SAND2007-0559C

Title: Novel ScGaN and YGaN Alloys for High Efficiency Light Emitters

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Project Team and Roles

Name	Role	Responsibilities	Fraction of time*
Robert M. Biefeld	P.M.	Project Manager	
Daniel D. Koleske**	P.I.	MOCVD growth and reports	0.40
Arthur J. Fischer	I.	LED “quick tests” and full fabrication	0.15
David M. Follstaedt	I.	TEM investigations	0.10
William R. Wampler	I.	RBS to determine alloy contents	0.10
Mary H. Crawford	I.	PL and IQE measurement	0.10
Stephen R. Lee	I.	XRD analysis	0.15

*Fraction of time includes any technical-support personnel allocated to each investigator.

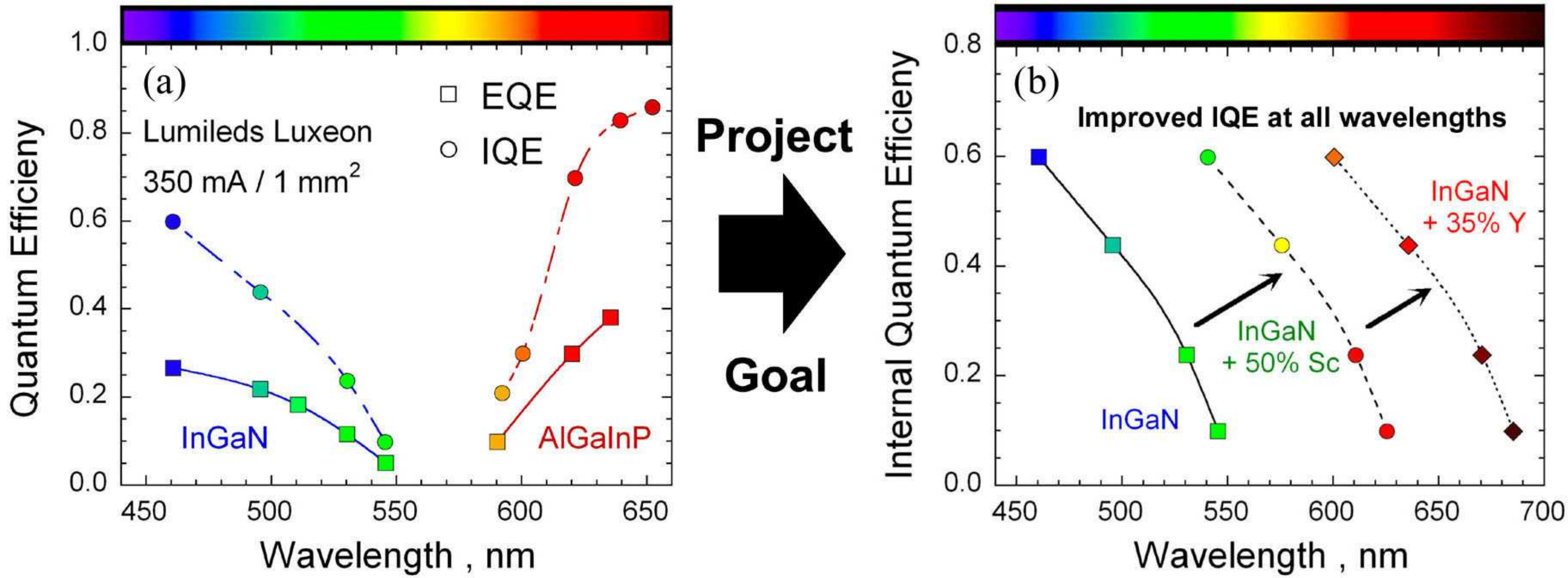
**Jerry Thaler was hired as a post-doc to work with Dan Koleske on the MOCVD growth research.

Project Objective

To red-shift the wavelength of the most efficient InGaN-based LEDs in the near UV and blue to longer wavelengths in the green, yellow, orange, and possibly red by adding Sc and Y to the QWs.

From Lumileds via Wetzel et al.

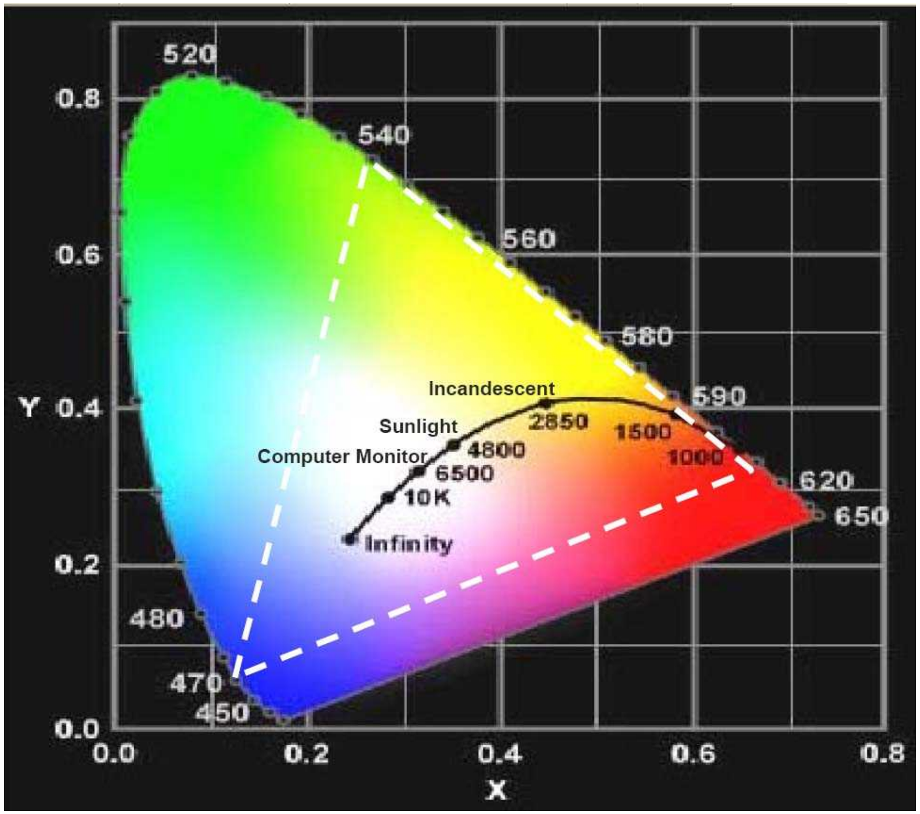
If successful, expected increase in IQE



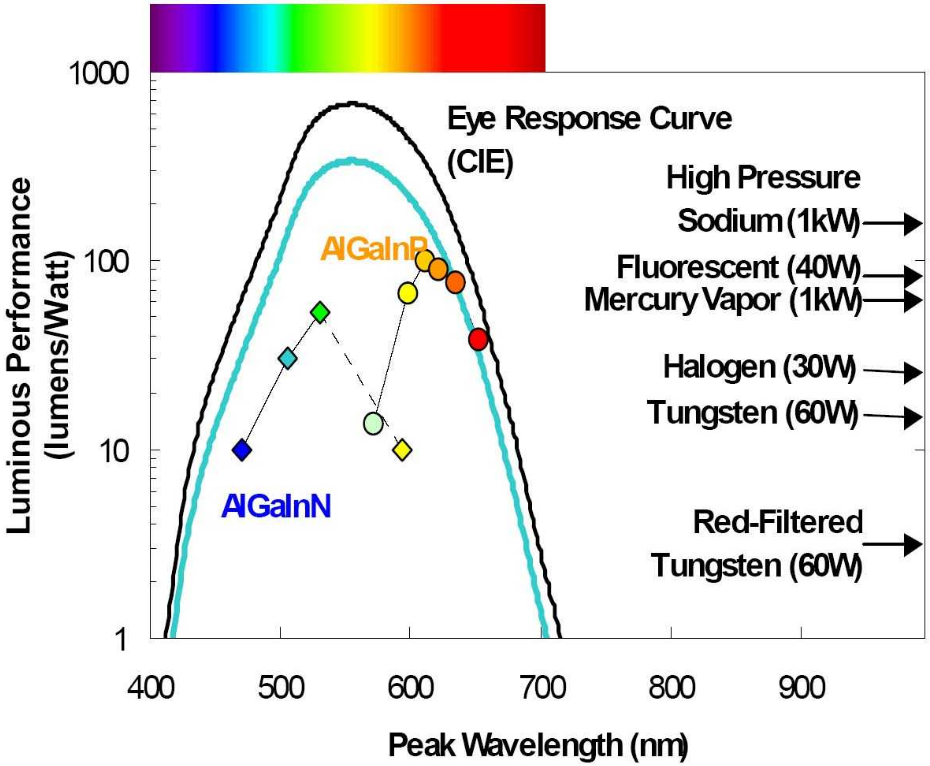
Bandgap of GaN = 3.4 eV, ScN = 2.15 eV, YN = 0.8 eV are assumed.

Achieving white light with an RGB approach

With RGB approach can achieve all colors within triangle



Eye most sensitive to 555 nm (green) light.

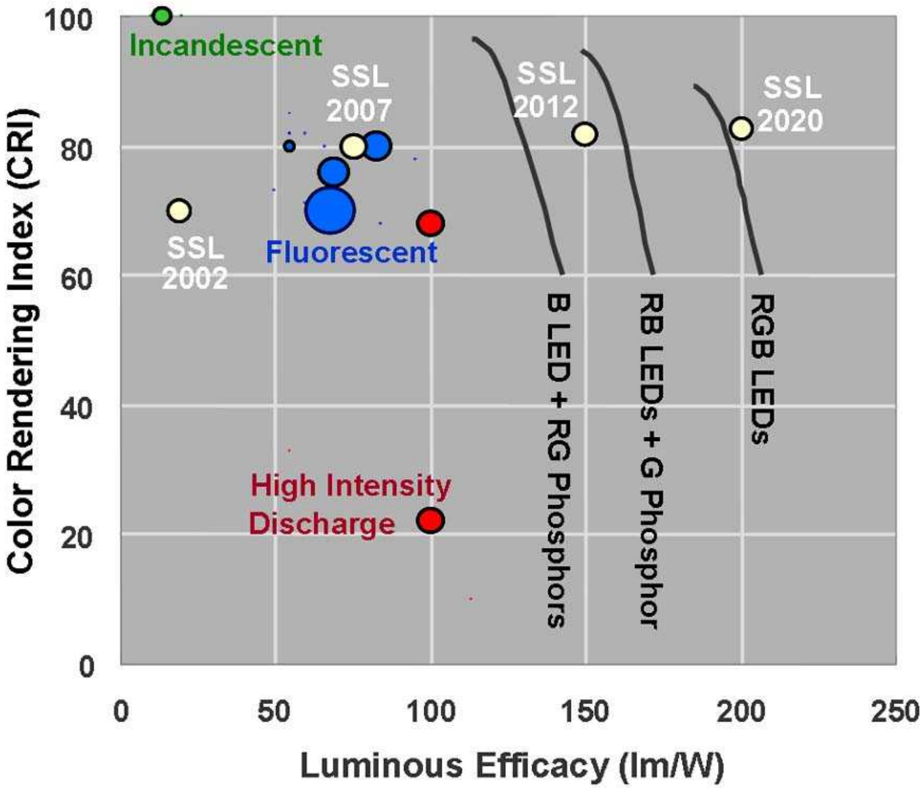


For tricolor approach (RGB) need a brighter green LED.

Expected Benefits

If this research is successful, companies that manufacture InGaN-based LEDs should be able to add Sc and Y to the InGaN quantum wells to produce high efficiency LEDs over the entire visible wavelength range.

Targets for CRI and luminous efficacy shown as white dots



*Estimate of the CRI based on the luminous efficacy was performed by Jeff Tsao (SNL) using a quantitative luminous-efficacy-CRI simulator developed by Yoshi Ohno at NIST. For the characteristics of the white light, we assume a constant color temperature of 4000K, with no allowed deviation from Planckian white. For the characteristics of the LEDs and phosphors we assumed: 50% efficiency and 20 nm linewidths for the LEDs and 90% efficiency and 80 nm linewidths for the phosphors. This calculation takes into account the stokes shift energy loss in the phosphors.

Tricolor RGB may be only approach to meet DOE SSL Goals

Concessions Necessary to Grow InGaN on GaN

- Lower growth temperature
  - GaN grown at 1000-1100 °C, InGaN grown at 700-800 °C
  - May introduce defects, impurities, metal inclusions, V-defects, changes in surface morphology – increased roughness, etc...
- Can only use N_2 carrier gas for growth, no H_2.
  - Surface H may be beneficial in reducing CH_x- fragments.
- Have to use higher NH_3 flow rates.
  - Lower NH_3 cracking efficiency – non-stoichiometric defects.
- Strain increases as indium content and thickness increase.
  - Have to work below the critical thickness – film coherency.
  - Strain relief produces defects.
  - May prevent growth of higher In content alloys to < 20 %.

What mechanisms limit the growth of high quality, higher In content InGaN alloys and InGaN/GaN quantum wells?

Despite more than a decade of research, InGaN materials growth is characterized by a complex interplay of phenomena that are still not entirely understood:

2D → 3D growth mode evolution with lower growth temperatures and higher Indium, (also depending on pressure, NH_3 flow, TMI flow, etc.)

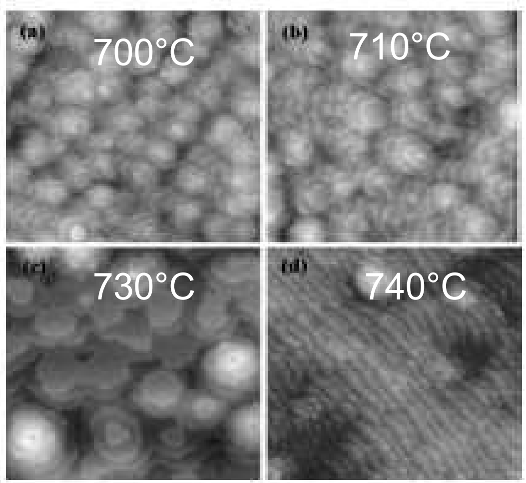


Figure from Oliver et al., JAP 97 013707 (2005)

Distinct morphological defects, depending on strain, growth temp, and defect populations

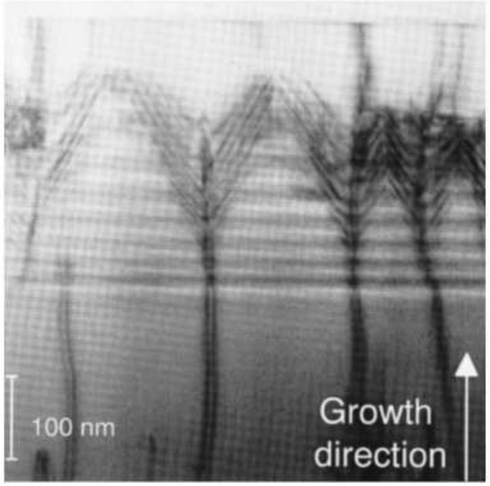


Figure from Scholz et al., Mat Sci Eng B 50, 238 (1997)

Inclusion growth at InGaN/GaN QW interface, depending on growth temp, hydrogen flow, leading to thermal instability

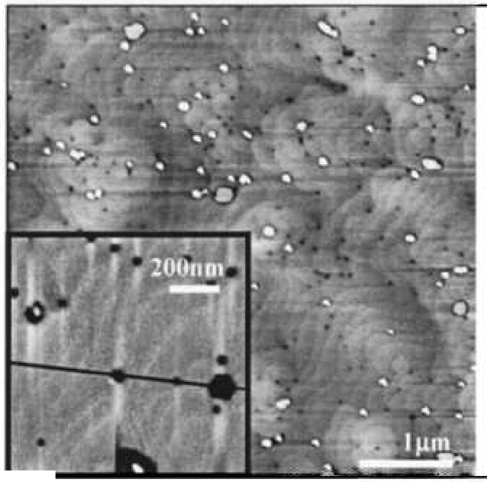
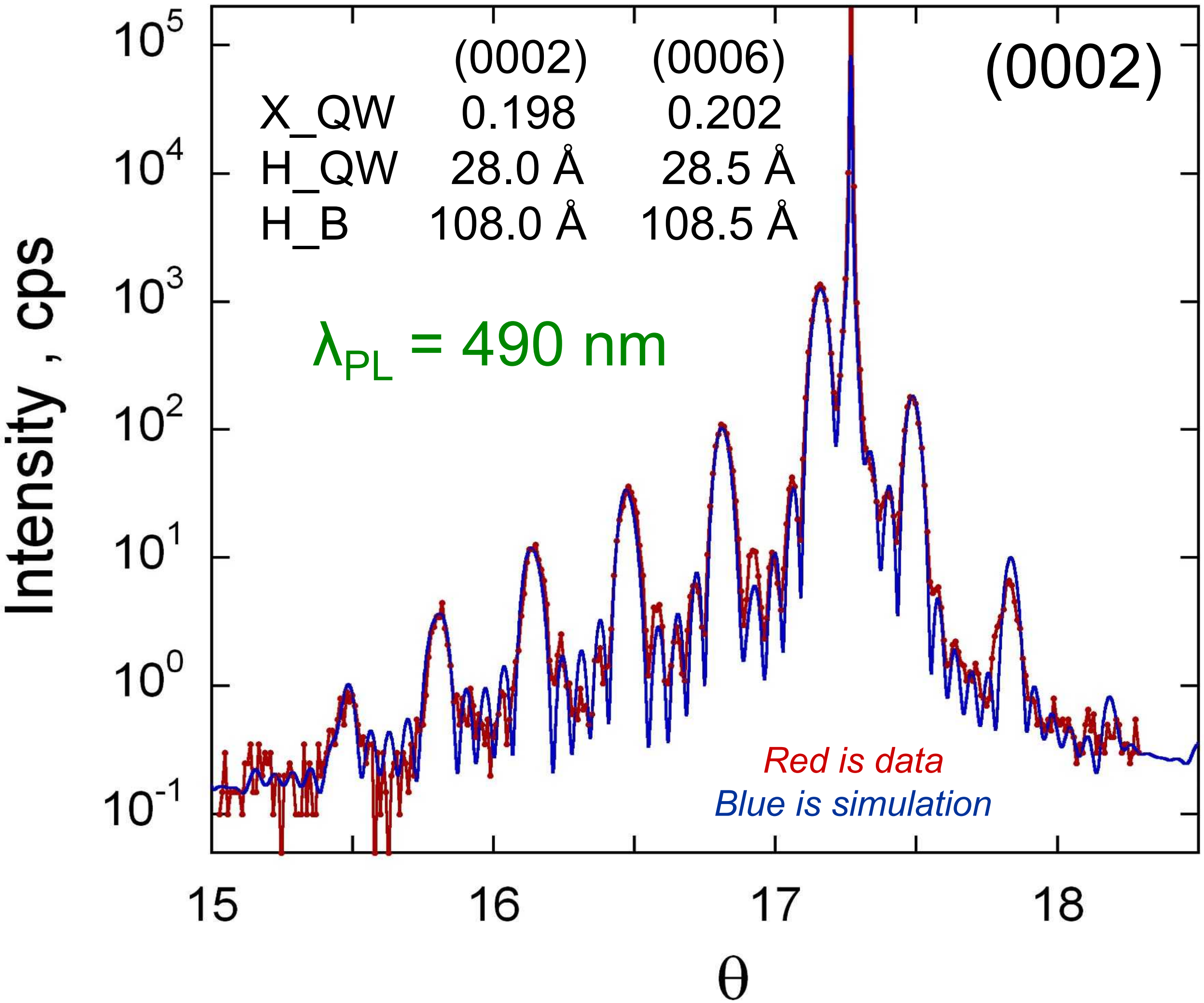


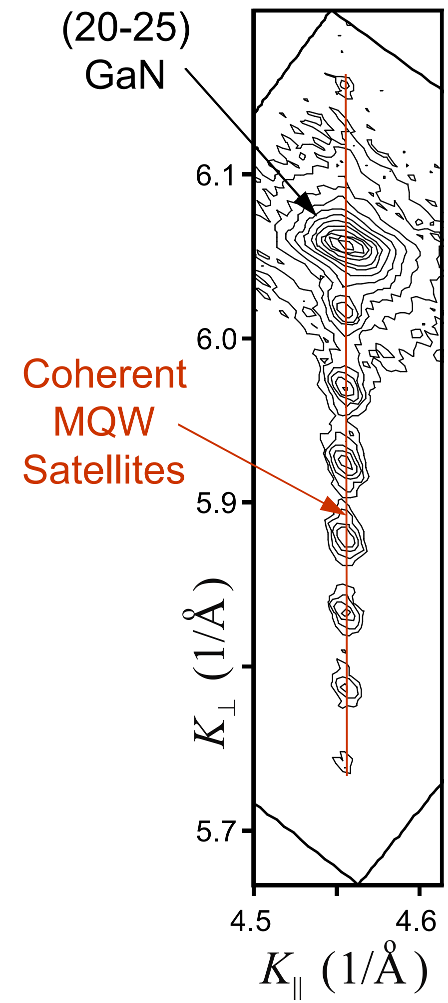
Figure from Ting et al., JAP 94 1461 (2003)

What limits the materials quality and performance of higher In content InGaN and InGaN/GaN MQWs? What limits the incorporation of indium?

Quantum wells are coherently strained

Both the dynamic diffraction simulation and reciprocal space maps suggest layer coherency.

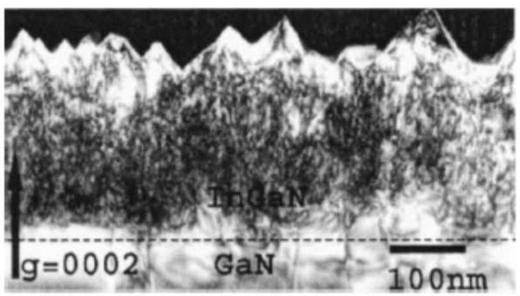




$K_{\parallel} \propto 1/a_{\parallel}$, broading is similar

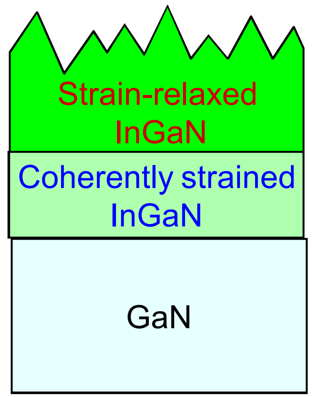
Impact of strain on indium incorporation

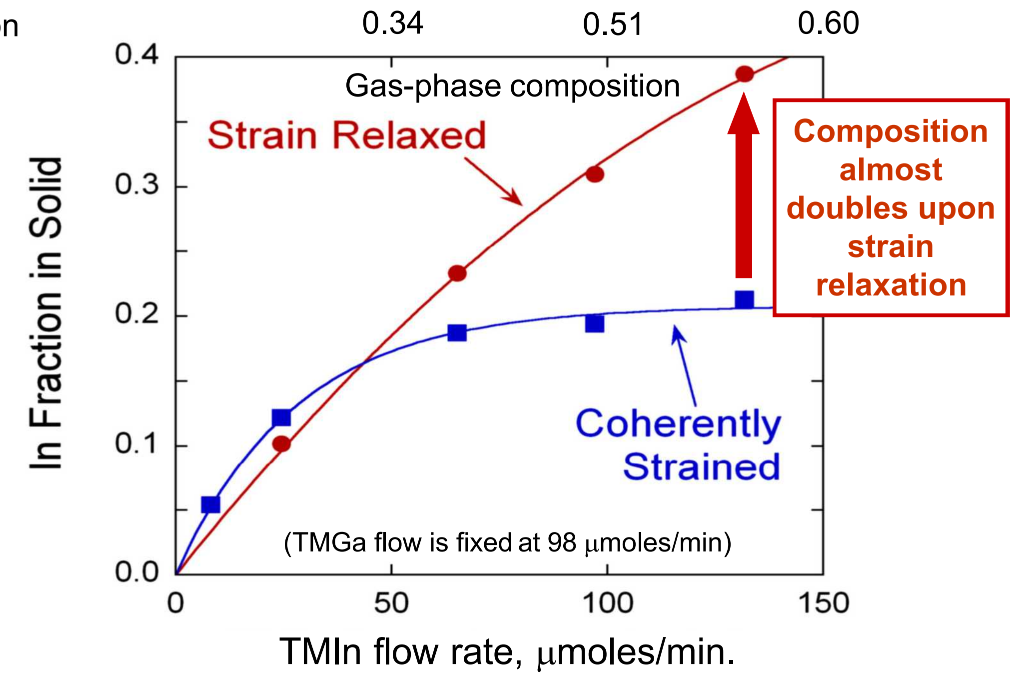
➢ strain plays a critical role in limiting indium incorporation



M. Rao, et al., APL 85, 1961 (2004).

~100-nm-thick InGaN on GaN at 760 C:





Related observations:

Z. Liliental-Weber, et al., J. Electron. Mat. **30** (2001) 439.

S. Pereira, et al., APL **80** (2002) 3913.

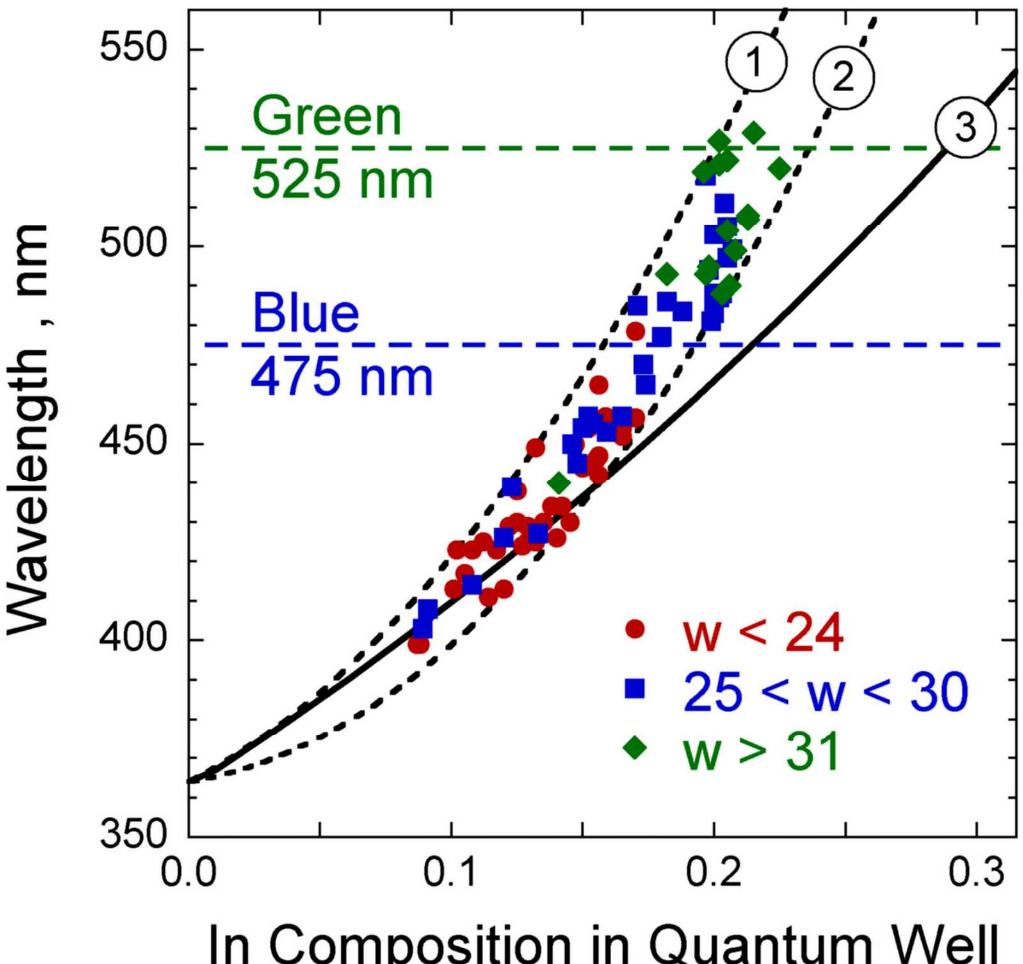
Shimizu, et al., JJAP **36** (1997) 3381.

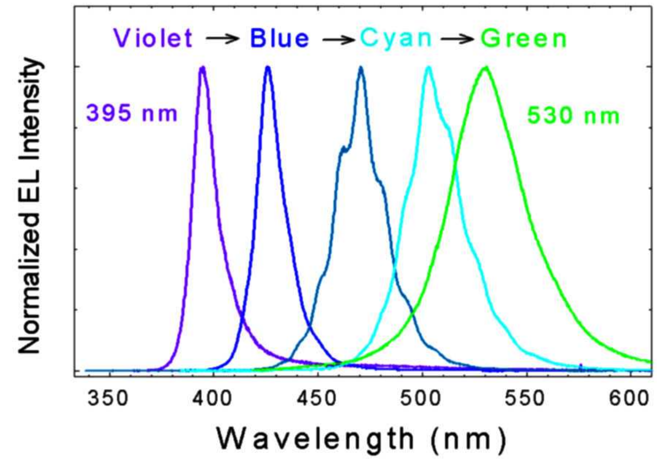
➢ Strain-relaxed InGaN templates could enable significantly higher In concentrations at reasonably high growth temperatures (~760°C) – Mike Coltrin – NETL project.

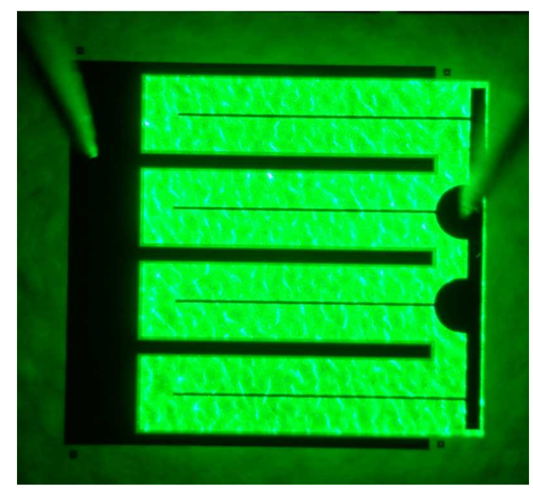
<u>Fundamental question</u>: How does indium incorporation of only 20 % influence green and longer wavelength emitters?

Green possible with 20% In and QW thickness of 30 Å

Line 3 is the bulk InGaN PL wavelength vs, indium composition







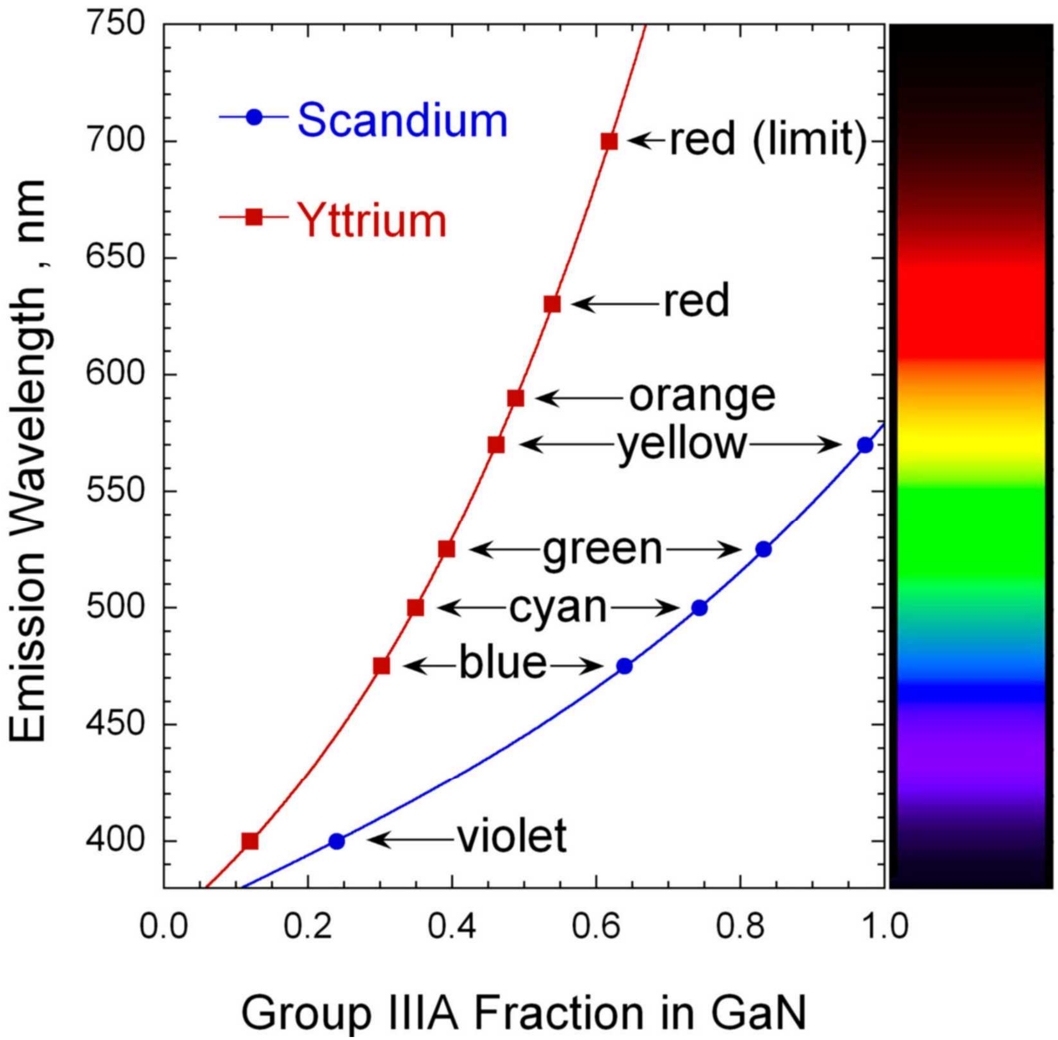
Green (527 nm) achieved with 20% indium content and a 30 Å thick QW, however output intensity is 1/3 that at 500 nm and 1/9 that at 423 nm.

Possible advantages of ScGaN or YGaN

- Same growth temperature as GaN.
  - GaN grown at 1000-1100 °C, since Sc and Y are more refractory – grow at higher temperatures.
  - Chemistry of Sc and Al are similar – AlGaN is grown at high T.
  - Reduced phase separation – AlGaN alloys are mixed.
- Can use both N_2 and H_2 carrier gases for growth.
  - Increased rehydrogenation and desorption of CH_x- fragments.
- Can use lower NH_3 flow rates.
  - Higher temperature leads to more efficient NH_3 cracking.
- No strain issues with ScGaN but strain issues with YGaN.
  - ScN has the same lattice constant as GaN.
  - YN lattice constant is larger than GaN, but not as large as InN.

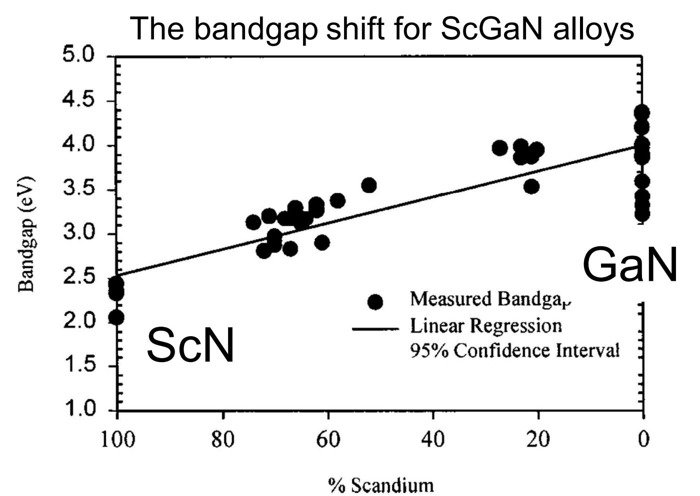
ScN and YN bandgaps are lower which should decrease the group III-nitride LED wavelengths.

Estimation of the emission wavelength for ScGaN and YGaN alloys.



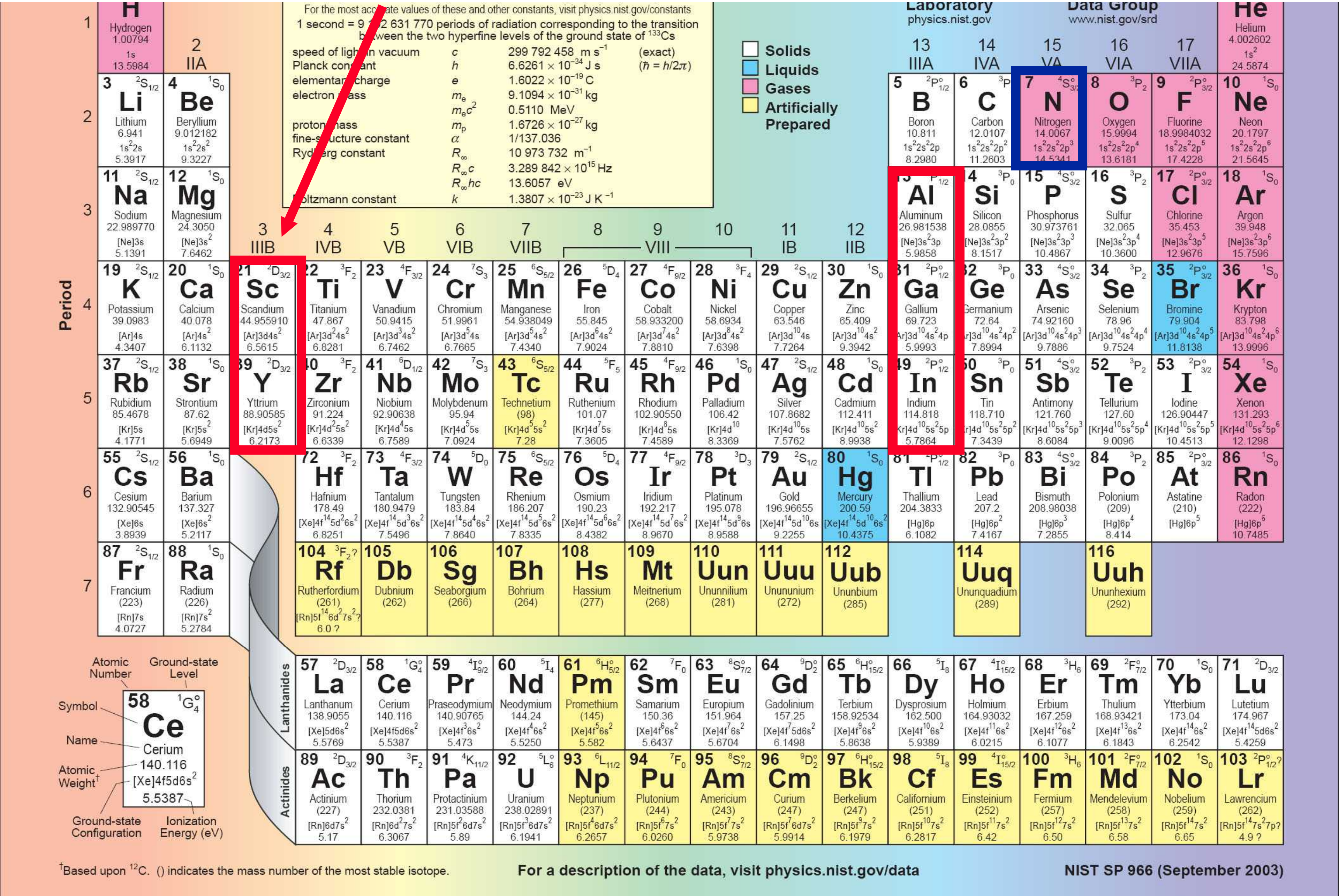
Calculated assuming that bandgaps energies are
3.4 eV for GaN,
2.15 eV for ScN,
0.8 eV for YN.
Assume that the bandgap changes linearly though out alloy mixture.

Should be able to cover all visible wavelengths. Same is true for InN.



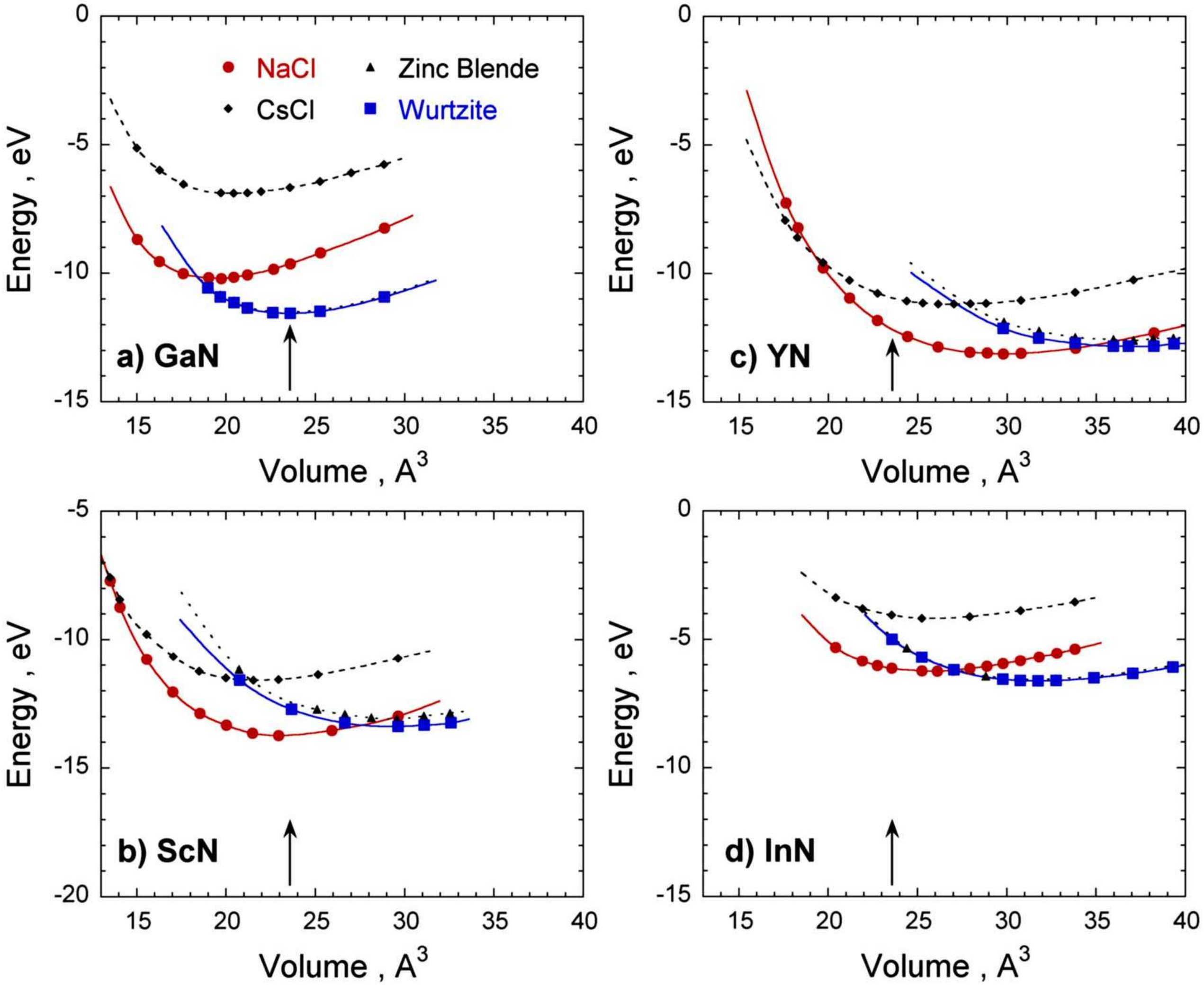
Little and Kordesch, Appl. Phys. Lett. 78, (2001)

Scandium and Yttrium “the other group III” metals



For coherent layers on GaN we might expect

DFT calculations using full potential inearized augmented plane wave (FP-LAPW) method.



From: L. Mancera, et al., phys. stat. sol. (b) 241, 2424 (2004).

Arrow denotes GaN volume at minimum energy.

Rock salt lattice constants for ScN, YN, and InN.

Note that coherent InGaN alloys can be grown on GaN up to 20 % indium, so this may not be a large concern.

Calculations by Moreno-Armenta et al., phys. stat. sol. (b) 238, 127 (2003), suggests that the wurtzite structure is preferred for ScGaN up to 65% Sc. The bandgap is also direct for wurtzite ScGaN and decreases in energy as Sc is added.

Possible issues with ScGaN or YGaN alloys

- Little is known about these alloys!
  - Are the bandgaps of ScGaN and YGaN alloys direct or indirect? Preferred lattice type on GaN?
  - Many other material parameters are also unknown.
  - ScGaN and YGaN alloys are disordered due to rock-salt lattice preference on wurtzite GaN.
- Issues with Sc and Y MO precursors.
  - Sc and Y form oxides, precursors might contain oxygen.
  - Low vapor pressure Sc and Y MOs – hard to deliver.
  - Precursors are new and untested in MOCVD growth.
- Chemistry of Sc (and Y) closer to Al than Ga or In.
  - AlN and AlGaN compounds harder to grow than GaN or low indium (< 5%) content InGaN films.
- Still have strain issues for YGaN films on GaN.

Subtask 1.1: Purchase and evaluate Sc and Y MO sources and modify the reactor is necessary.

- **Evaluate Sc and Y metalorganic (MO) sources.**
  - **<u>Compound</u>:** Initially we will explore substituted cyclopentadienyl MOs for deliver of Sc and Y precursors. Later other sources will also be evaluated. Work with Epichem.
  - **<u>Compatibility</u>:** The sources will be evaluated for compatibility with the reactor environment, vapor pressure measured, and maximum growth rates determined.
  - **<u>Purity</u>:** The sources will also need to be purified for the later stages of this work, due to the high oxygen content in starting Sc and Y precursors.
- **Modifications to the MOCVD reactor may also be necessary.**
  - **<u>Delivery</u>:** May need to add separate bubbler lines for MO delivery, heating of the MO lines, and increasing the mass flow controller size to deliver adequate MO.
  - **<u>Maintenance</u>:** The effect of using Sc and Y MOs on the reactor will also need to be evaluated. May need increased reactor maintenance.

Subtask 1.2: Add Sc and/or Y to conventional blue and green InGaN based LEDs.

- **Add Sc and/or Y directly to current InGaN based LEDs to:**
  - determine if the wavelengths of these blue and green LEDs can be extended to longer wavelengths.
  - Have quick “proof-of-concept” to validate the entire proposal and possibly uncover potential problems.
- **Once we have the precursors, we plan to start this work in a custom designed high speed rotating disk reactor.**
- **We are also hiring a post-doc to devote 100 % of their time on this project under Dan Koleske’s direction.**

Subtask 1.3: Develop growth and characterization capabilities for ScGaN and YGaN alloys.

- **Once growth of ScGaN and YGaN alloys commences we will need rapid feedback to determine the optical and structural properties of the alloys.**
  - ScGaN and YGaN will be grown on GaN on sapphire.
    - Reason: these alloys will have thicknesses of 20 to 30 Å and will be put into GaN based LEDs.
  - Growth conditions such as temperature, pressure, and flow rates will be evaluated to increase Sc and Y content.
  - Characterization such as X-ray, RBS, photoluminescence (PL) and secondary ion mass spectroscopy (SIMS) will be used to determine the Sc and Y content in the alloys.
  - During this subtask ScGaN alloys with 20 % Sc content (392 nm) and YGaN with 10% Y content (395 nm) will be demonstrated.

Have expertise in X-ray, RBS, and PL characterization of nitrides at Sandia

Subtask 1.4: Demonstrate ScGaN with 50% Sc content and YGaN with 30% Y content.

- **This subtask is a continuation of subtask 1.3, however,**
  - the Sc content in the alloy will be increased to 50% (446 nm).
  - the Y content in the alloy will be increased to 30% (475 nm).
  - XRD will be used to verify the crystal structure of the ScGaN and YGaN alloys.
  - SIMS used to determine Sc and Y content.
  - PL will be used to determine the wavelength shift vs. Sc and Y content in the alloys.

Subtask 1.5: Determine PL wavelength dependence on the Sc and Y contents in alloys.

- **For this subtask, the alloy growth will be varied to improve the crystalline structure.**
  - Growth parameters that most influence the crystalline structure will be determined.
  - PL will be used to determine the wavelength shift as a function of Sc and Y content in the alloys.
  - The alloy content will be determined using XRD, RBS, and possibly SIMS if needed.
  - At the conclusion of this subtask, we should know the Sc and Y contents that will be needed to achieve, green, yellow and orange wavelengths.

Budget Period Tasks and Schedule

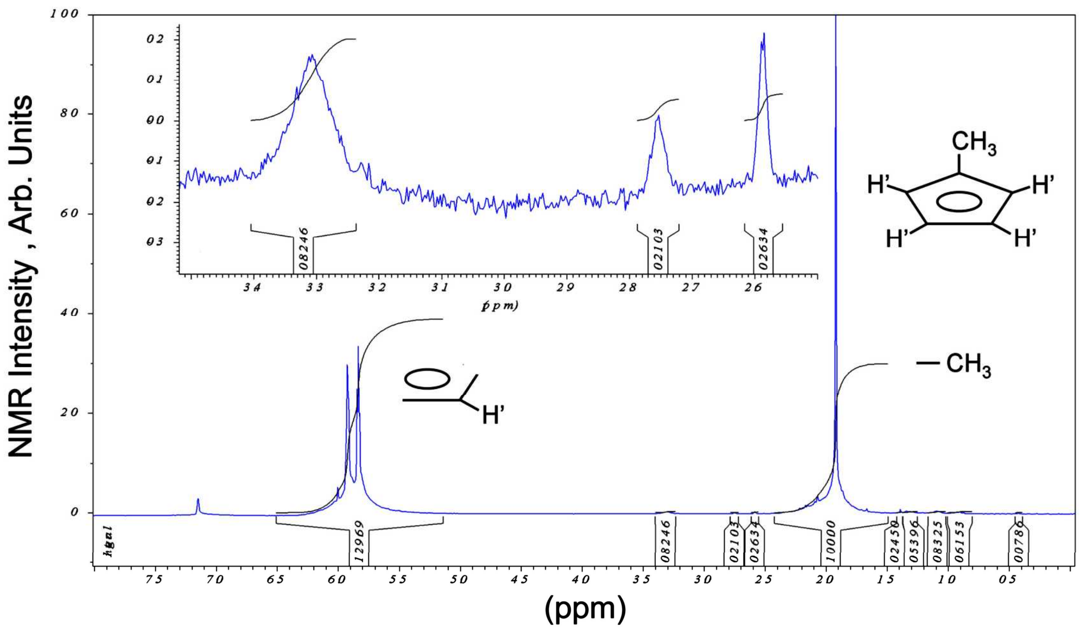
- **Task 1 - MOCVD growth of ScGaN and YGaN alloys – year 1.**
  - **Goal:** develop ScGaN and YGaN alloys and use them as active layers in green and yellow LEDs.
  - **Work will include**
    - evaluating MO precursors,
    - investigating the growth of ScGaN and YGaN,
    - developing methods to characterize the Sc and Y content
    - determine to what degree ScGaN and YGaN alloys increase the PL emission wavelength.
- **Task 2 - Increase brightness of InScGaN and InYGaN LEDs - year 2.**
  - **Goal:** develop ScGaN and YGaN based MQWs and LEDs with green and longer emitting wavelengths.
  - **Work will include**
    - Determining MQW wavelengths using PL and LED wavelengths and power output through "quick-test" and full LED fabrication.
    - Increase Sc and Y contents to produce the desired green, yellow, and orange wavelengths.
    - Determine feasibility of InScGaN and InYGaN based-LEDs.

Budget Period Milestones

Task 1 (First Year)	**MOCVD growth of ScGaN and YGaN alloys.**	**Completion Time**
Milestone 1.1	Purchase and evaluate metalorganic scandium and yttrium sources and modify reactor. (Critical to 1.3)	Month 2
Milestone 1.2	Add Sc and/or Y to conventional blue and green InGaN-based LEDs. - Achieve a wavelength shift of 20 nm without loss in output power.	Month 5
Milestone 1.3	Develop ScGaN and YGaN growth and character-ization capabilities. -Achieve ScGaN alloys with 20% Sc (392 nm) and YGaN alloys with 10% Y (395 nm). (Critical to 1.4)	Month 7
Milestone 1.4	Achieve ScGaN alloys with 50% Sc (446 nm) and YGaN alloys with 30% Y (475 nm). (Critical to 1.5)	Month 9
Milestone 1.5	Determine PL wavelength dependence on Sc and Y contents in alloys. - Determine target Sc and Y concentration needed in alloys to achieve green, yellow, and orange LEDs. (Critical to Task 2)	Month 12

Characterization of yttrium precursor

NMR spectra of the tris-methylcyclopentadienylyttrium, $(Mecp)_3Y$. Hydrogen peaks from the cyclo-pentadienyl ring (labeled H’) occur near 5.9 ppm and hydrogen peaks form the methyl groups (labeled H) occur near 2.0 ppm. From the NMR, the material does not show any organic impurities. There appears to be some oxygen species in <100 ppm concentration.



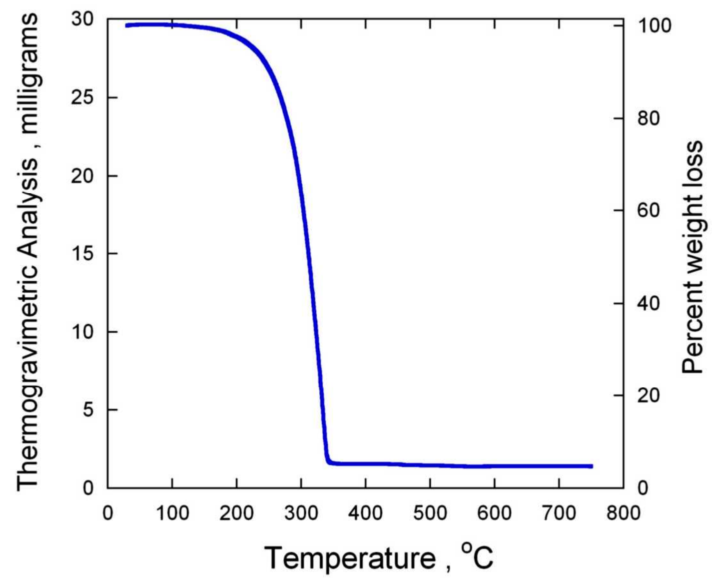
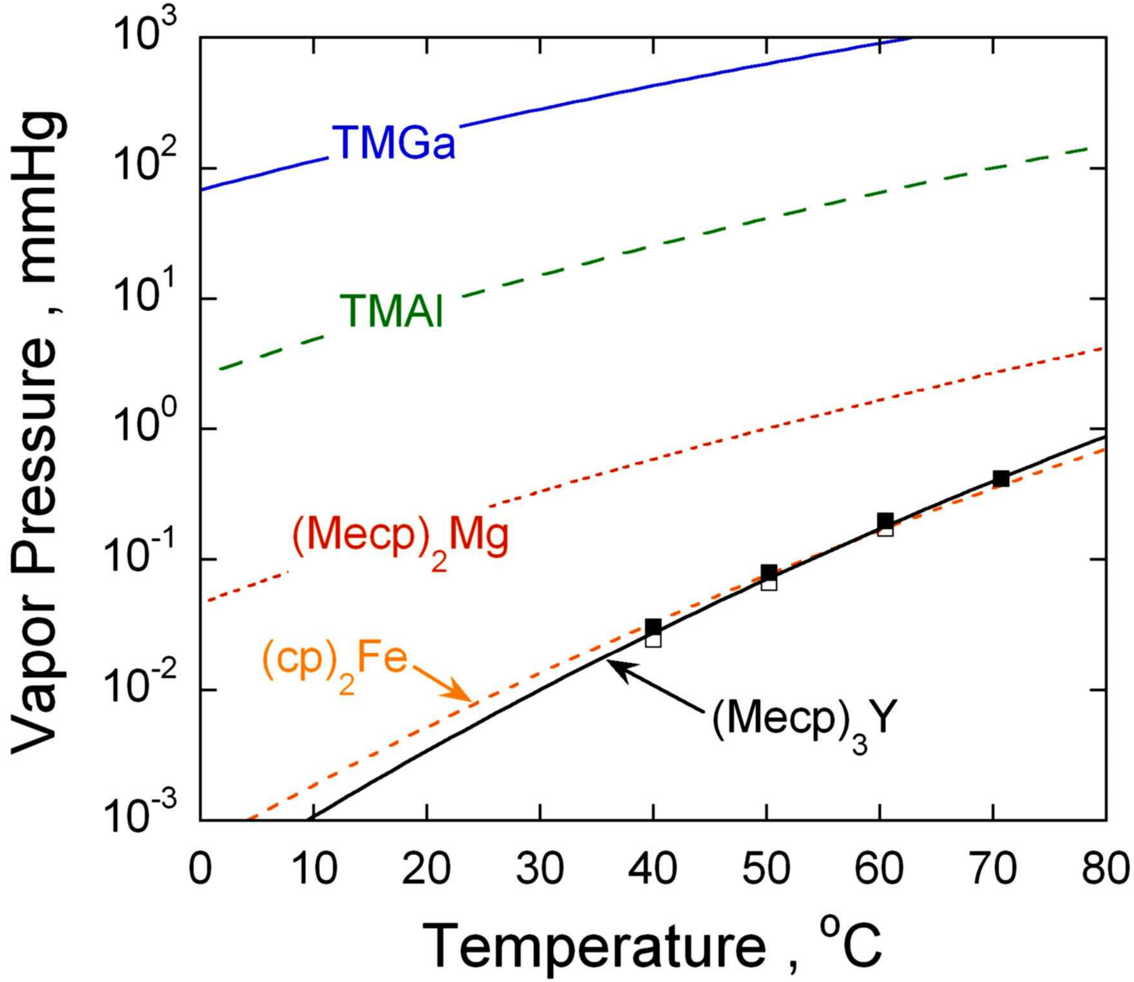


Fig. 2. Thermogravimetric (TGA) analysis of the yttrium precursor. The TGA analysis indicated a very clean material with a low residue of < 5 %, while residue due to the yttrium metal alone would have been around 27 %.

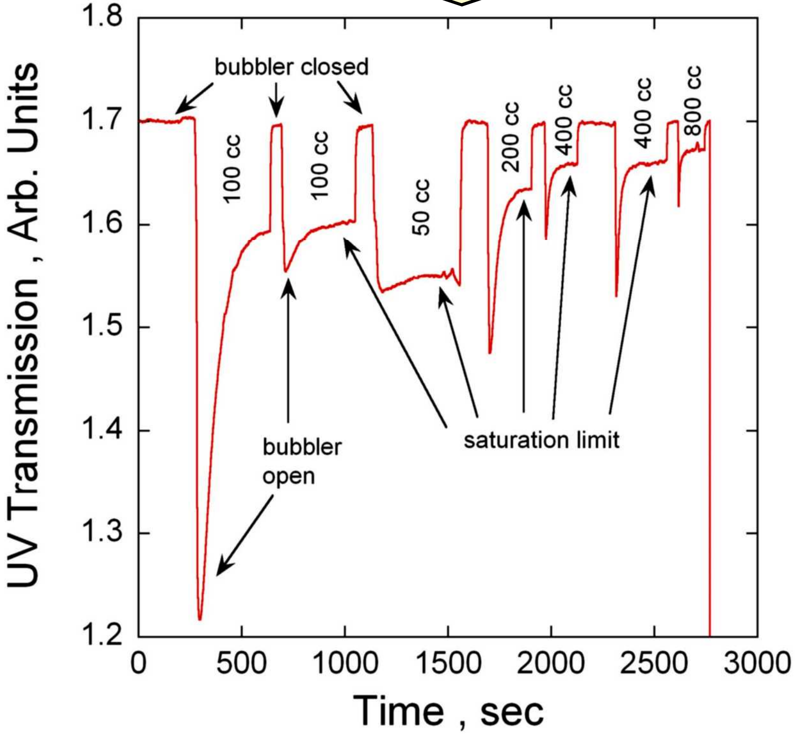
Yttrium precursor has a low vapor pressure

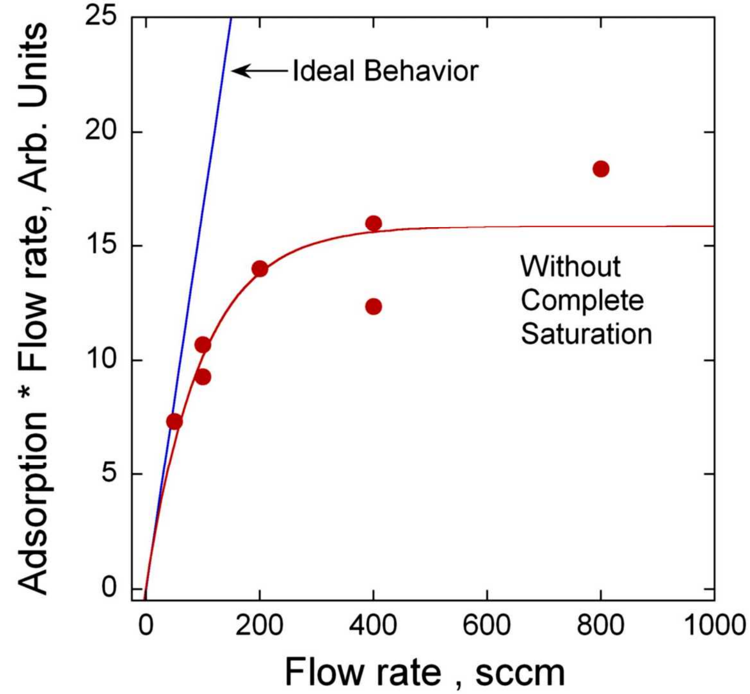


Vapor pressure curves vs. temperature for the $(Mecp)_3Y$ compound (open and filled squares and black solid line) and other common metalorganic precursors used for growth and doping of the group III nitrides.

UV transmission measurement of precursor delivery

The UV transmission through the cell for different bubbler flow rates is shown. The bubbler loop pressure was held at 600 torr and bubbler temperature at 50.7 °C. Note that once the bubbler is first opened there is a larger decrease in the UV transmission due to an increase in the absorption from the cyclopentadienyl groups flowing through the UV cell. Flow conditions ranged from 50 to 800 sccm.





Using the UV transmission data, the product of the UV absorption and the flow rate through the bubbler is plotted vs. the flow rate. This product should be proportional to the molar flow rate out of the bubbler. If the precursor saturates the gas phase then the ideal behavior is observed and the molar flow rate depends linearly on the flow rate through the bubbler. However if the precursor does not saturate the vapor phase then the molar flow rate will be sub-linear as shown by the data in red.