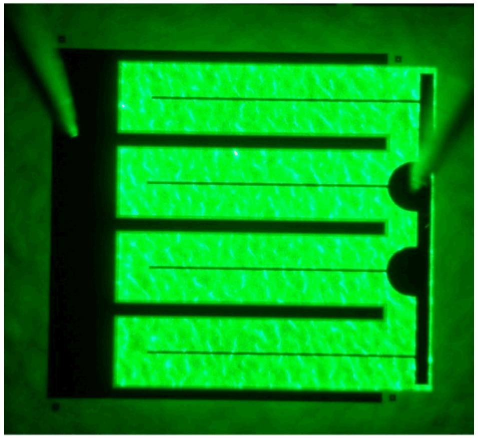


Determined from XRD

Range of PL emission wavelengths



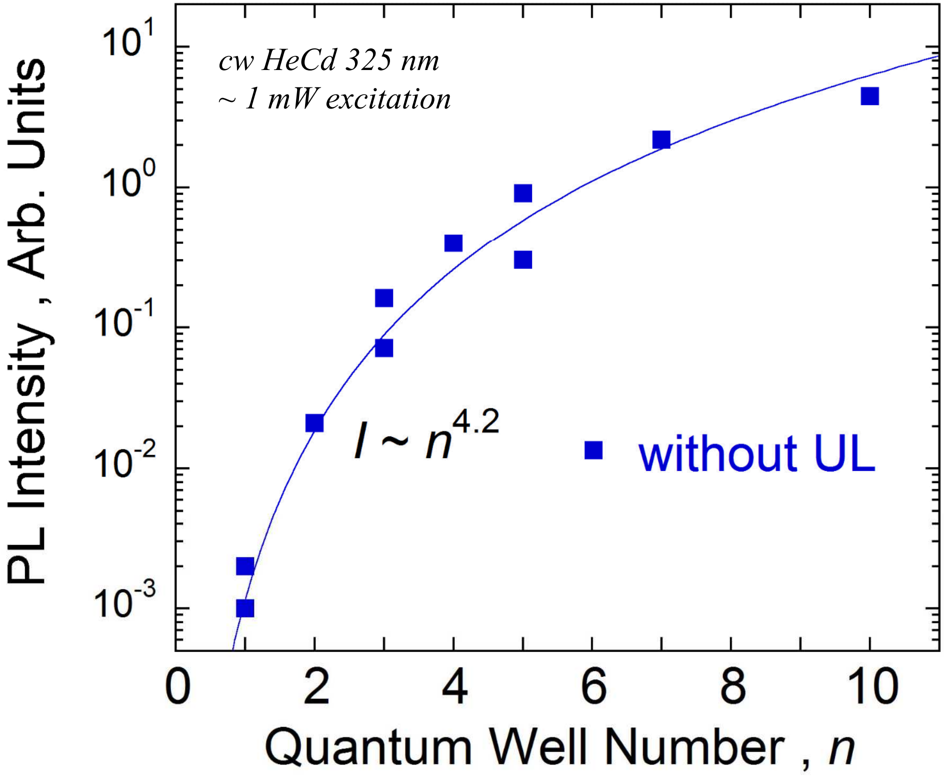
Strong polarization fields decrease the amount of indium needed to reach longer wavelengths



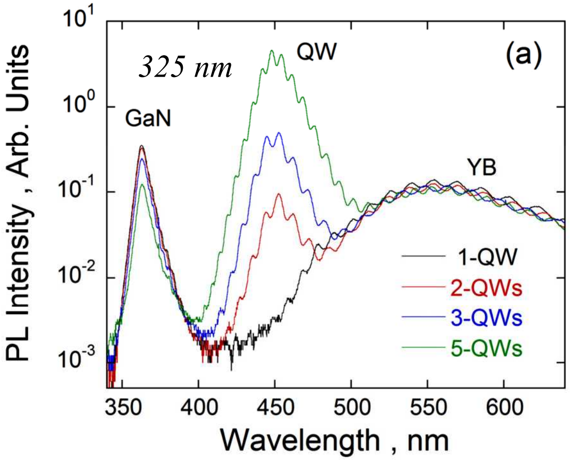
LED fabrication by Art Fischer

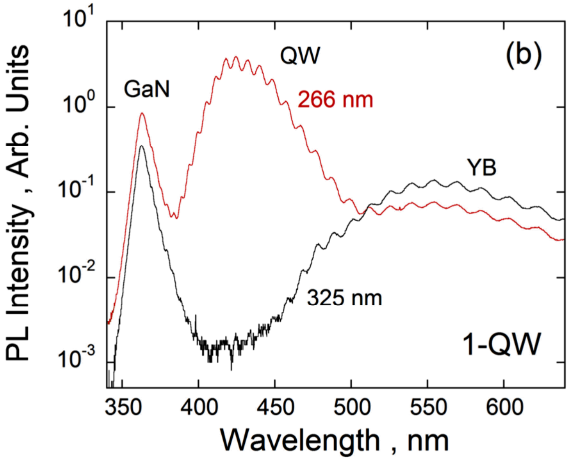
PL emission intensity versus number of QWs

Growth conditions - InGaN QWs at 770 ºC, GaN barriers at 800 ºC, P = 300 torr, λ = 440 nm.



Laser penetration depth taken into account

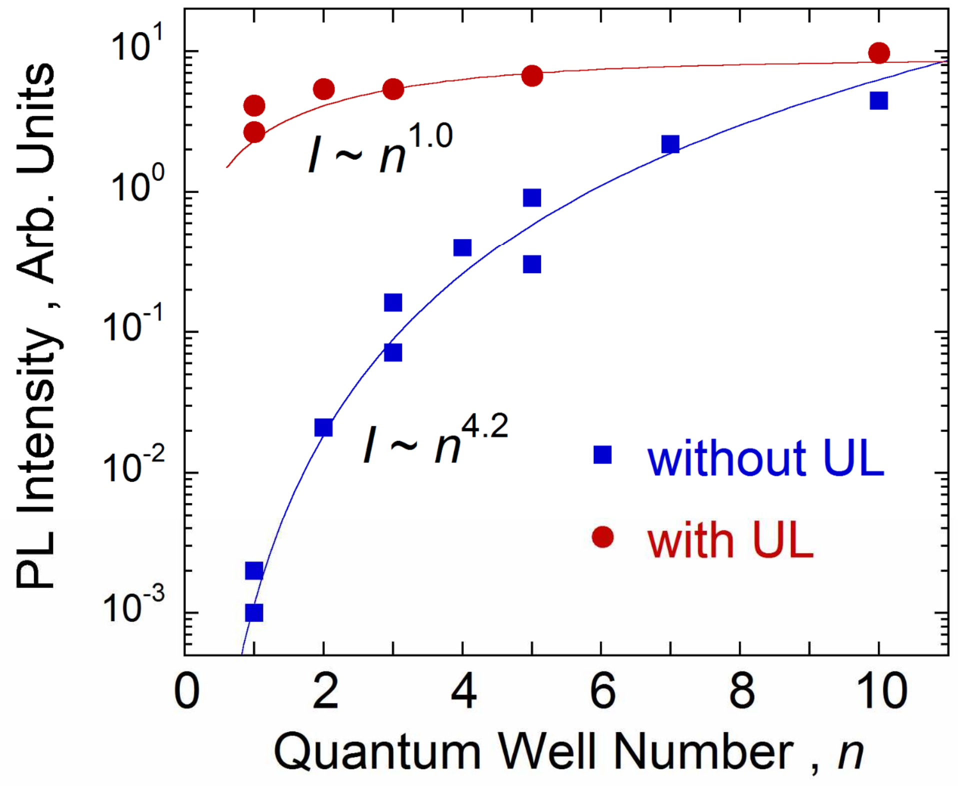




Much higher peak power achieved using the pulsed 266 nm laser.

Improved PL intensity using an InGaN underlayer

Growth conditions - InGaN underlayer (UL) at 850 ºC, P = 300 torr, 180 nm thick, 3 – 4 % indium.



Laser penetration depth taken into account

For each added QW expect the PL intensity to scale with the number of QWs.

Expect

I_{PL} ~ number of QWs or $I_{PL} \sim n^1$

Instead without UL

$I_{PL} \sim n^{4.2}$

And with UL

$I_{PL} \sim n^{1.0}$

Instead of using an UL can just increase the number of QWs.

Some groups use short period superlattices to improve emission intensity.

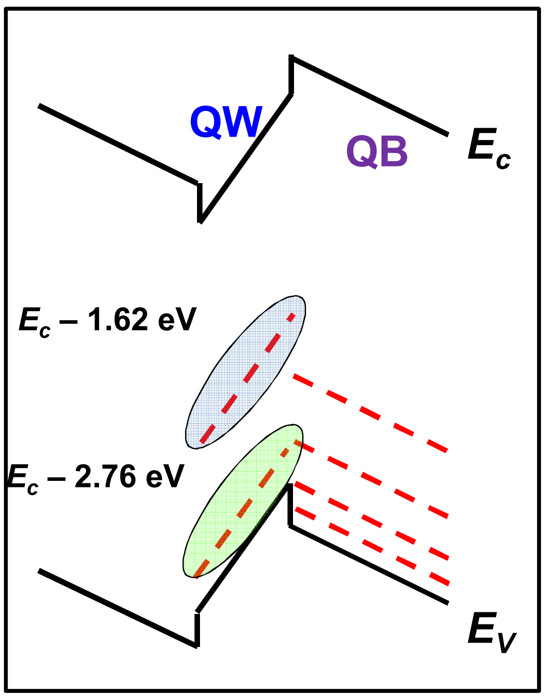
Not sure of the exact mechanism for PL improvement!

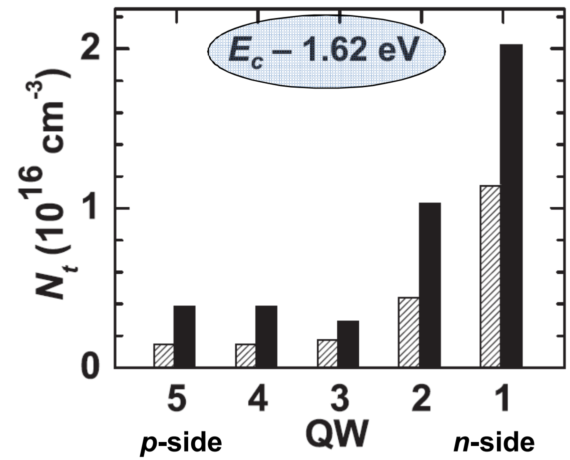
Higher defect concentrations in first QW

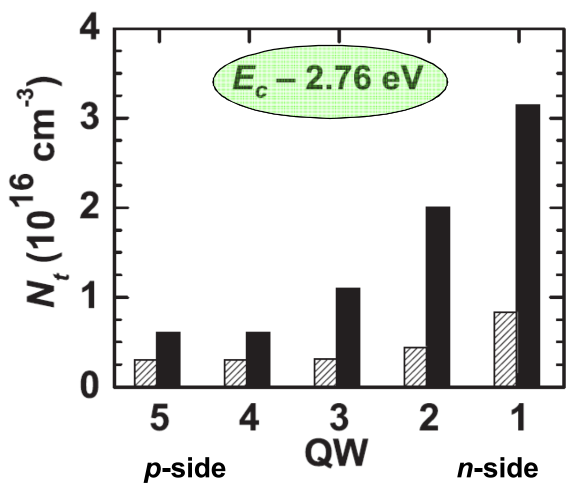
See Armstrong et al. APL 101, 162102 (2012) for more details.

Deep Level Optical Spectroscopy (DLOS) by Andy Armstrong and Tania Henry for 440 nm LEDs grown on two different dislocation density GaN templates.

TDD = 3 × 10^9 cm^{-2} (solid black bars)
TDD = 5 × 10^8 cm^{-2} (hatched bars)







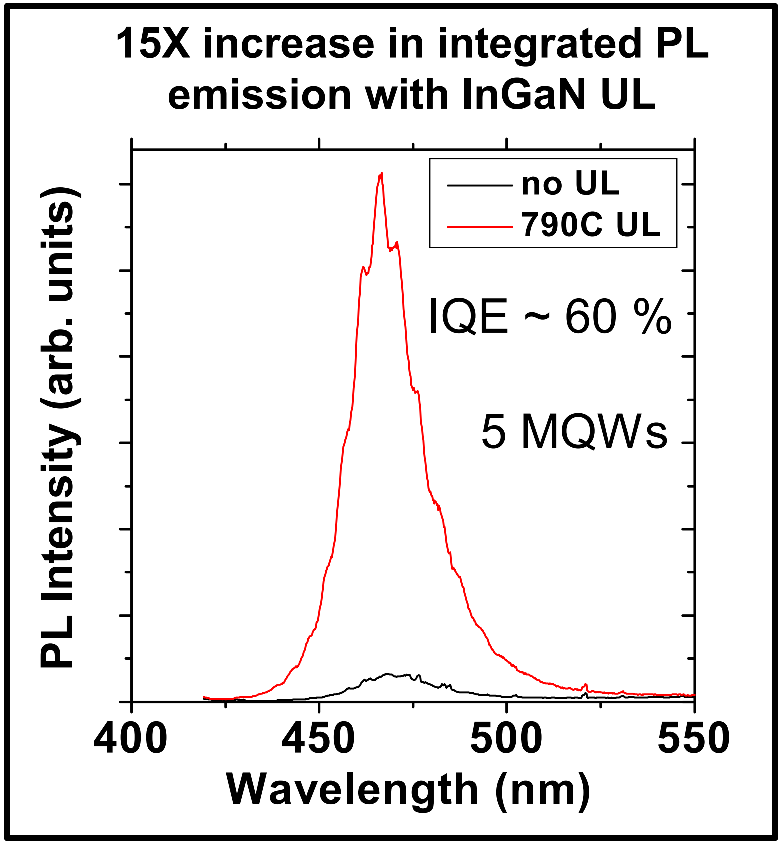
InGaN QW defect level

Potential non-radiative recombination center (NCR)
More in 1st than 5th QW for both defect levels shown.

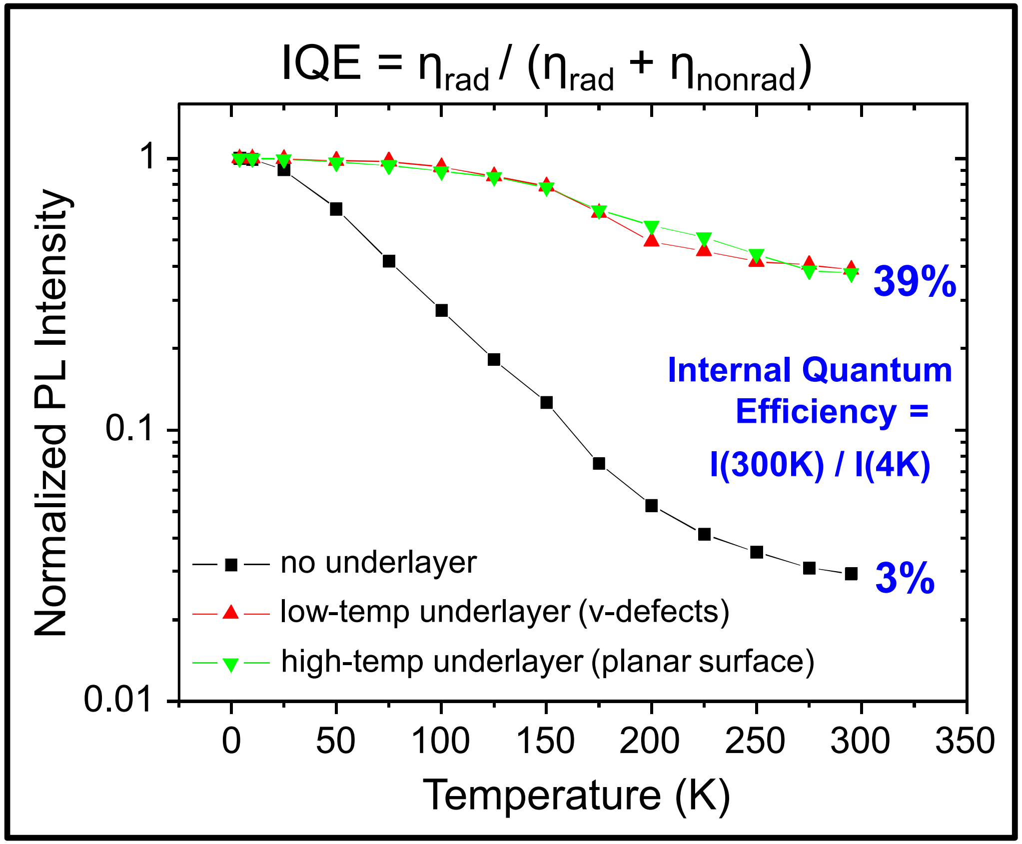
Point defects in the GaN barrier can also be NCRs. GaN barriers also have unique defect levels due to low temperature growth.

InGaN underlayers increase IQE of MQWs

UL especially help emission of single QWs



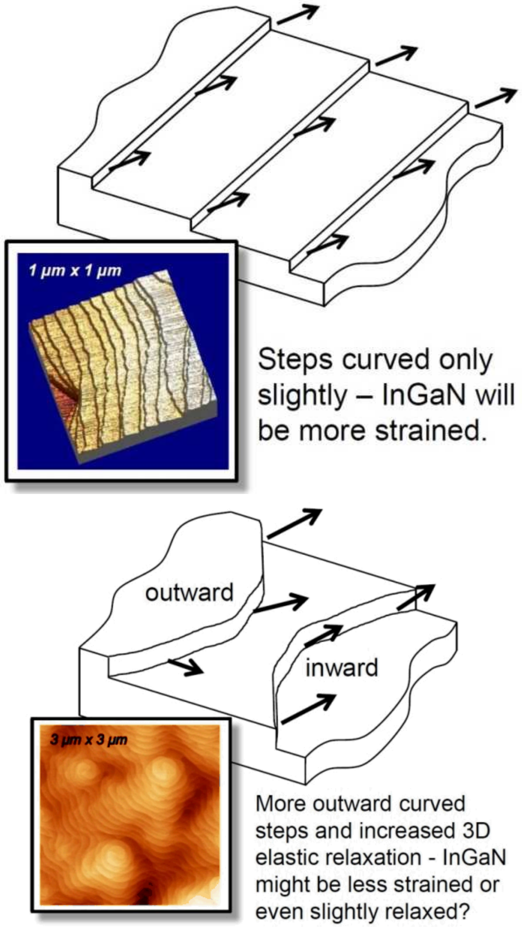
Temperature dependent PL studies by Mary Crawford



Underlayers enhance efficiency compared to same MQW with no underlayer.

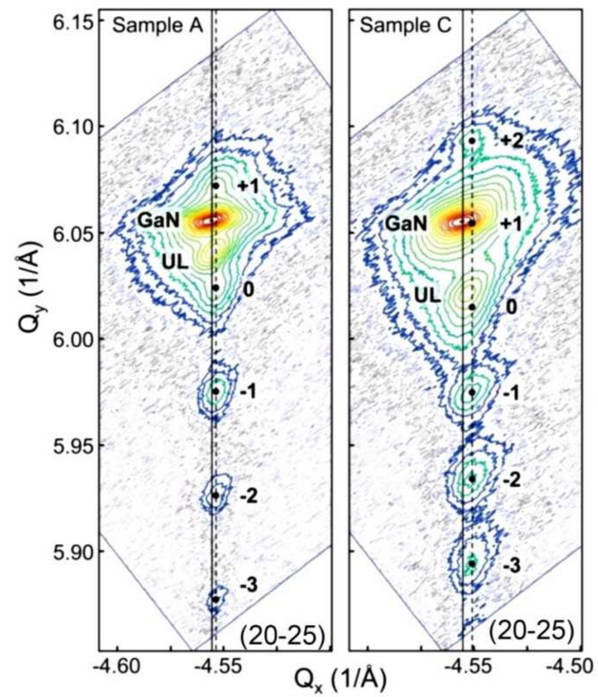
MQWs on thick InGaN provide some strain relief

Have achieved IQE of 90 % in blue QWs in APL 101, 241104 (2012).



S.R. Lee et al. JCG 355 (2012) 63.

Strain relaxation is observed in k-space maps for MQWs on ULs.

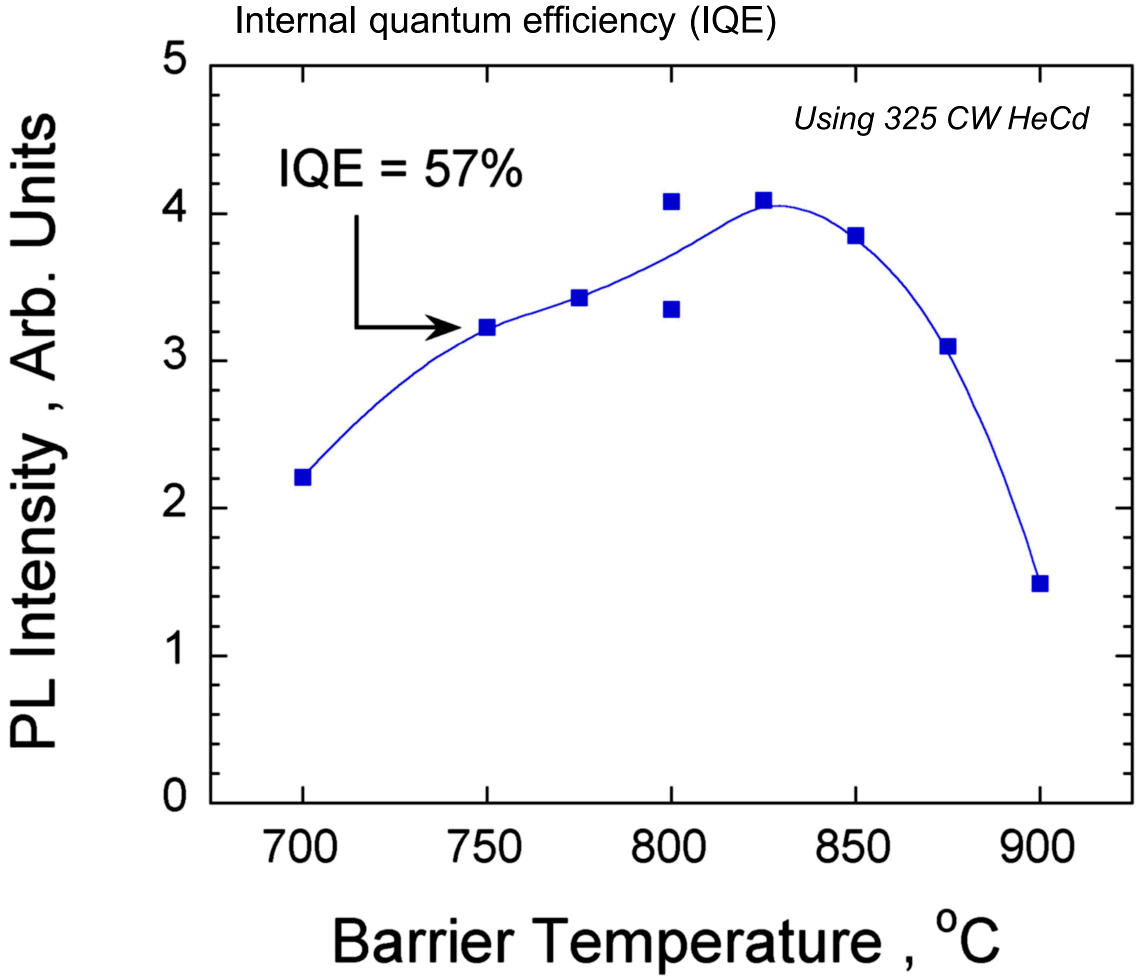


Sample A - InGaN UL and a 5-period $In_{0.17}Ga_{0.83}N/GaN$ MQW – 2.8% per QW.

Sample C - InGaN UL and a 10-period $In_{0.20}Ga_{0.80}N/GaN$ MQW – 4.2% per QW.

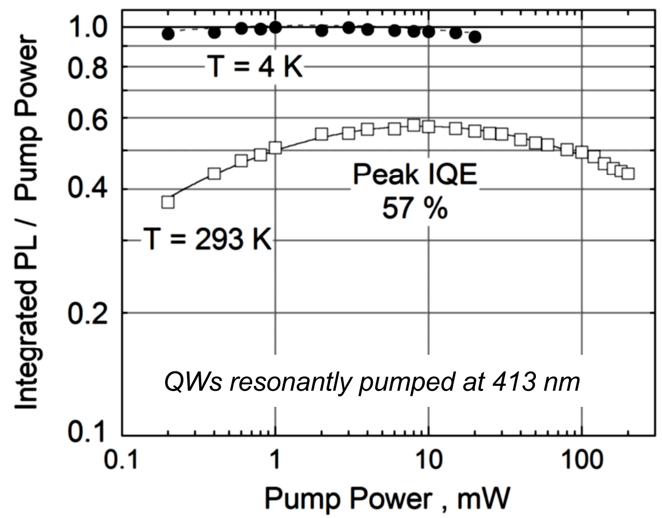
outward curving steps > inward curving steps

Influence of GaN barrier temperature on PL



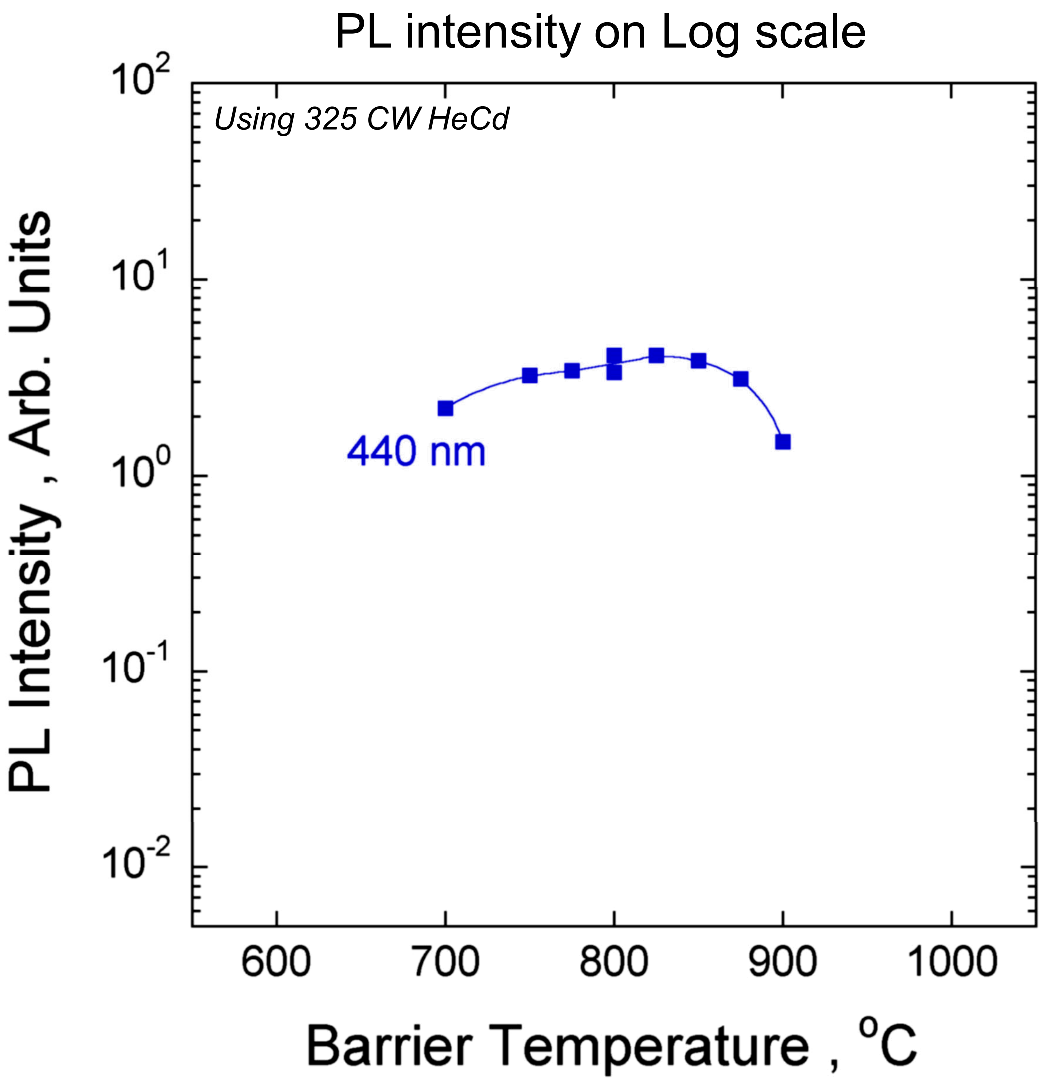
Growth conditions – 5 MQW structures grown on InGaN UL at 770 ºC using different GaN barrier growth temperatures. Verified with XRD.

IQE = I_{PL} at T=300K/ I_{PL} at T = 4K

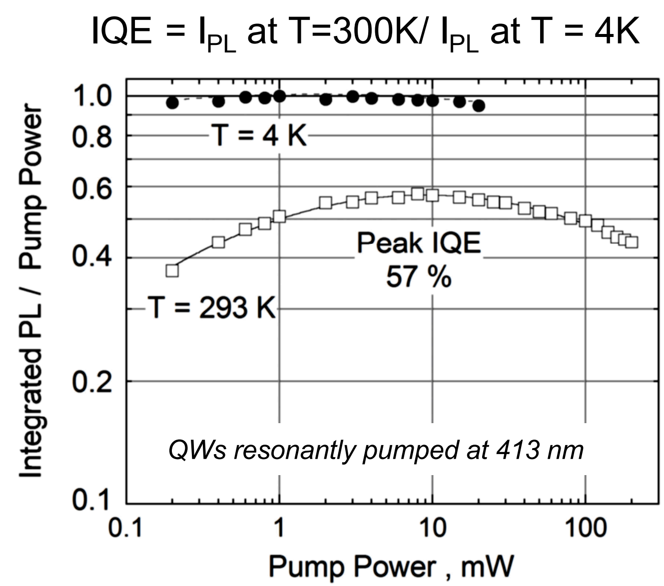


PL intensity changes by a factor of 2.5x and is fairly constant from 750 to 875 °C

Influence of GaN barrier temperature on PL



Growth conditions – 5 MQW structures grown on InGaN UL at 770 ºC using different GaN barrier growth temperatures. Verified with XRD.



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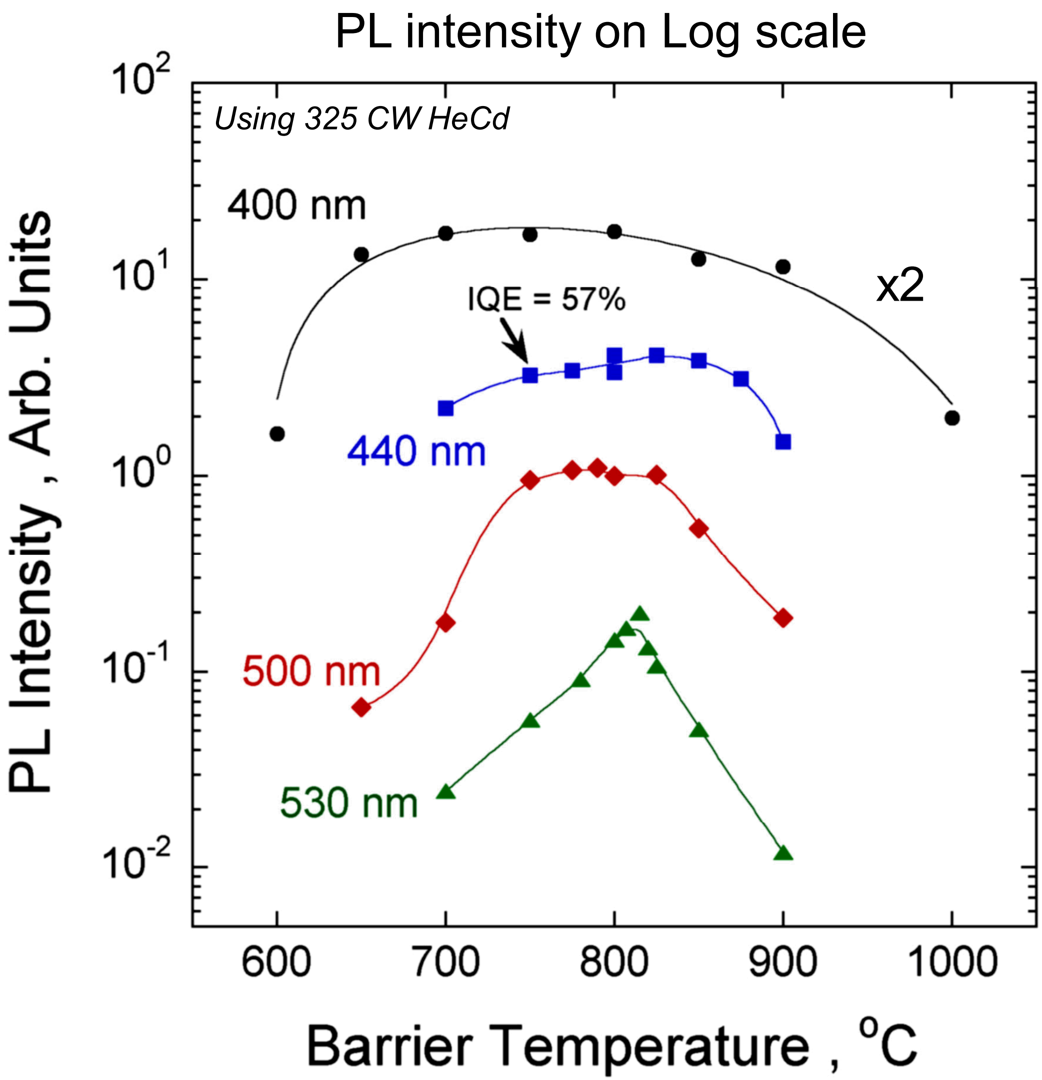
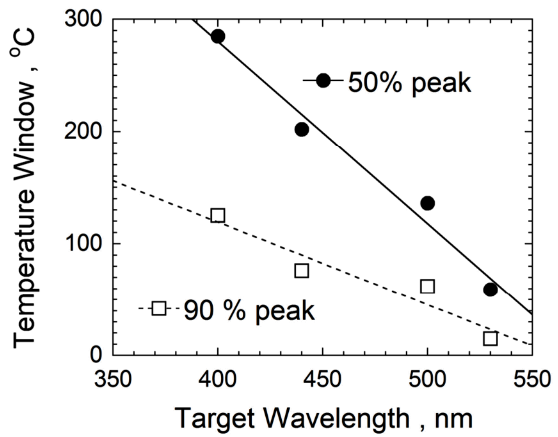
Influence of GaN barrier temperature on PL



Growth conditions

QW growth temperature varied along with the GaN barrier temperature.

T_{QW} = 790 °C for 400 nm, 2 min.
T_{QW} = 770 °C for 440 nm, 2 min.
T_{QW} = 750 °C for 500 nm, 2.1 min.
T_{QW} = 740 °C for 530 nm, 2.2 min.

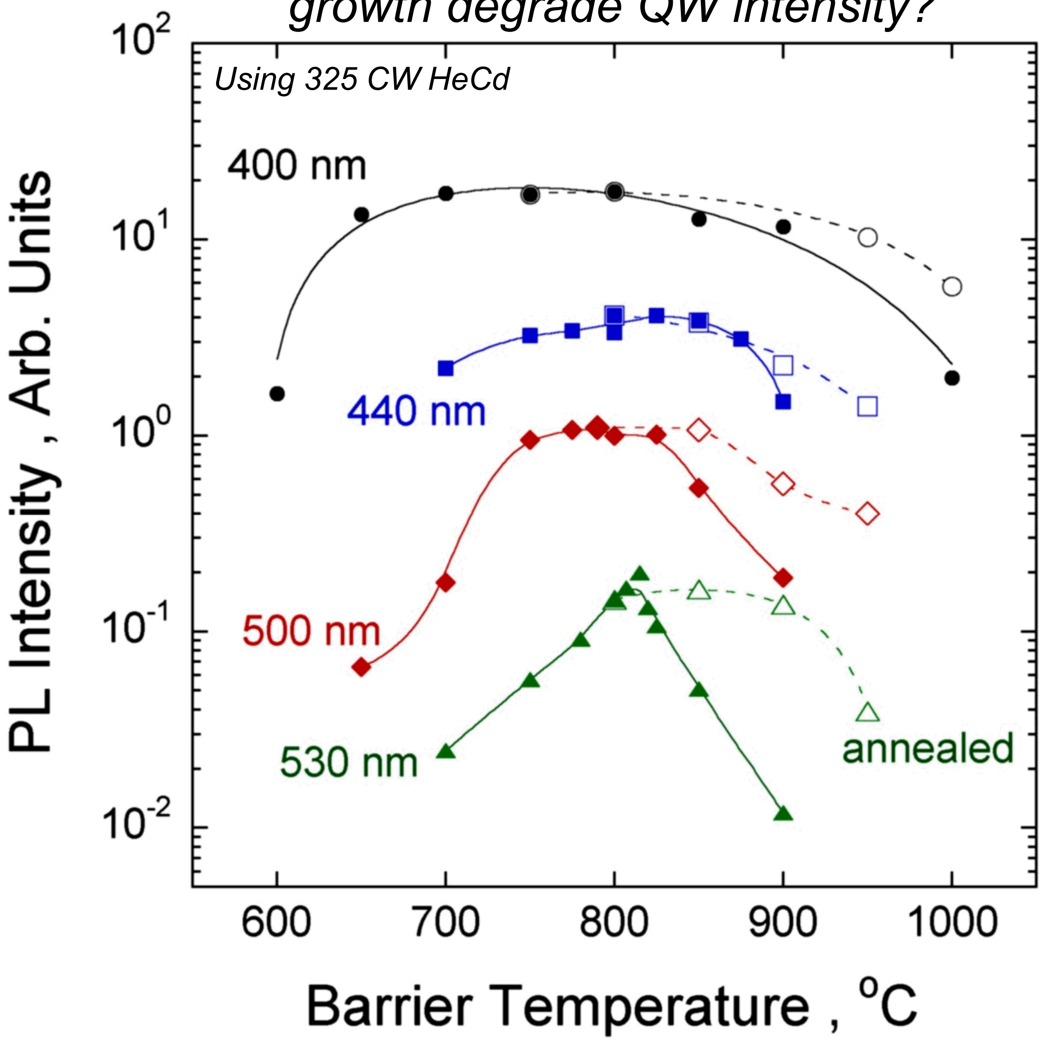


Larger growth temperature window for shorter wavelength MQWs.

Barrier growth conditions not as critical at shorter wavelengths?

Influence of GaN barrier temperature on PL

Does high temperature GaN barrier growth degrade QW intensity?



<u>InGaN decomposes as the temperature increases</u>

(Thaler et al. JCG 311, 2933 (2010))

For bulk InGaN films, the PL intensity decreased prior to any measurable decrease in XRD peak intensities as the annealing temperature increased. Annealing generates NRCs.

Quartered best QW wafers and annealed them for 30 additional minutes at temperatures higher than the initial GaN barrier growth conditions.

Observe some decrease in the PL intensity but does not account for entire decrease in PL intensity.

Surprisingly observe least degradation for 530 nm QWs for T ≤ 900 ºC.

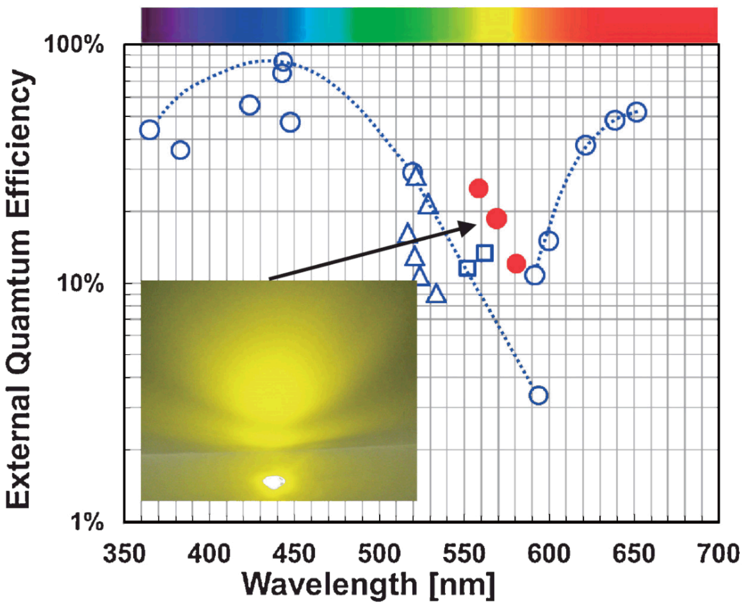
Advanced Stuff

AlGaN capping InGaN quantum wells.
Use hydrogen to etch InGaN.

AlGaN capping of InGaN QWs

Work from Toshiba Corporation Research and Development Center

Saito et al. APEX 6, 111004 (2013)

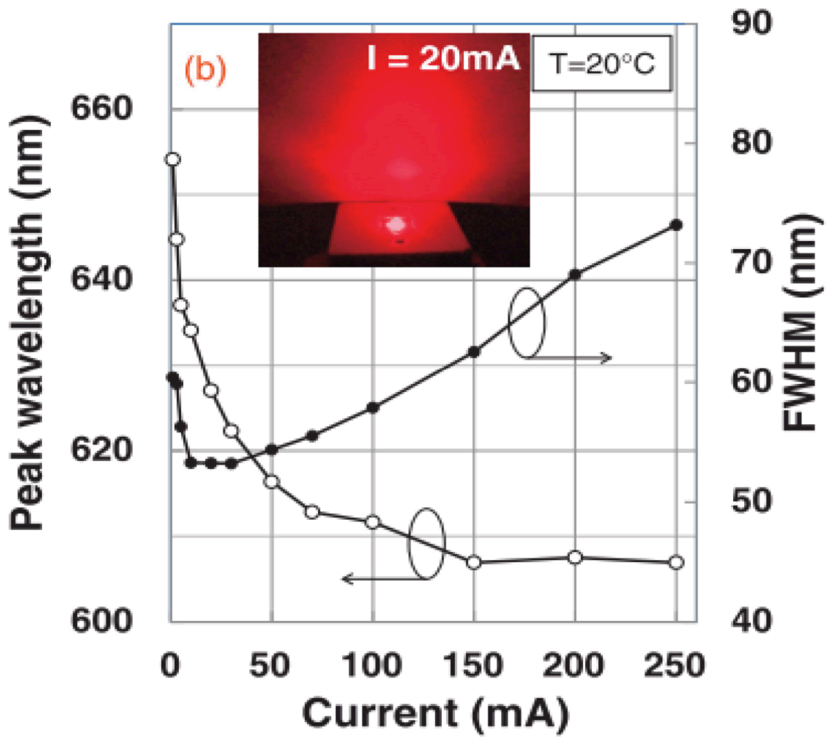


11.0 mW and 24.7% EQE for a 559 nm green-yellow LED and

4.7 mW and 13.3% for a 576nm yellow LED with the injection current of 20mA were achieved.

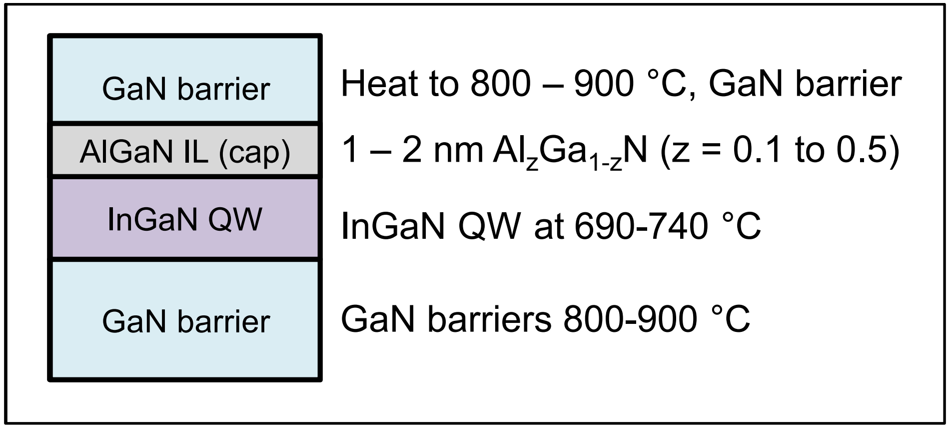
Hwang et al. APEX 7, 071003 (2014)

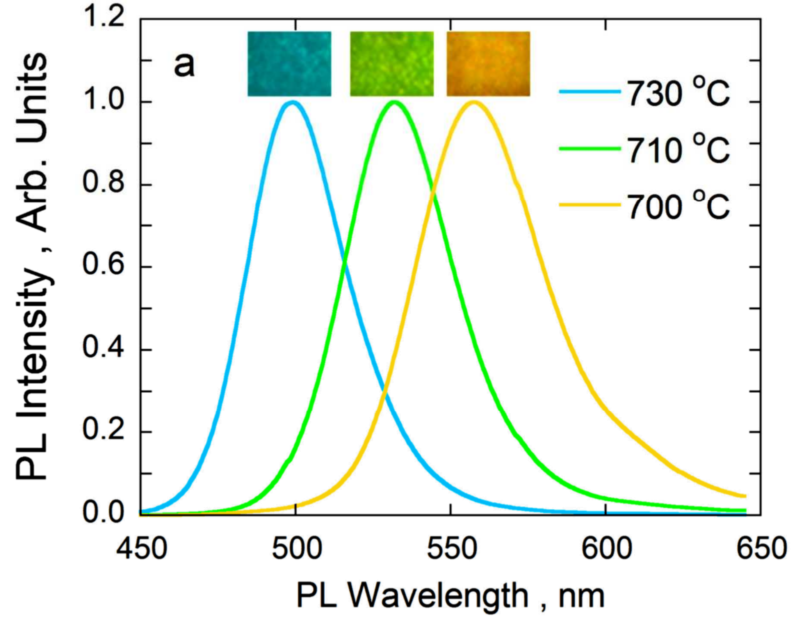
1.1 mW and 2.9% EQE at 629 nm for an injection current of 20 mA

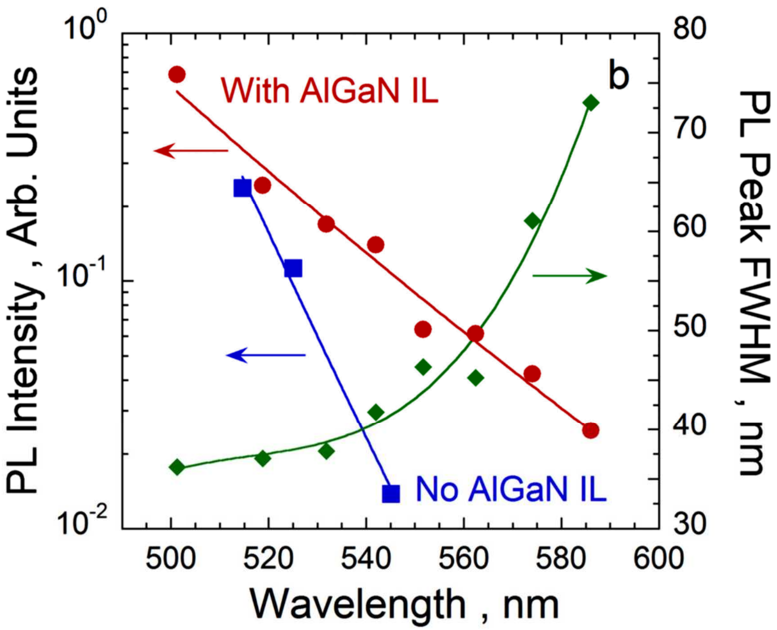


Longer wavelength QWs with AlGaN cap

Manuscript submitted to Journal of Crystal Growth

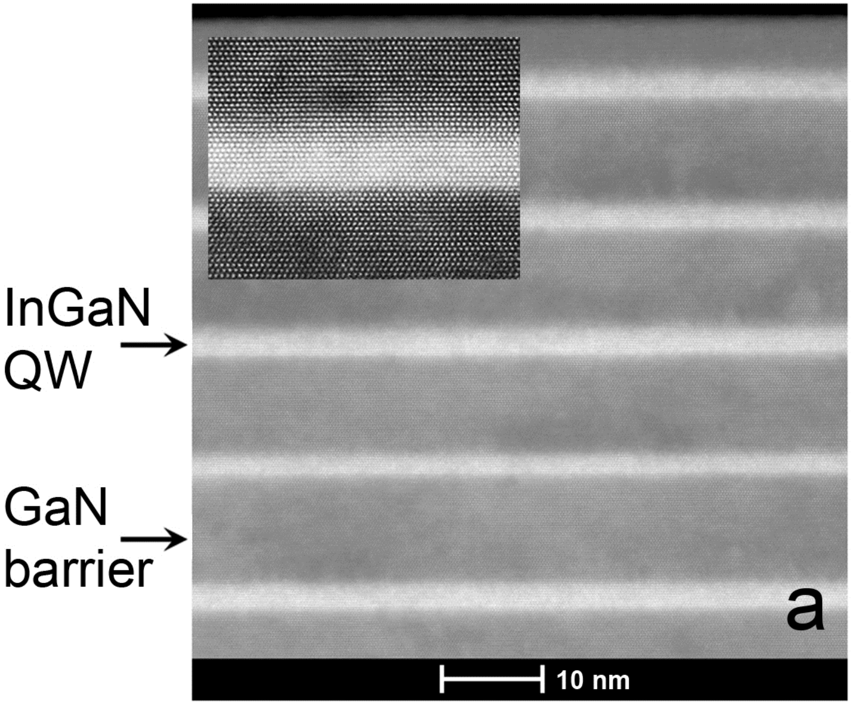




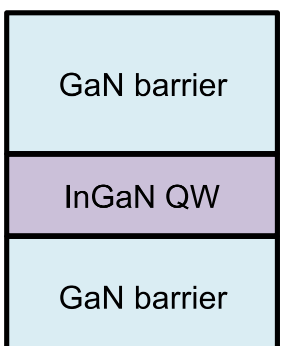


- QW growth temperature can be lowered well below metal precipitation temperature ~ 730 °C.
- AlGaN capped QWs have ~10x higher PL intensity compared to uncapped QWs for wavelengths greater than 540 nm.

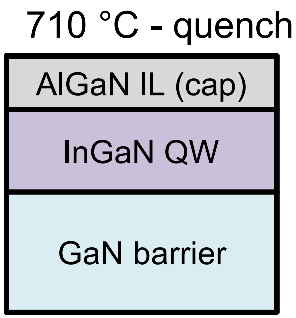
XTEM images with and without AlGaN cap

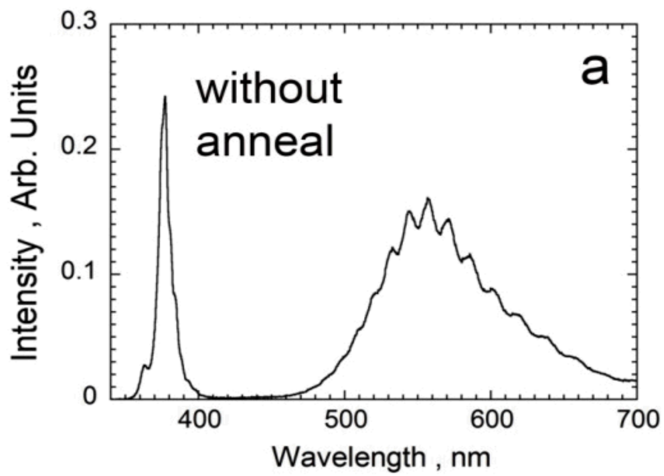


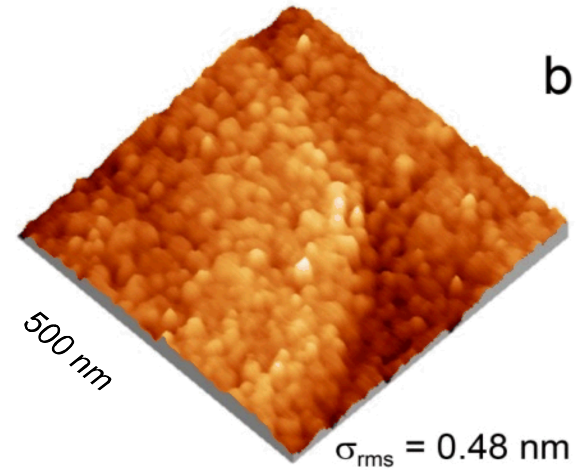
Indium protruding into GaN barriers



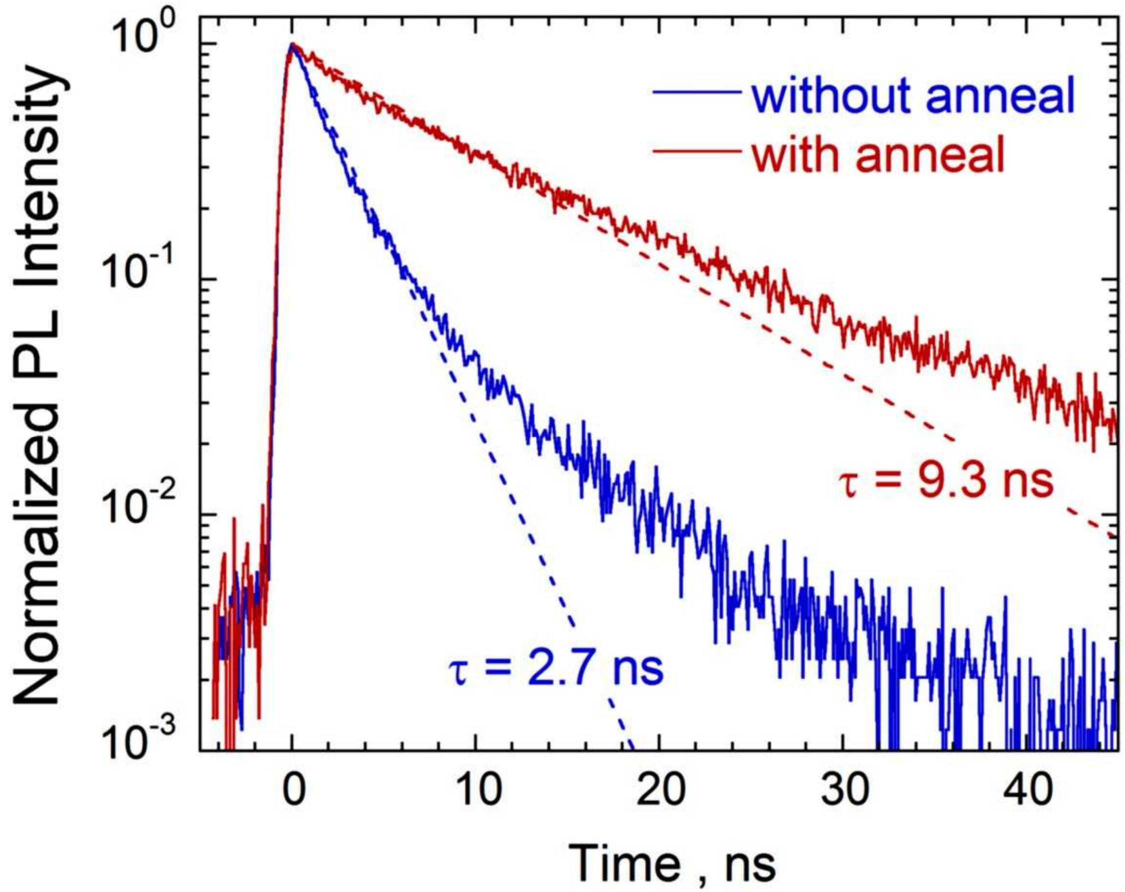
When does the PL intensity improve?





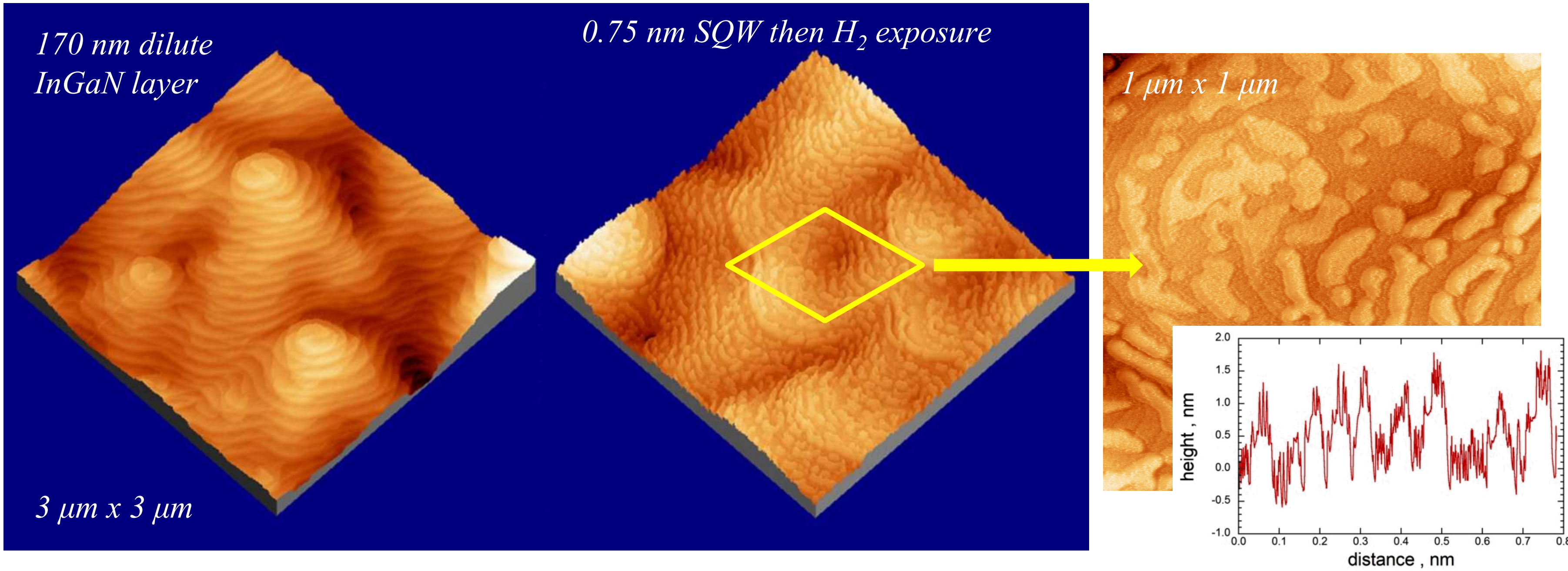


Time resolved photoluminescence



Annealing decreases non-radiative recombination centers which increases PL lifetime.

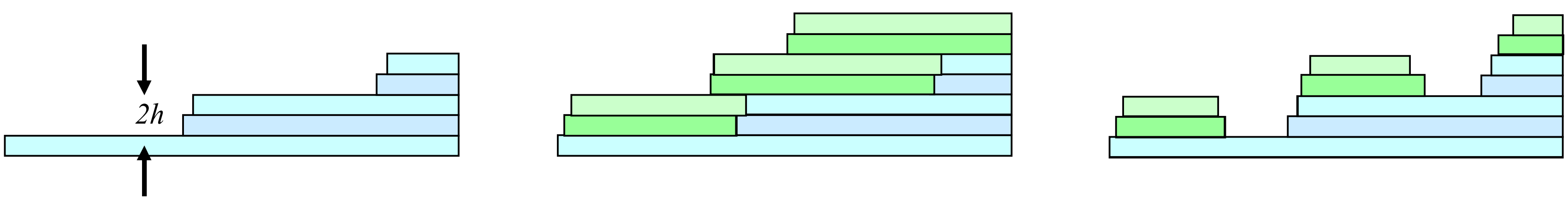
Hydrogen: The magic InGaN eraser



Dilute InGaN layer
(170 nm thick)

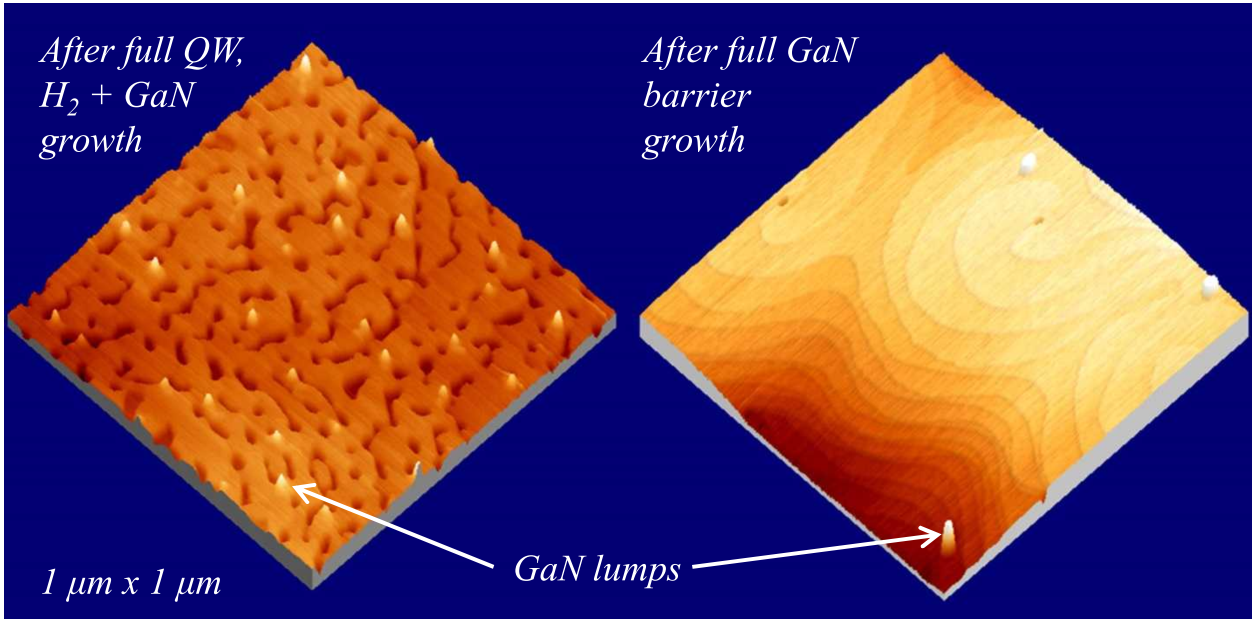
Grow $In_{0.14}Ga_{0.84}N$ QW
(about ¼ thickness of typical QW)

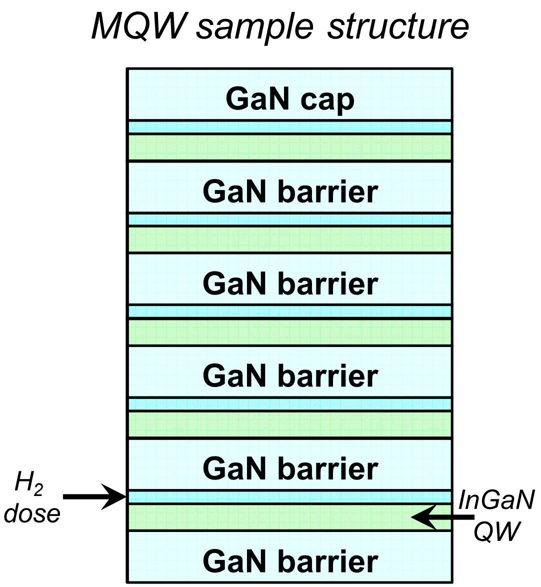
Add 2 SLM H_2 for ¼ min.
(discontinuous QW etching)



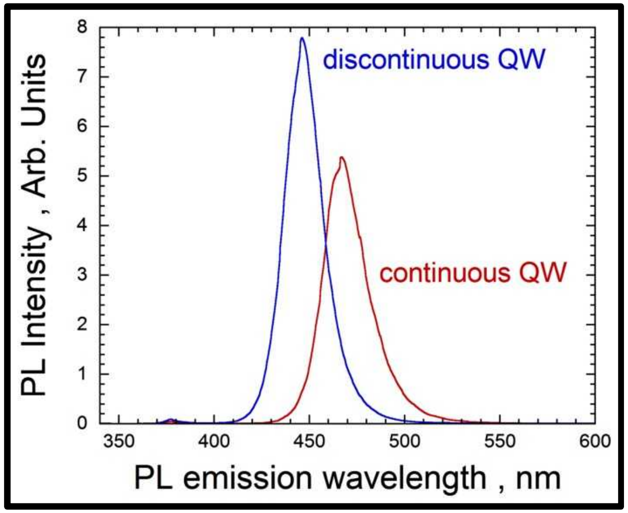
InGaN islands preferentially line outer step edge – lower strain region

Hydrogen can produce discontinuous QWs





- Holes in InGaN are the entire QW thickness.
- Ga atoms left over from the InGaN etching result in GaN lumps.
- PL emission intensity improved in discontinuous QWs

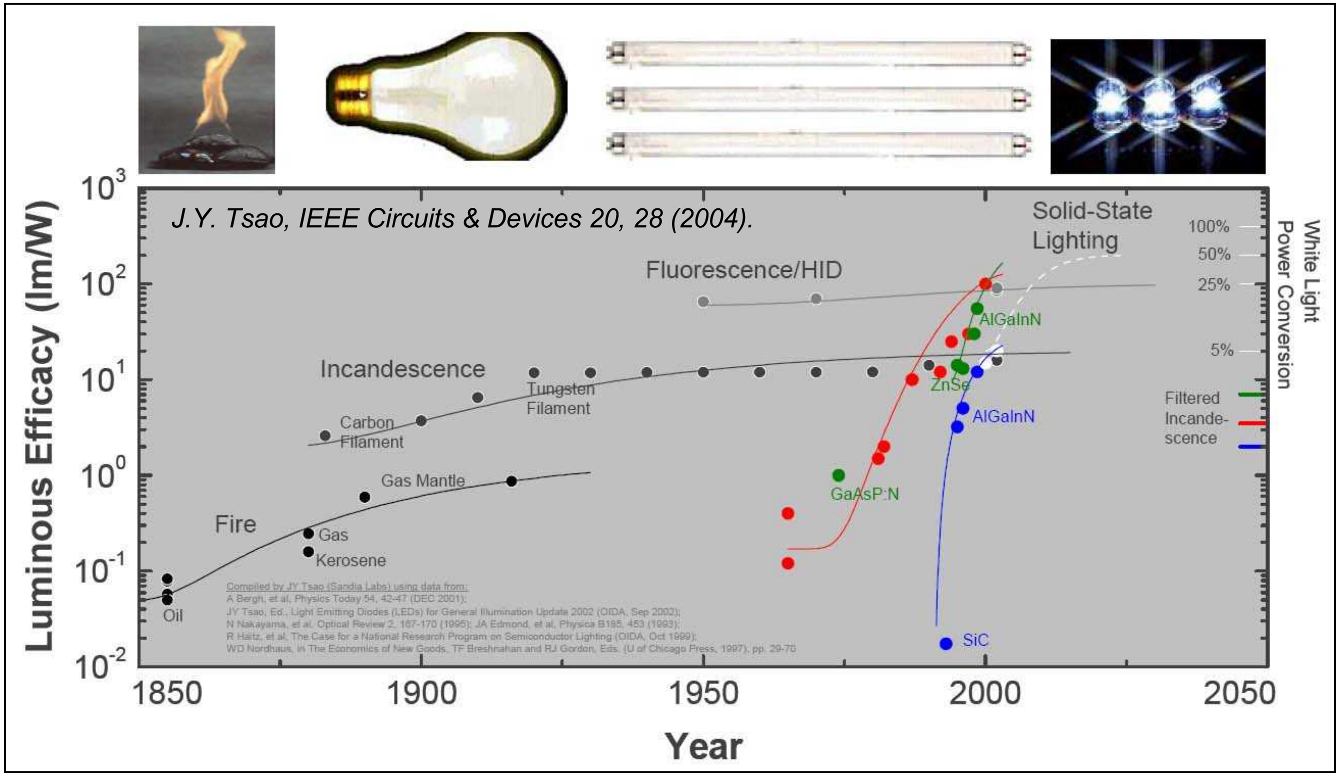


What's Next?
Beyond solid state lighting to power electronics

Status of Solid State Lighting?

Sandia National Laboratories

Luminous efficacy from conventional light sources has stagnated for the last 50 years



DOE has a stated goal of producing SSL with 50% wall-plug efficiency by 2025 (> 200 lm/W)

On Feb. 2013, Cree XLamp - CCT= 4400K, 0.35 A, 276 lm/W

Power Conversion Efficiency

Incandescent ~ 5%

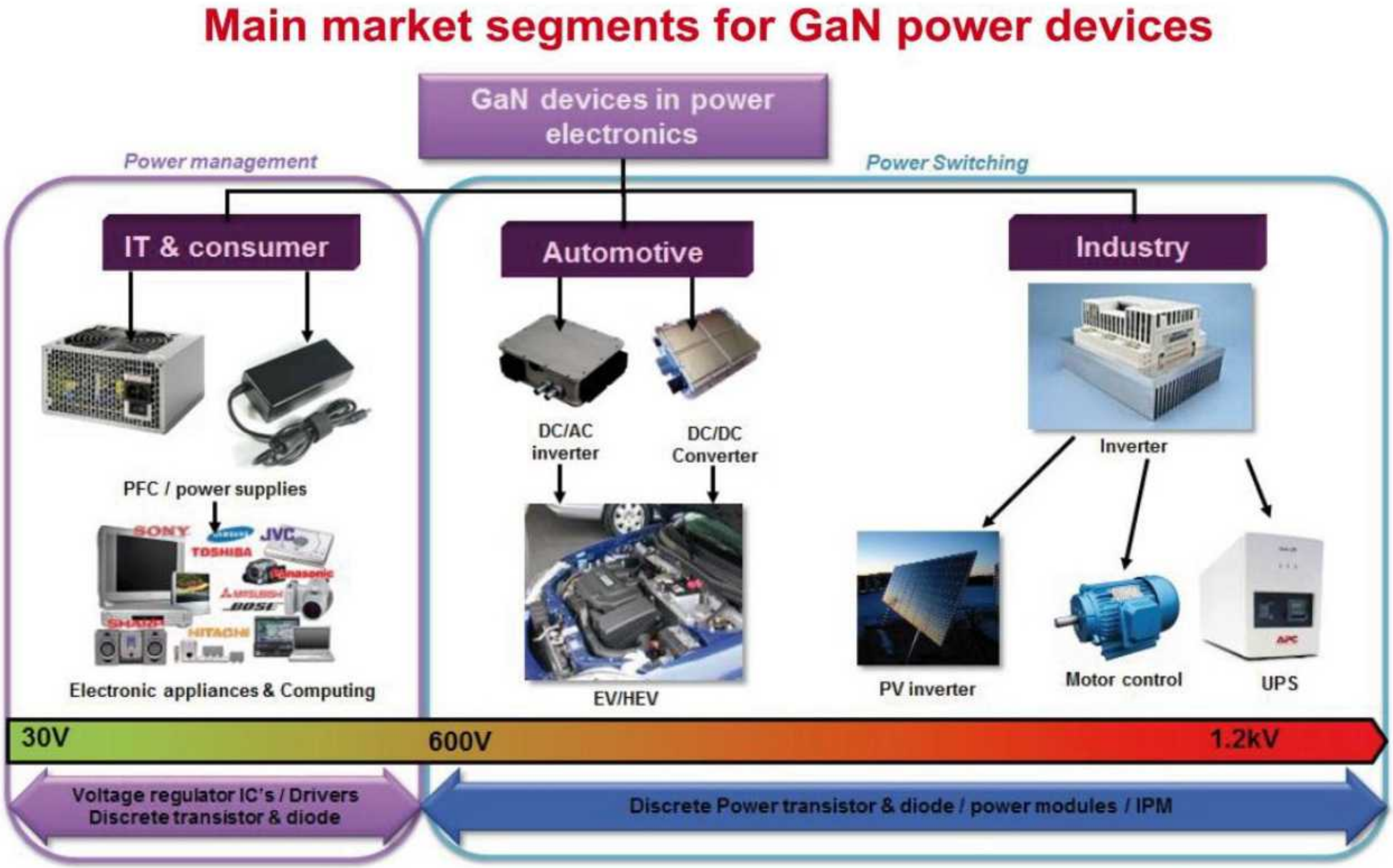
Fluorescent ~ 20%

SSL Goal ~ 50%

LED package ~ mid 1990's

Cree® XLamp CXA3590
10,000-18,000 lumens
maximum current 150 A

Power Electronics



YOLE DÉVELOPPEMENT

Thanks to:

Sandia Colleagues:

A. A. Allerman – AlGaN MOVPE
S. R. Lee – XRD analysis
A. Armstrong - DLOS
M. E. Coltrin – modeling
M. H. Crawford – PL, LED studies
A. J. Fischer – PL, photonics
J. J. Wierer, Jr – solar cell
G. Thaler – MOCVD growth
J. R. Creighton – InGaN chemistry
G. T. Wang – nanowire growth
K. C. Cross - AFM

D. M. Follstaedt – TEM microscopy
N. A. Missert – CL imaging
J. J. Figiel – MOVPE tech.
J. M. Kempisty – MOVPE tech.
L. J. Alessi – MOVPE tech.
D. L. Alliman – MOVPE tech.
M. L. Smith – processing
P. G. Katula – XTEM
J. Y. Tsao – chief scientist
R. M. Biefeld – manager 1126
D. L. Barton – manager 1123