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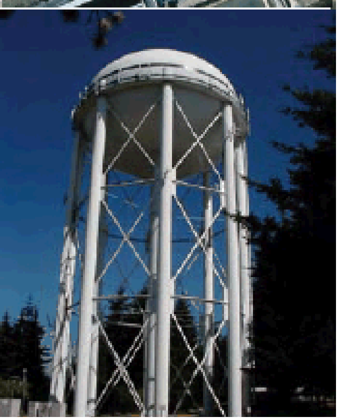

Ultraviolet Semiconductor Materials for Next-Generation Water Security

Mary H. Crawford

Sandia National Labs

Semiconductor Material and Device Sciences Dept.

Org. 01123

Acknowledgements: A. A. Allerman, A. M. Armstrong, M. A. Miller, J. J. Wierer, N. A. Modine and A.F. Wright

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Water Security

Key Aspect: Robust water quality assurance
(terrorist attacks, natural disasters, etc)

Potential Strategy:

Supplement centralized water treatment facilities with distributed point-of-entry (POE) and point-of-use (POU) systems*

Desired Attributes:

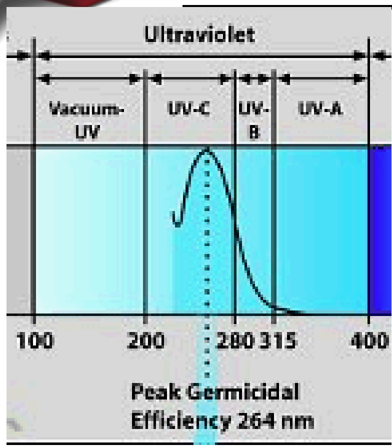
- broadly effective *(biological, chemical)*
- high reliability, low maintenance
- low cost, low energy consumption
- low environmental impact *(manufacture, use, disposal)*

Attributes for New Functionality:

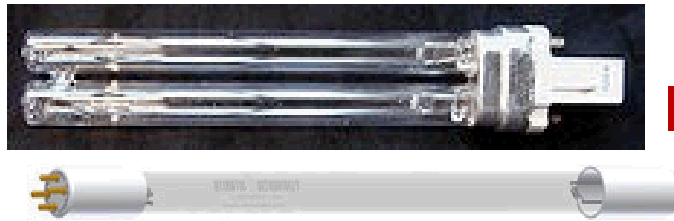
- no power requirements or solar-powered
- "smart" integration of sensing and purification functions
- communication between networked POE/POU systems

*I. Silverstein, EPA Feb. 2006 Figures from EPA water.epa.gov/infrastructure/water security

Next-Generation UV Sources for Water Purification



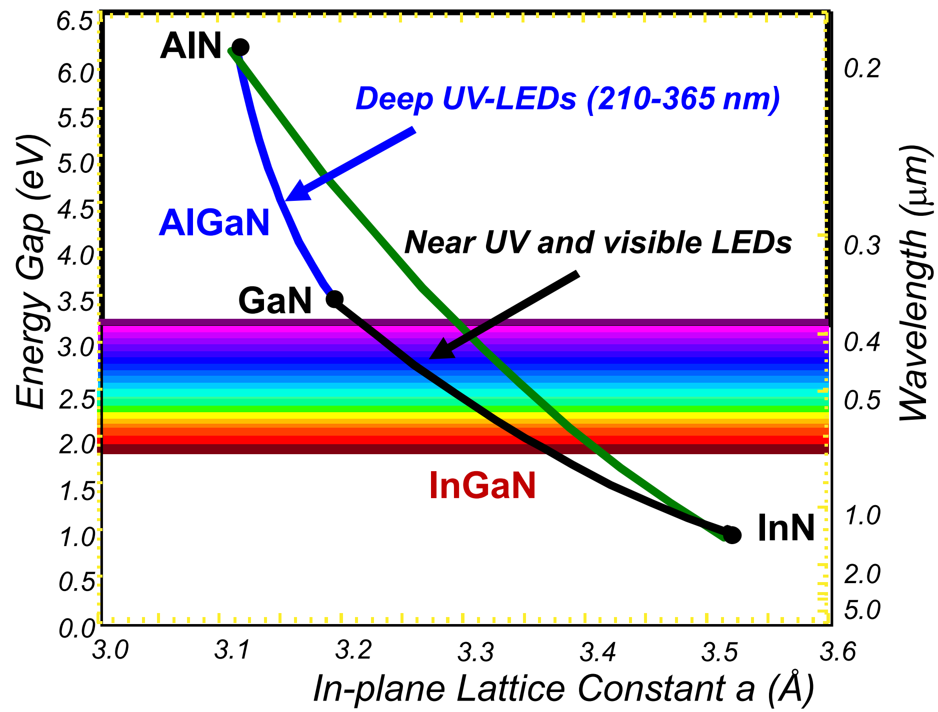
Hg Lamps → Solid-state (LEDs)



254 nm

210-365 nm

AlGaInN Semiconductor System



UV LED Advantages:

- **Avoids hazards of Hg disposal**
- **Integration with control electronics**
- **Low power /solar power**
- **Instant turn-on**
- **Wavelength tunable *(340 nm /265 nm for fluorescence sensing/purification)***

Limitations:

- **Present devices only ~2% efficient**

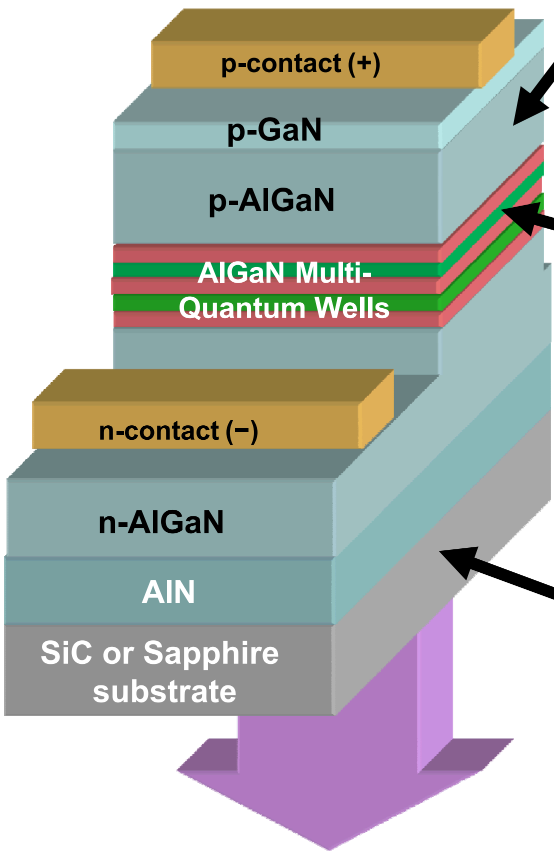
→ Estimate > 10% efficiency is needed for practical implementation

→ Materials breakthroughs needed!

LED image from s-et.com

Materials challenges for realizing high performance AlGaN deep UV LEDs

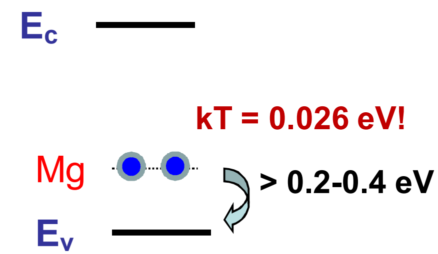
AlGaN Deep UV LED (p-n junction device)



Bottom emission

p-type AlGaN is very difficult

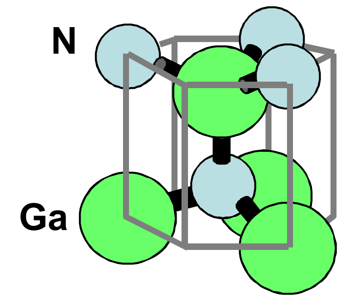
- → Large acceptor ionization energies
- → Compensating defects
- → P-GaN is better, but absorbs deep-UV!



AlGaN Quantum Wells have low optical efficiency

- → Non-radiative crystalline defects (e.g., impurities, vacancies)

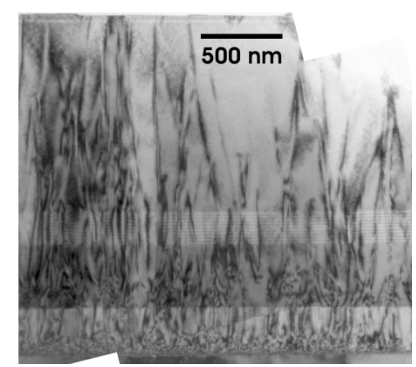
GaN Unit Cell



Lack of AlGaN Substrates

- → high densities of extended defects (threading dislocations) > 10^9 cm^{-2}
- → Reduced device efficiency and operational lifetime

TEM image of AlGaN on sapphire



Sapphire substrate

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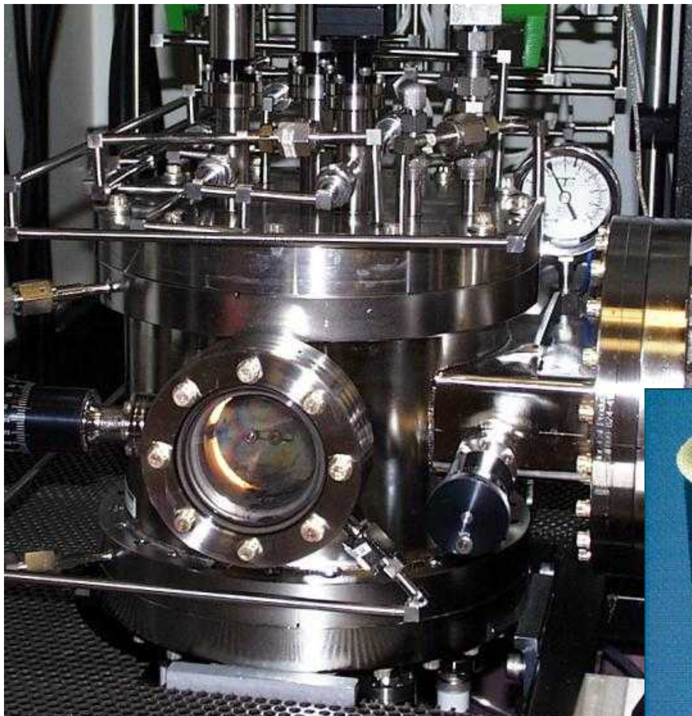
Epitaxial Growth of Nitride Semiconductors by Metal-organic Vapor Phase Epitaxy at Sandia

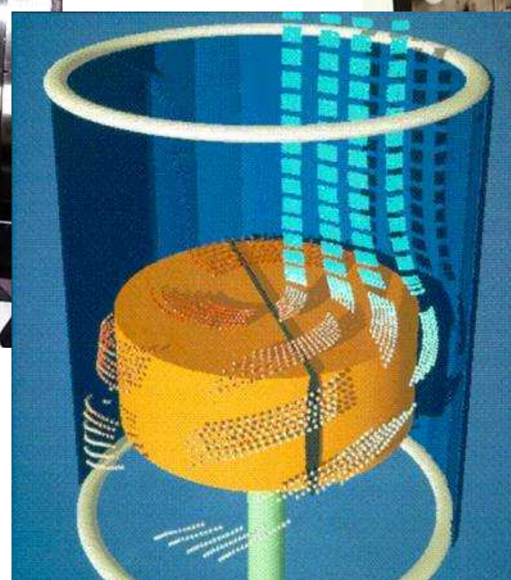
Veeco D-125 Rotating Disk MOVPE System



AlGaN Growth

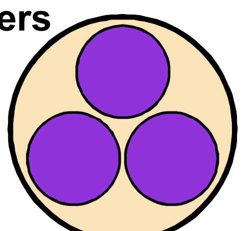
Sources: **TMGa, TMAl, NH_3**
Temp: **1035-1100°C**
Pressure: **75-300 torr**
Growth rates: **0.3-1 μm/hour**

Dopants:
n-type: **SiH_4**
p-type: **Cp_2Mg**



Rotation ~ 1500 rpm

3 two-inch wafers



Andrew Allerman,
Org. 01126

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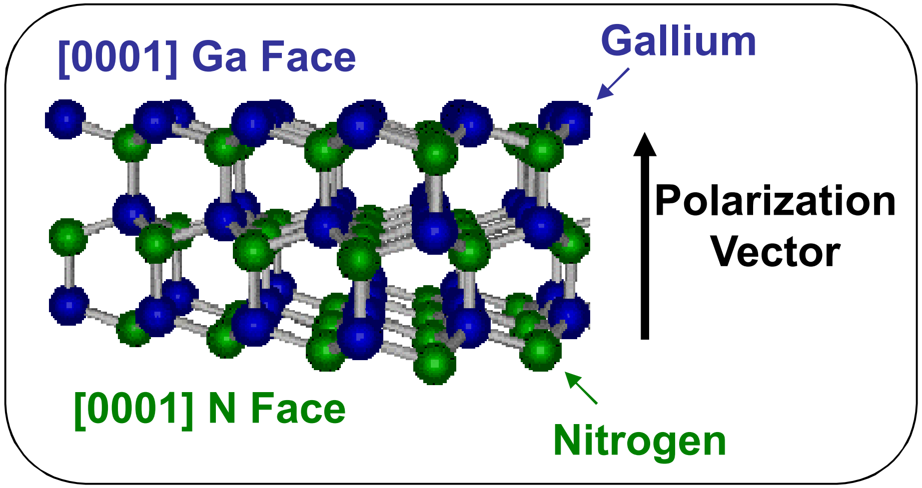
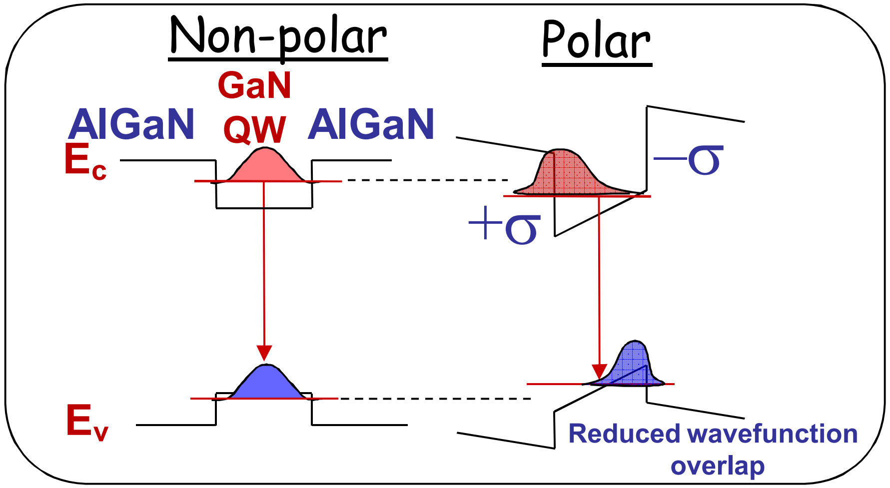
Proposed P-type Doping Solution: Mg-doped Short-Period Superlattice

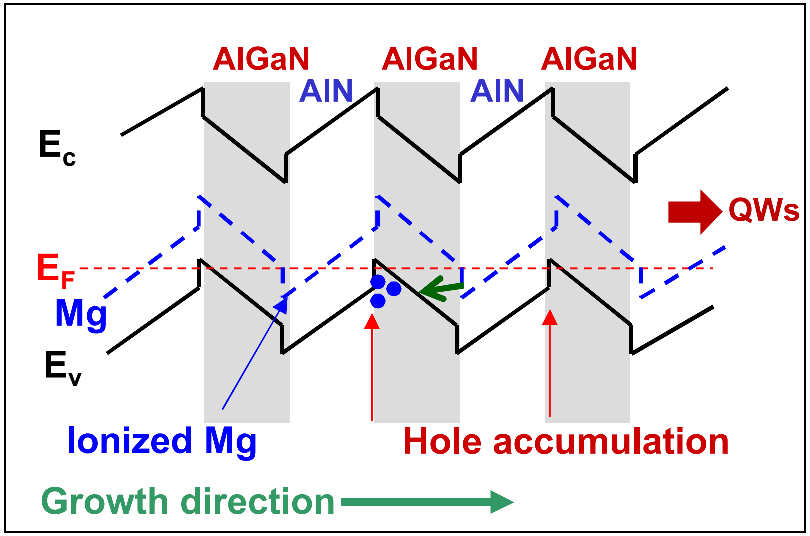
Wurzite GaN crystal structure



Polarization effect on GaN quantum well



Mg-doped Polarization Superlattice



- Manipulation of polarization fields alters electronic states and enables hole accumulation
- Use of “ultrathin” layers (5-15Å) in the SL enables:
  - high effective bandgap of random alloy (Al~0.60)
  - possibility of tunneling-assisted vertical transport

→ **Deep-UV-Transparent Hole Injector**

Nikishin et al
JAP (2005)
(MBE growth)

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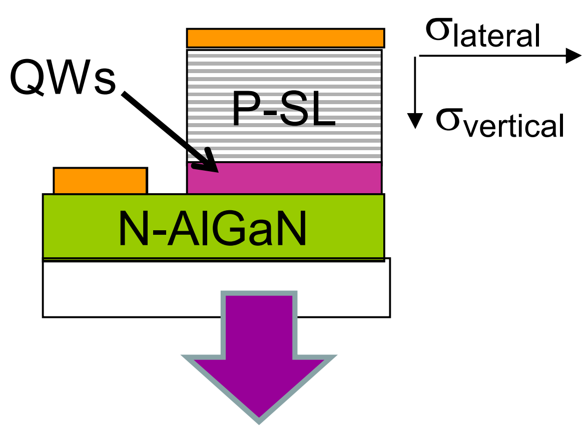
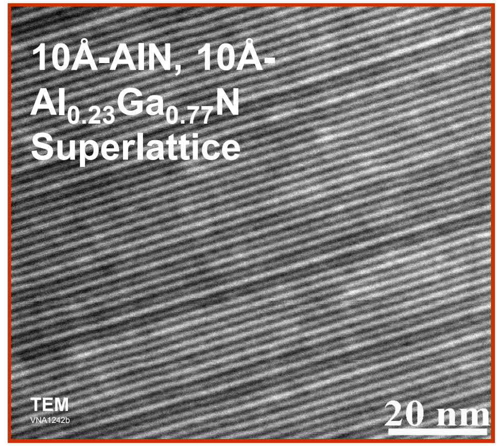
Progress to Date on Mg-doped SPSLs

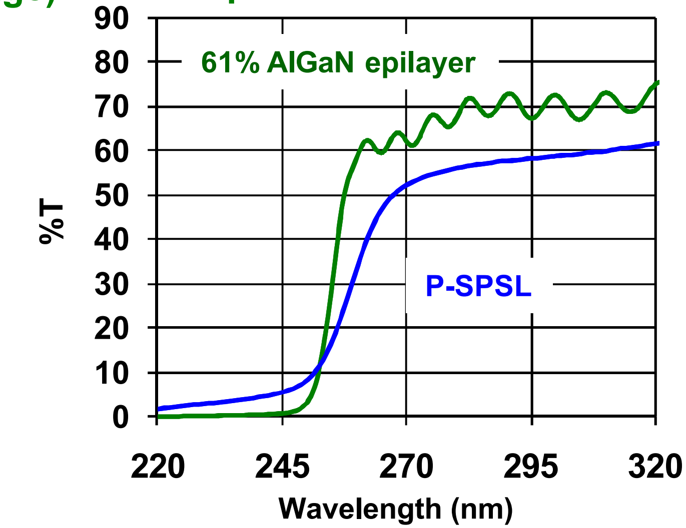
Proposed p-SPSL LED



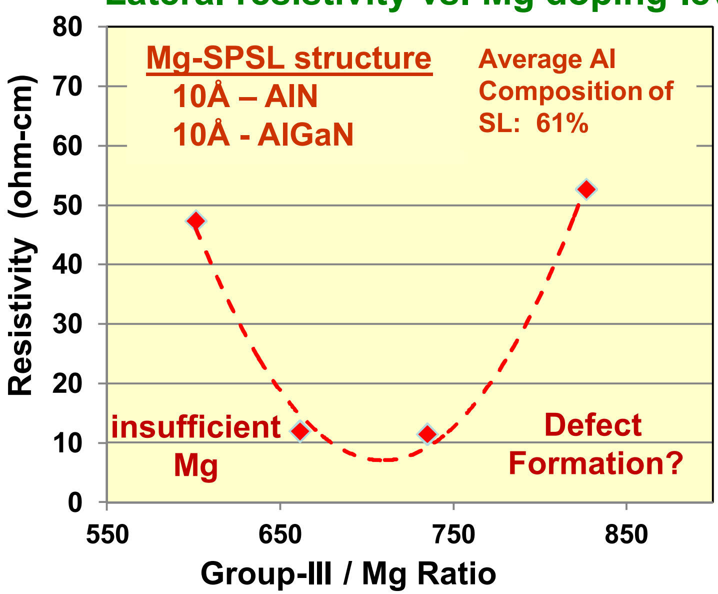
Structural Properties (TEM image)



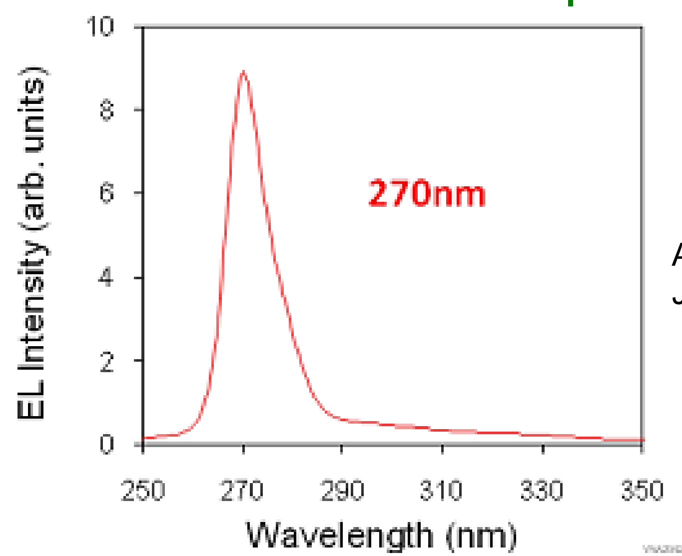
Optical Transmission



Lateral resistivity vs. Mg doping level



Electroluminescence from p-SPSL LED



Improvement of vertical conductivity still needed

A. A. Allerman et al, J Crystal Growth, (2010)

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Application of Novel Tools to Study Point Defects

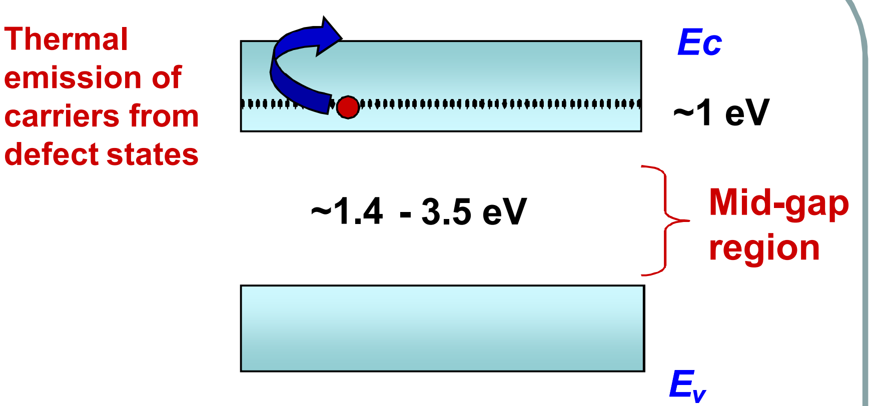
Motivation

→ Point defects (*vacancies, impurities, etc*.) may cause non-radiative recombination, dopant compensation, defect-assisted carrier tunneling from active region

Challenge

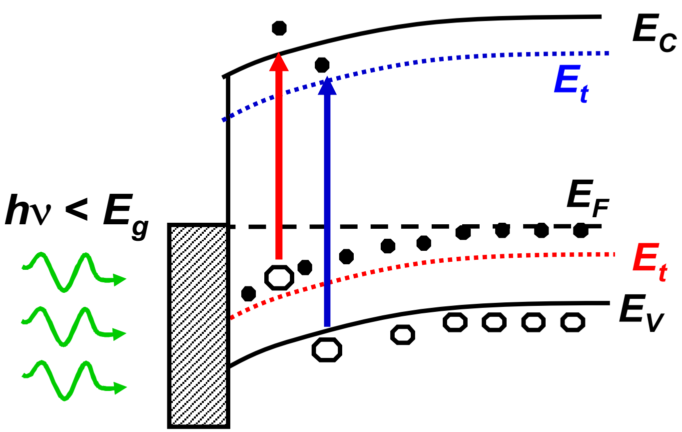
→ Most common experimental techniques (e.g., DLTS) can't probe entire bandgap

Deep Level Transient Spectroscopy



→ limited to ~ 1 eV of Ec, Ev
→ cannot probe mid-gap non-radiative centers

Deep Level Optical Spectroscopy



→ photo-capacitance technique
→ application of tunable light excitation to access entire bandgap

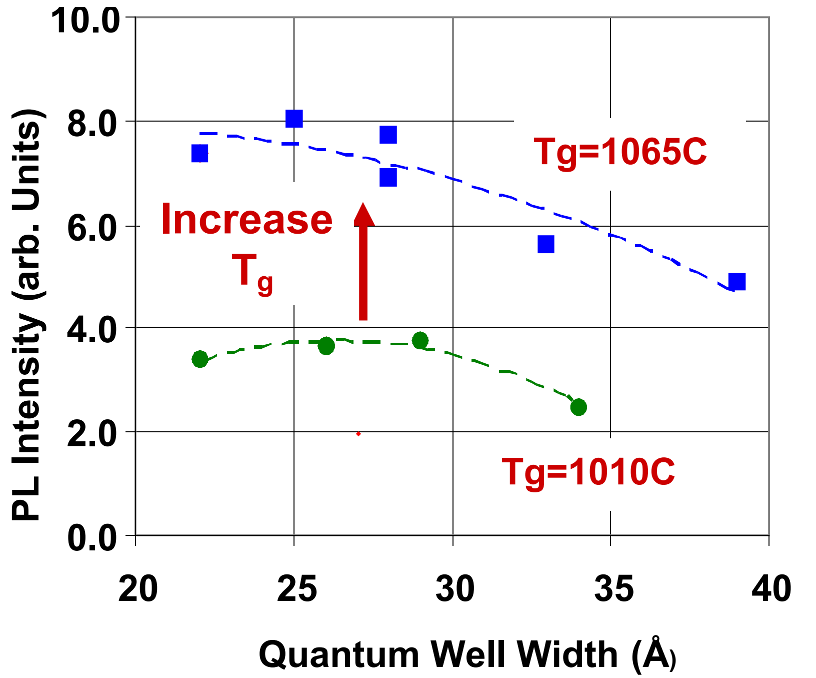
Andrew Armstrong, Org. 01123

Combination of photoluminescence and DLOS to study impact of QW growth temperature

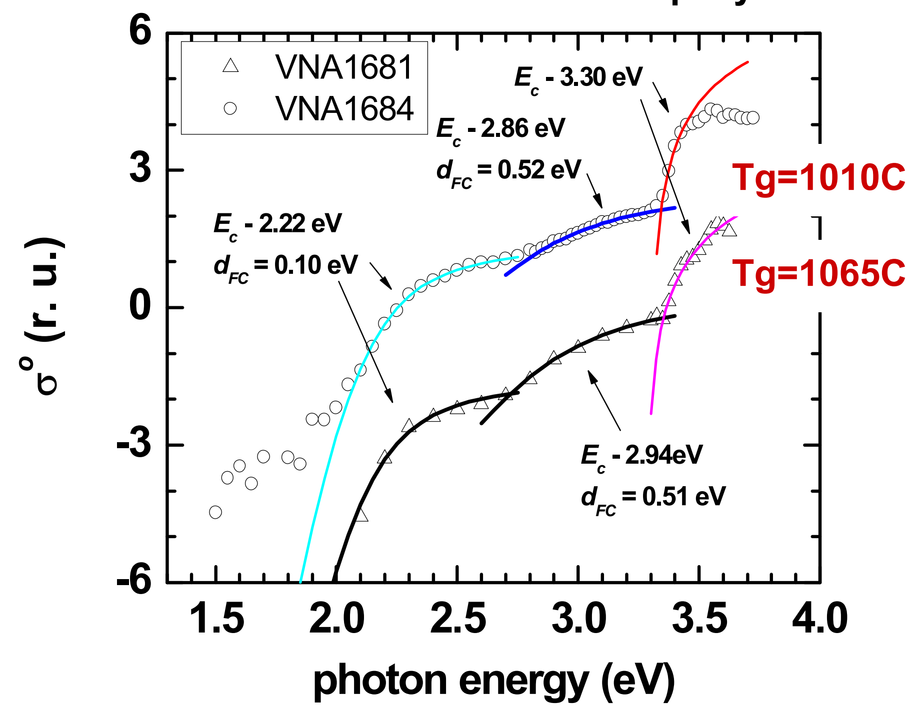
Materials Growth Conditions → Defect Properties → Materials Performance

Impact of growth temperature on AlGaN quantum well luminescence

Photoluminescence of 340 nm AlGaN QWs



DLOS data of related AlGaN Epilayers



→ Change in growth temp does not introduce new defect levels

Model used to fit DLOS data: Paessler JAP 96, 715 (2004)

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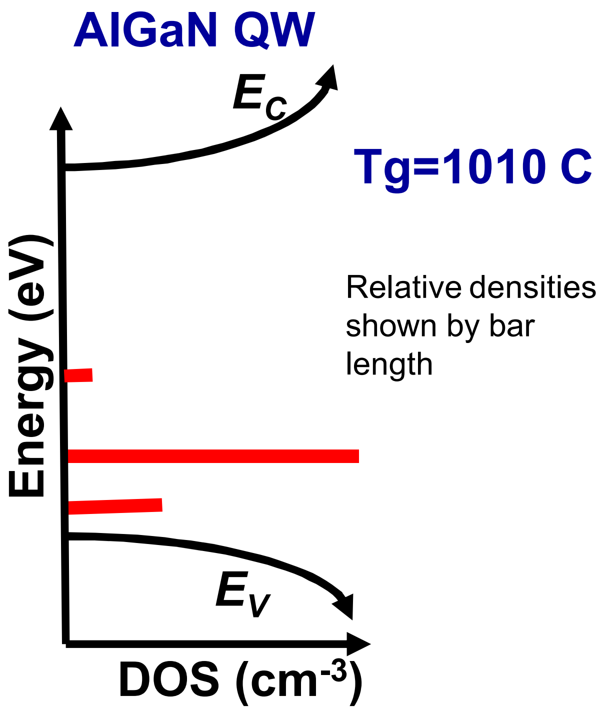
Combination of photoluminescence and DLOS to study impact of QW growth temperature

Lighted CV measurements to determine densities of deep levels (cm^{-3})

Trap Energy	Tg *1065°C*	Tg *1010°C*	*Change*
Ec-2.22 eV	2.5e15	1.1e16	4.4X
Ec-2.90 eV	2.7e16	9.0e16	3.3X
Ec-3.30 eV	7.7e15	3.0e16	3.8X



- ~3-4X increase in deep level density across the spectrum with lower Tg
- Increased defect density correlated with ~ 3X decrease in PL deep level intensity

First *quantitative* correlation of AlGaN growth conditions, increased deep level densities, and lower luminescence intensity

A. Armstrong, et al., submitted to Appl. Phys. Lett.

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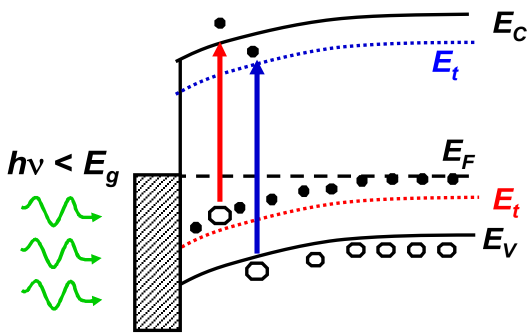
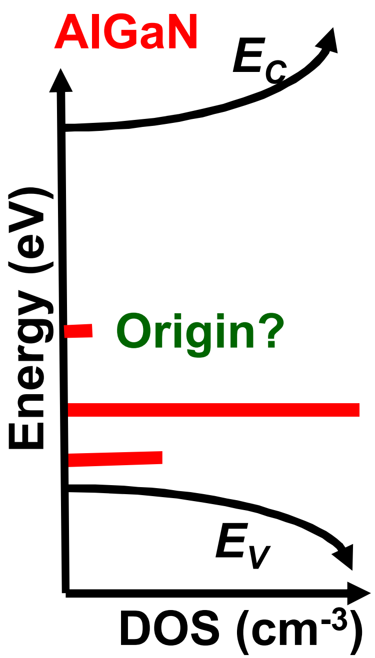
Identification of physical origin of defect levels: Experiment and Theory

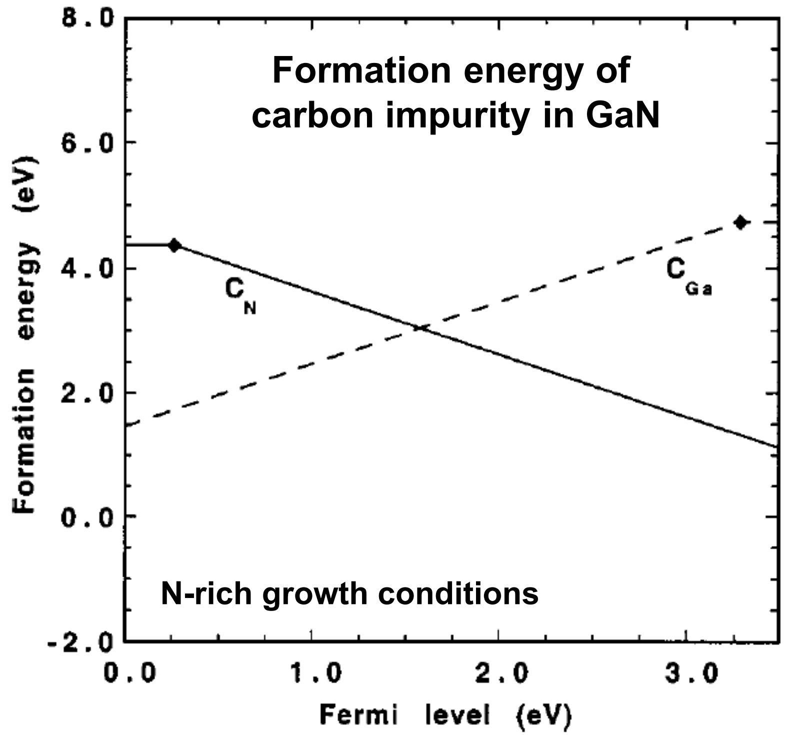
Experiment: DLOS

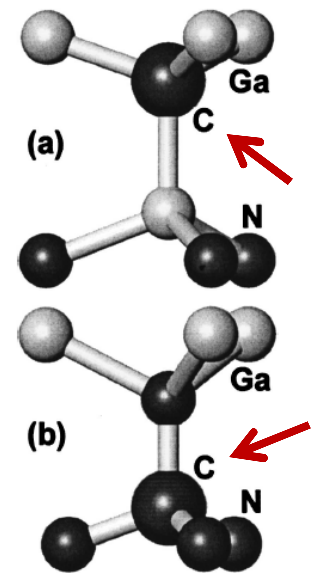




Andy Armstrong (01123)

Theory: Density Functional Theory





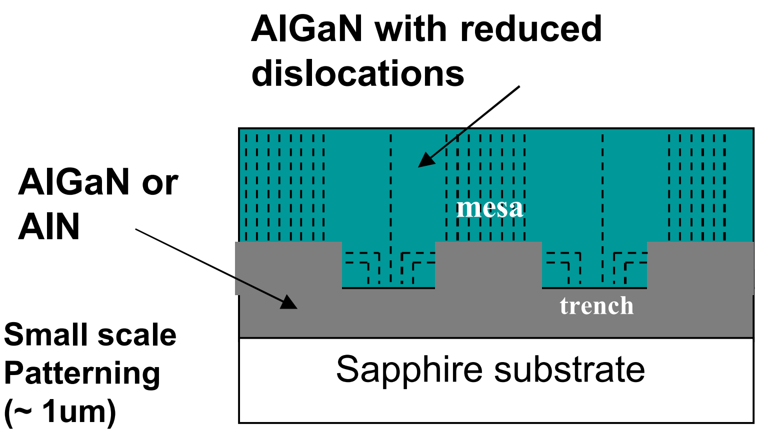
A. F. Wright, JAP 92, 2575 (2002)

- Formation energies of defects
- Energies of defect levels
- Capture cross-sections

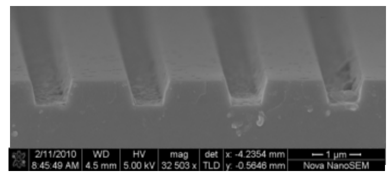
Alan Wright (01112)
Normand Modine (01132)

Materials Engineering for Mitigation of Extended Defects

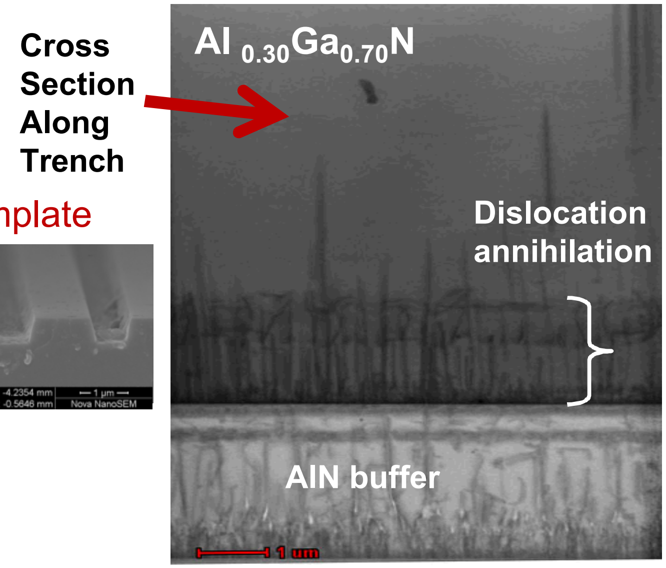
AlGaN Growth on Corrugated Templates



Starting template

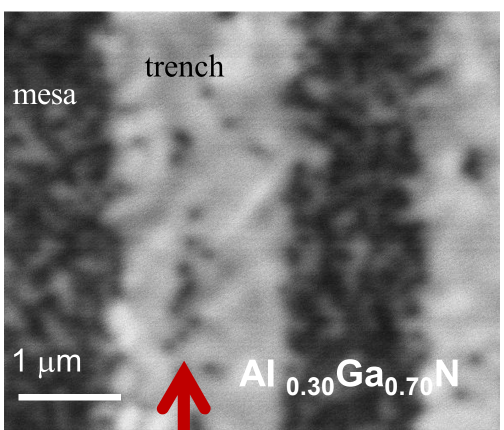


TEM of AlGaN Epilayer

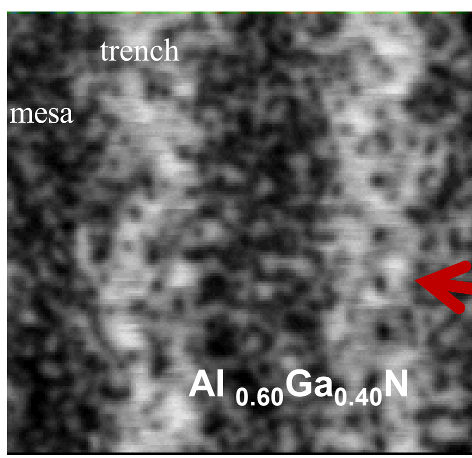


- Dislocations largely annihilated in ~1.5 microns of growth!

CL of 340 nm AlGaN QWs



CL of 280 nm AlGaN QWs



Demonstration of viability in germicidal region (< 300 nm)

- 10-30X TD reduction in $Al_{0.30}Ga_{0.70}N$ (340 nm), to 2-4 e8 cm^{-2} in trenches

A. Allerman

Iida et al., J. Crystal Growth (2007)
Kueller et al., J. Crystal Growth (2010)

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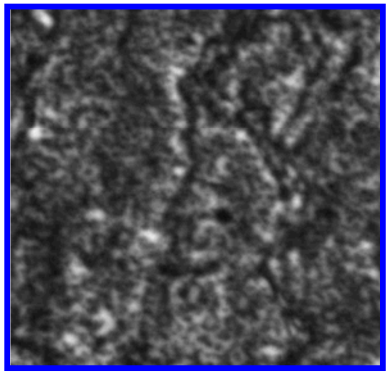
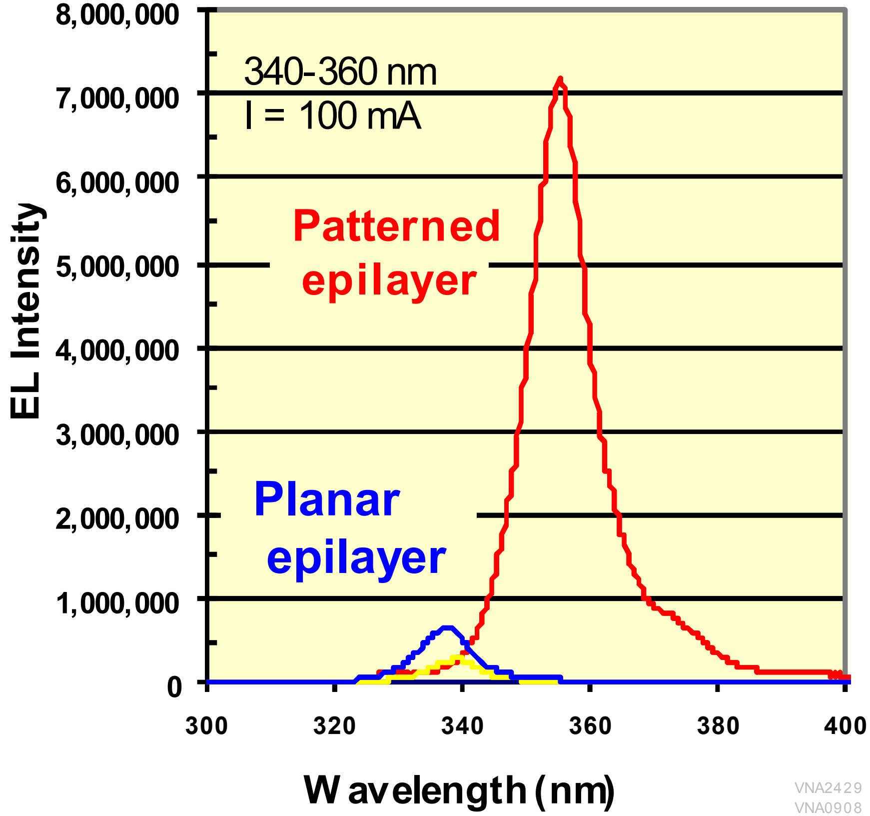
Impact of Dislocation Reduction

Electroluminescence of p-n Junction structure

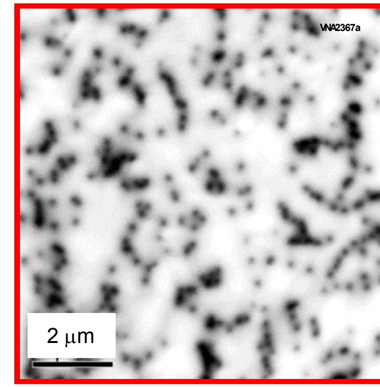
CL from planar AlGaN epilayer



$Al_{0.30}Ga_{0.70}N$
No patterning



CL from patterned AlGaN epilayer



$Al_{0.30}Ga_{0.70}N$

- ***10x increase* in LED emission with patterned AlGaN template!**
- **Improved CL (reduced dislocations) leads to improved EL**
- **Presently working toward implementation in deeper UV LEDs**

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Summary

Goal: develop novel UV sources based on LEDs to enable point-of-use water purification systems with enhanced capabilities

- Requires overcoming major materials challenges of AlGaN alloys, Including fundamental limitations to p-type doping, and the effects of point and extended defects
- Developed Mg-doped polarization superlattices as a means to circumvent thermal activation of p-type dopants and achieve hole Injection with a deep UV transparent structure; 1^{st} generation LEDs with emission in the germicidal region
- Applied DLOS to achieve new insights into the correlation of AlGaN growth conditions, defect properties, and materials performance; potential to understand and control defect populations
- Advancing patterned-growth defect-reduction approaches to higher Al-content AlGaN devices, relevant to germicidal region of the spectrum

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