Background Story of the Invention of Efficient Blue InGaN Light Emitting Diodes

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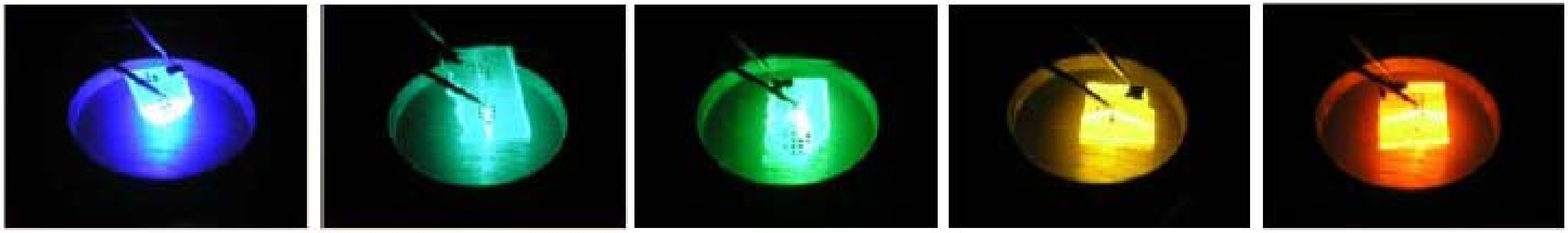
MATERIALS AND ECE DEPARTMENTS

UNIVERSITY OF CALIFORNIA, SANTA BARBARA,



2014 NOBEL LECTURE IN PHYSICS

Outline

1) **Introduction**: What is an LED?

2) **Material of Choice**: ZnSe vs. GaN

3) **The Beginning**: GaN on Sapphire

4) **Enabling the LED**: InGaN

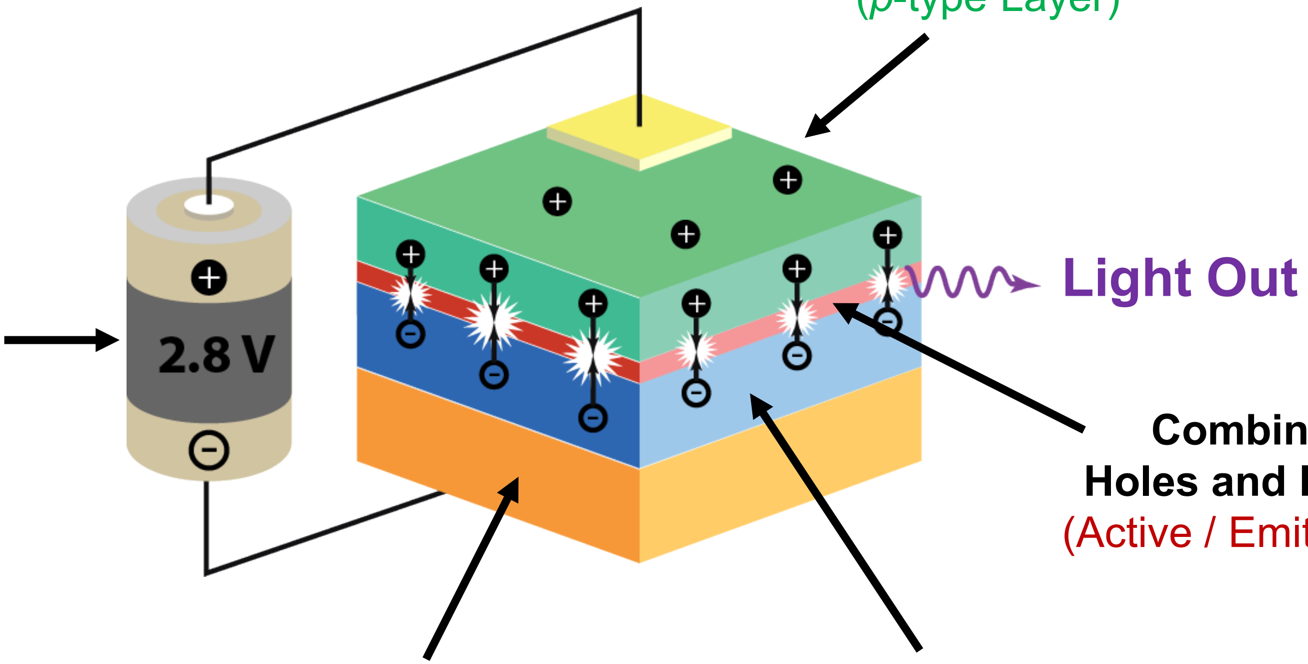
5) **Historical Perspective**

The LED

ENERGY EFFICIENT WHITE LIGHT

What is an LED?

A Light Emitting Diode (LED) produces light of a single color by combining holes and electrons in a semiconductor.



Source of Holes
(*p*-type Layer)

External Source of Electrons
(Battery)

Light Out

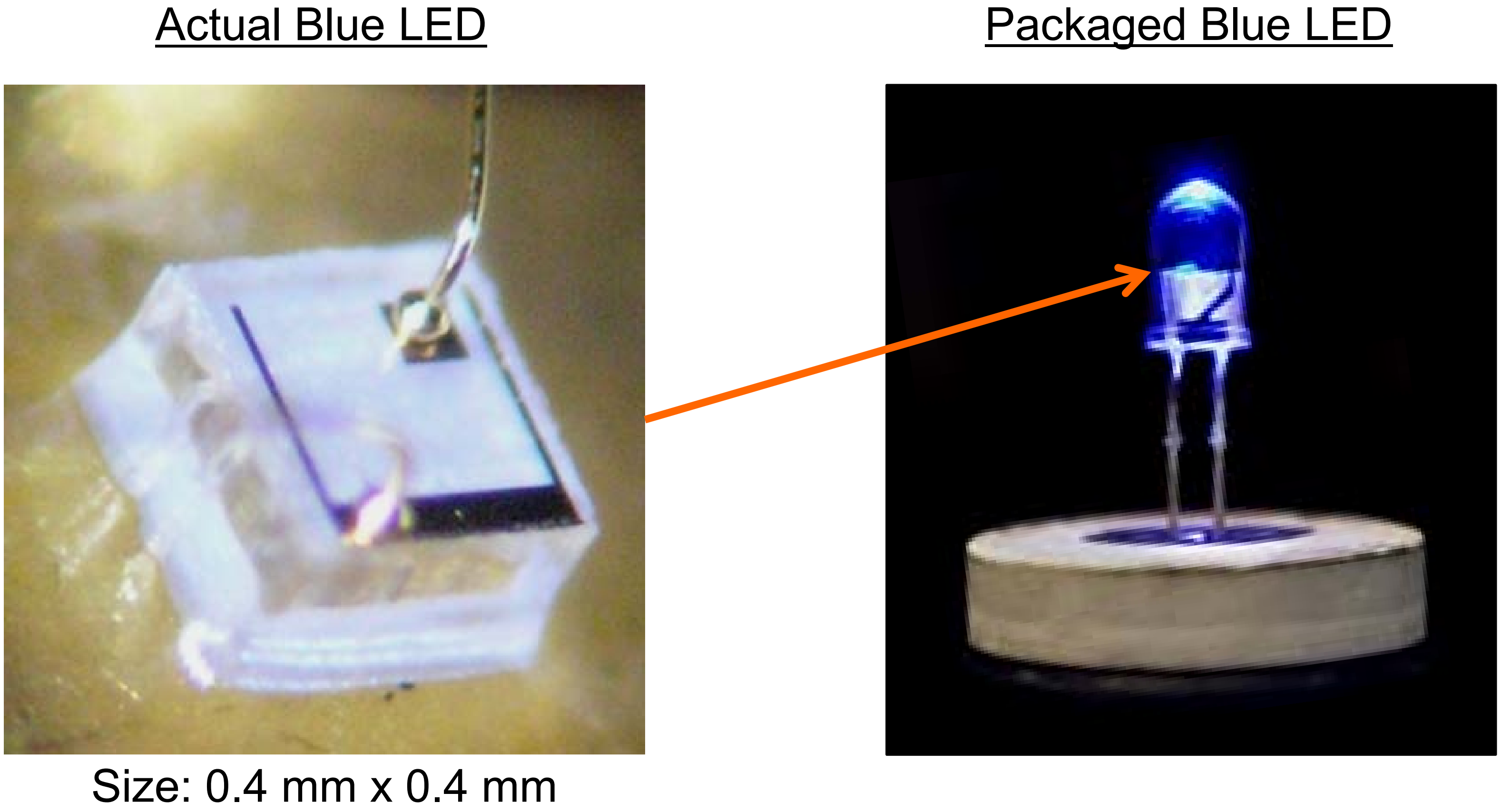
Combining of Holes and Electrons
(Active / Emitting Layer)

Substrate
(Foundation)

Source of Electrons
(*n*-type Layer)

What is an LED?

A Light Emitting Diode (LED) produces light of a single color by combining holes and electrons in a semiconductor.


Actual Blue LED

Packaged Blue LED

Size: 0.4 mm x 0.4 mm

White LED: Combining Colors

White Light: Blue + Other colors (red, yellow, green)

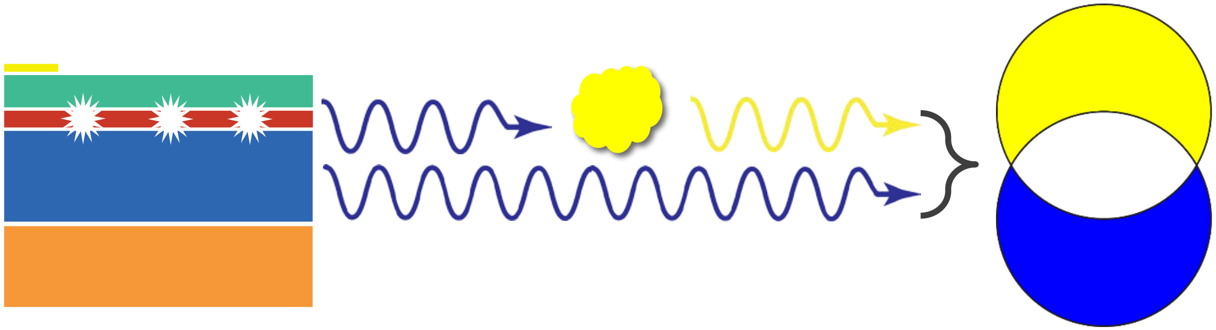
Other Colors: Convert Blue LED Light to Yellow using Phosphor.

Blue LED

Phosphor
Convert:
Blue → Yellow

White Light
= Blue + Yellow

White LED



S. Pimputkar et al., *Nature Photonics* **3** (2009) 180—182

Applications for InGaN-Based LEDs

Solid State Lighting

Decorative Lighting

Automobile Lighting

Displays

Agriculture

Indoor Lighting

Energy Savings Impact

~ **40 % Electricity Savings (261 TWh)** in USA in 2030 due to LEDs

Eliminates the need for **30+** 1000 MW **Power Plants** by 2030

Avoids Generating ~ **185 million tons of CO_2**

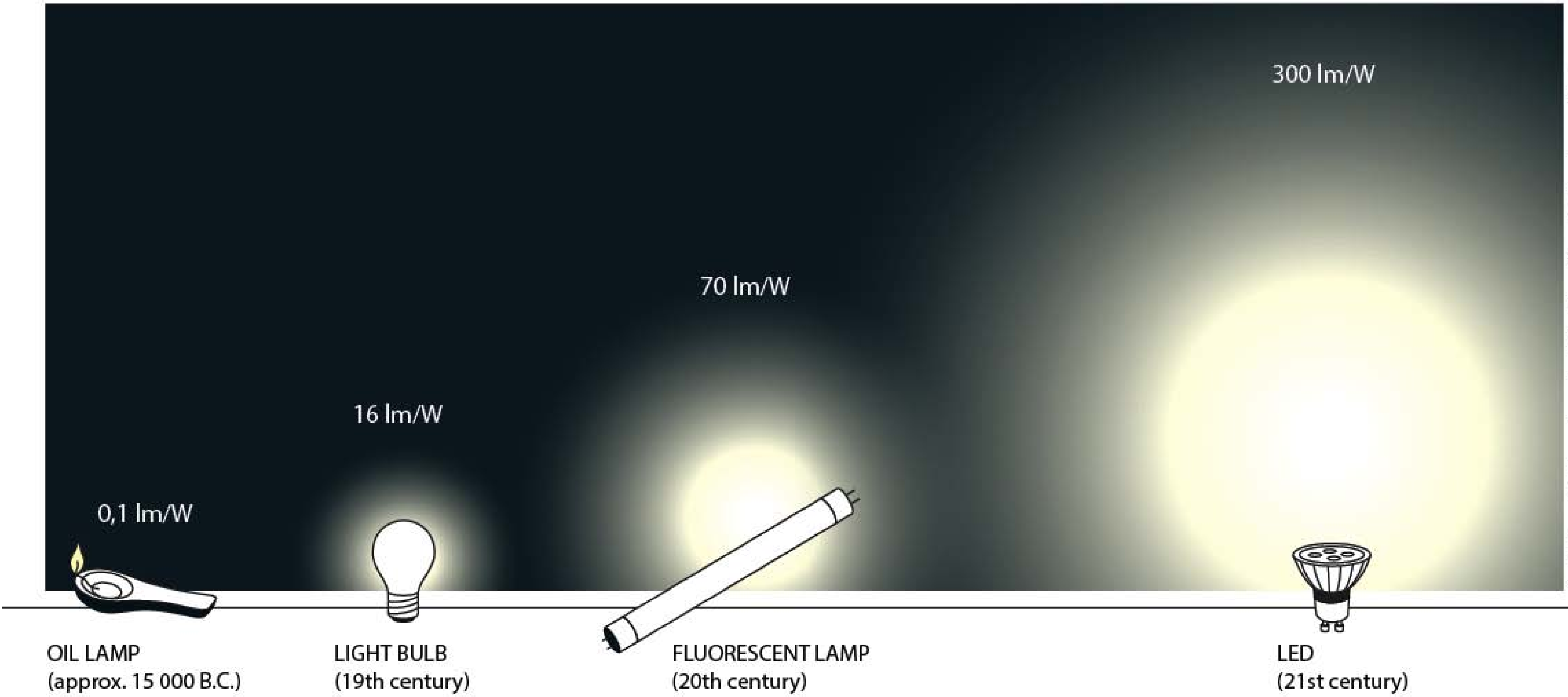


Illustration: © Johan Jarnestad/The Royal Swedish Academy of Sciences

Sources: www.nobelprize.org, US Department of Energy

1980s:
ZnSe vs. GaN

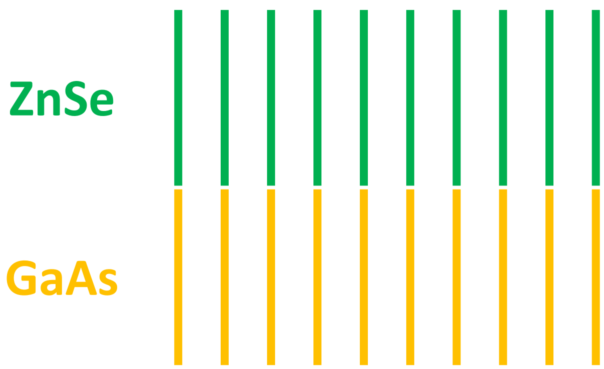
II-VI VS. III-N IN THE LATE ‘80S

Candidates for Blue LEDs: ZnSe vs. GaN

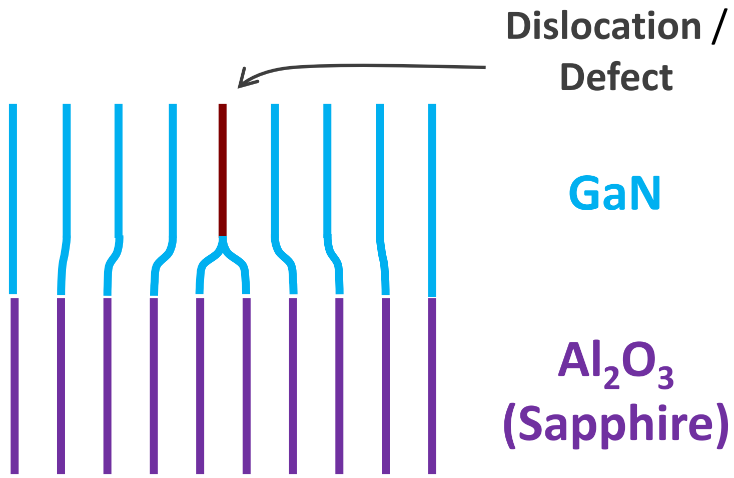
Semiconductors that possess the required properties to *efficiently* generate blue light: **ZnSe** and **GaN**

BUT … How does one ***create*** ZnSe / GaN?

Single crystal growth of material on top of different, available single crystal:

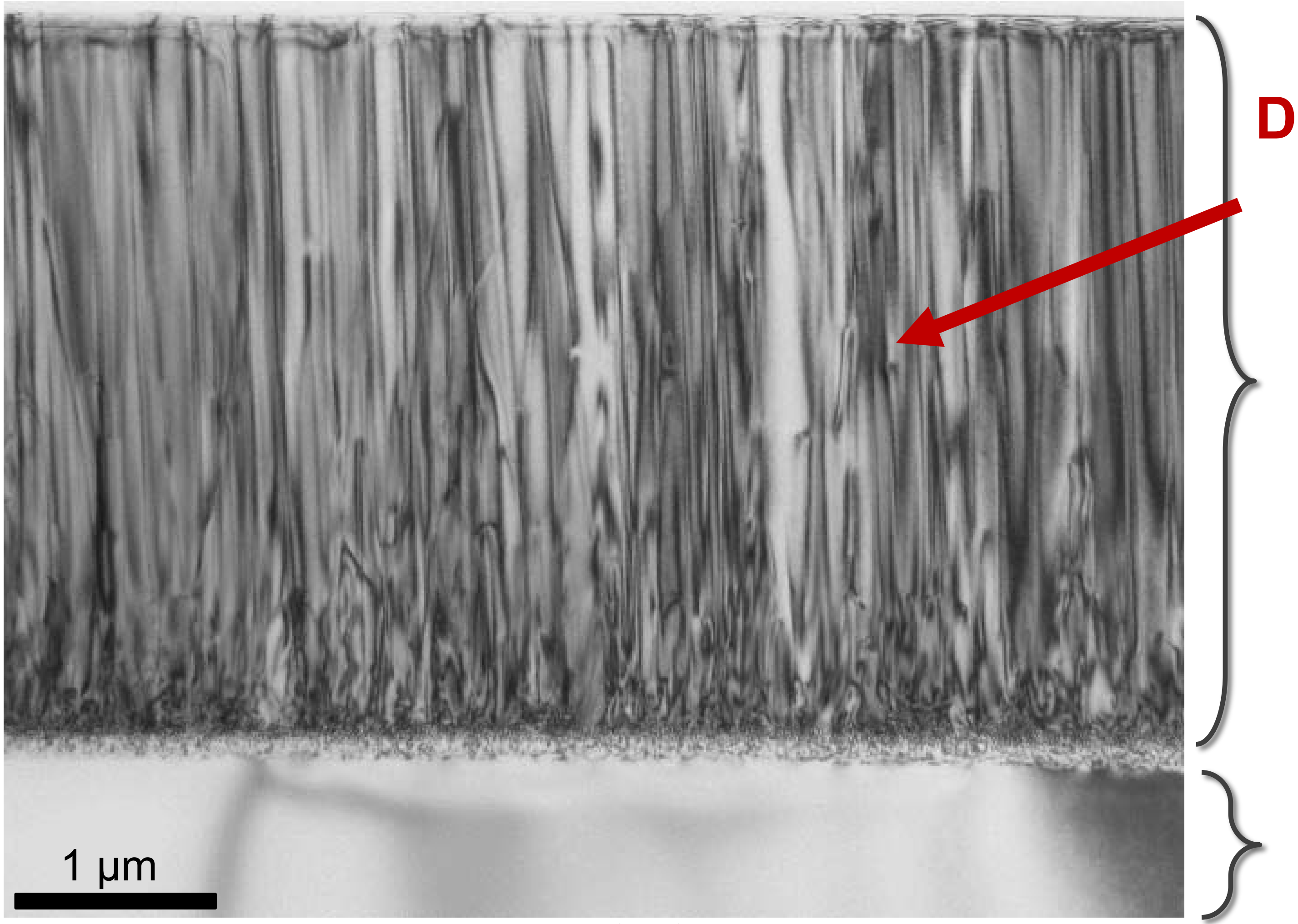


0 % Lattice Mismatch
Few Dislocations (Defects)



16 % Lattice Mismatch
Significant Dislocations (Defects)

GaN on Sapphire: Heavily Defected



Cross section Transmission Electron Microscope (TEM) of GaN on Sapphire, F. Wu *et al.*, UCSB

Too many Dislocations/ Defects

GaN

Sapphire

(Al_2O_3)

1989: ZnSe vs. GaN for Blue LED

ZnSe on GaAs Substrate

- **High Crystal Quality**: Dislocation density < 1×10^3 cm^{-2}
- **Very Active Research**: > 99 % of researchers

GaN on Sapphire Substrate

- **Poor Crystal Quality**: Dislocation density > 1×10^9 cm^{-2}
- **Little Research**: < 1 % of researchers

Interest at 1992 JSAP Conference:

- **ZnSe** – Great Interest: *~ 500 Audience*
- **GaN** – Little Interest: *< 10 Audience*
- **GaN Actively Discouraged**:
  - "GaN has no future"
  - "GaN people have to move to ZnSe material"

1989: Starting Point of Research

Seeking to get Ph.D. by writing papers

- Very few papers written for GaN
- Great topic to publish lots of papers!

Working at a small company:

- Small Budget
- One Researcher

Commonly accepted in 1970s—1980s:

- LEDs need dislocation density < 1x10^3 cm^{-2}

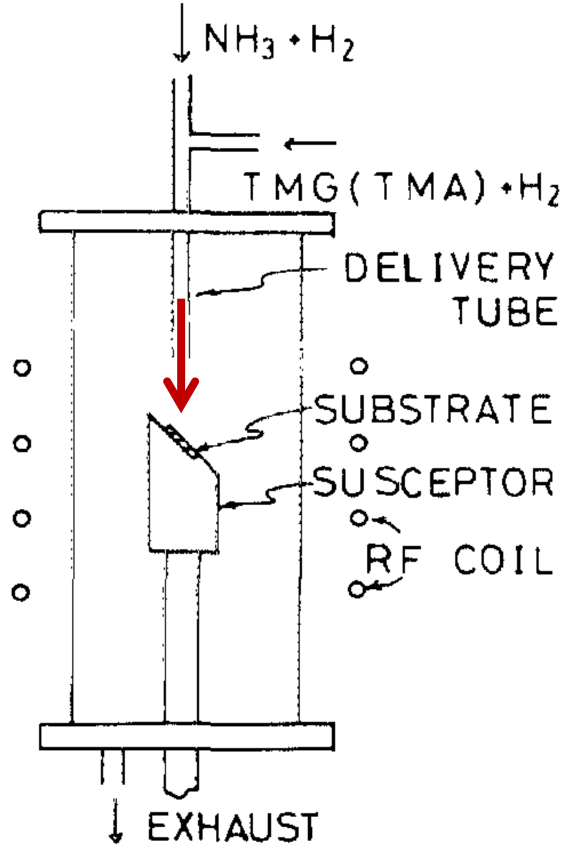
Never thought I could invent blue LED using GaN…

Development of GaN

GAN MATURES

MOCVD GaN before 1990s

MOCVD Reactor



H. Amano, N. Sawaki, I. Akasaki, Y. Toyoda, *Appl. Phys. Lett.*, **48** (1986) 353—355

MOCVD System:

- High carrier gas velocity: **~ 4.25 m/s**
- Poor uniformity
- Poor scalability
- Poor reproducibility
- Poor control

AlN Buffer Layers:

- **Crack free** GaN growth
- **High Structural Quality GaN**

But …

- **Al causes significant problems in MOCVD reactor**, undesired

Invention: Two-Flow MOCVD

1991: S. Nakamura *et al.*, *Appl. Phys. Lett.*, **58** (1991) 2021—2023

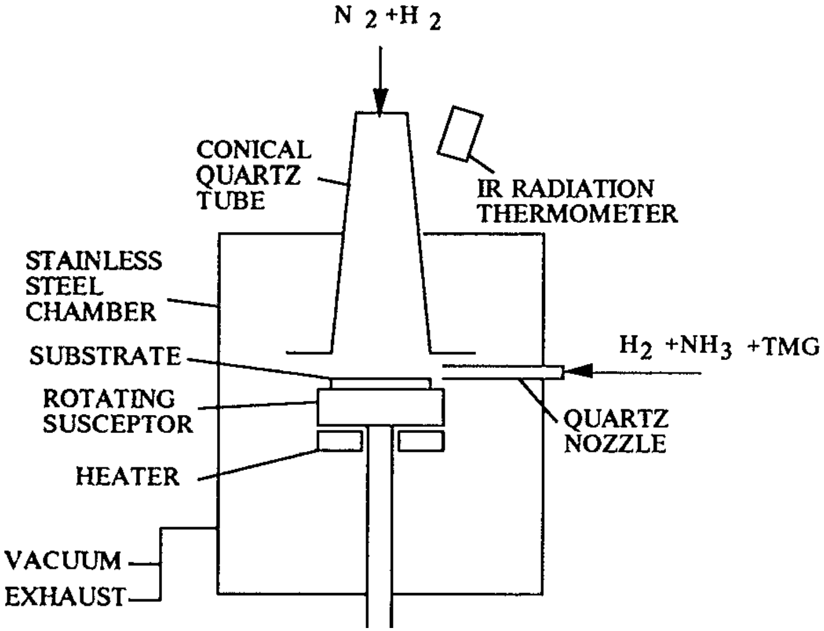
Invention of **Two-Flow** MOCVD System

(MOCVD: Metal-Organic Chemical Vapor Deposition)

Reproducible, uniform**,** high quality GaN growth possible

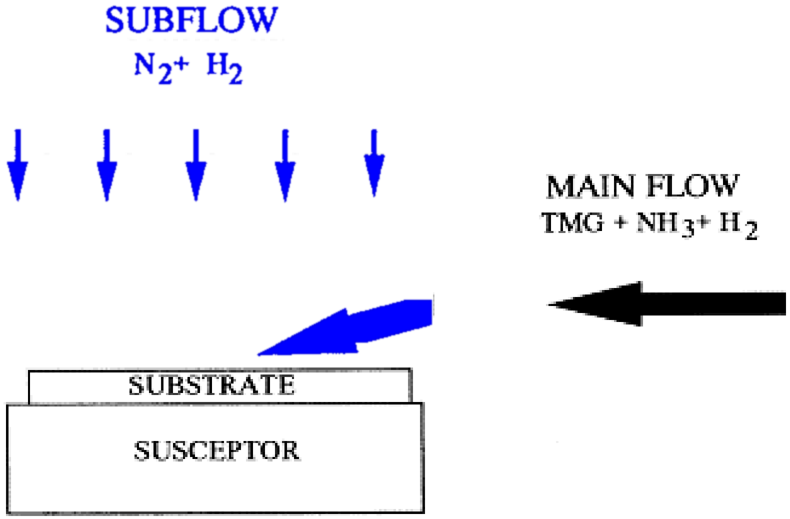
Low carrier gas velocity: ~ 1 m/s

Schematic of Two-Flow MOCVD



Main Breakthrough:

Subflow to gently "push" gases down and improve thermal boundary layer



First MOCVD GaN Buffer Layer

1991: S. Nakamura, *Jpn. J. Appl. Phys.*, **30** (1991) L1705—L1707

GaN Buffer Layer on Sapphire substrate:

High Quality GaN Growth

Smooth and Flat Surface over 2” Substrate

Highest Hall mobilities reported to date:

No Buffer: 50 cm^2/V s

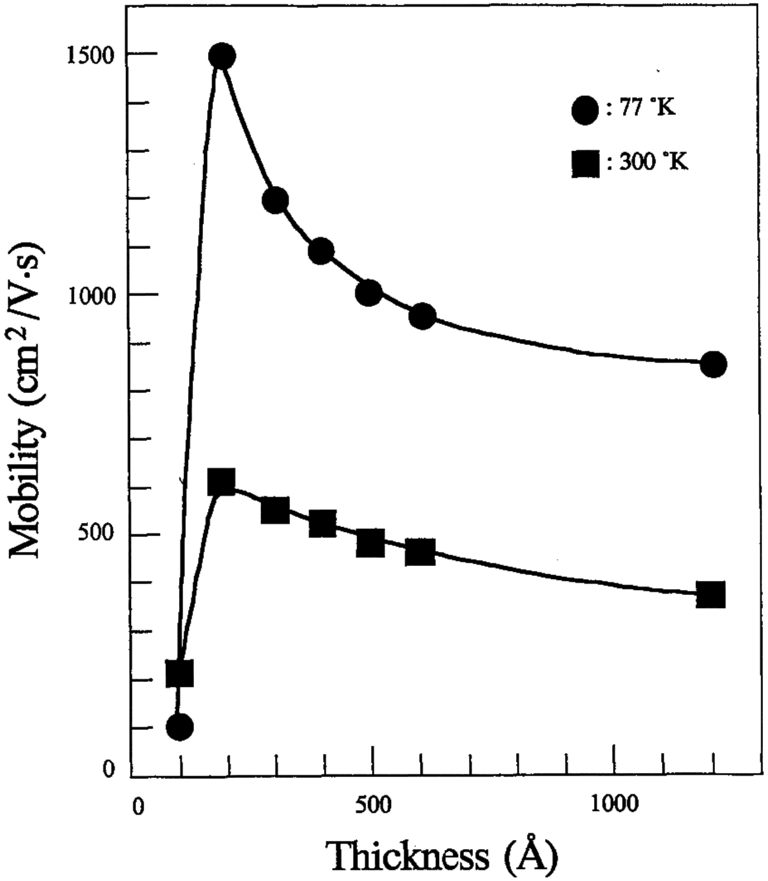
AlN Buffer: 450 cm^2/V s

Two-Flow {

No Buffer: 200 cm^2/V s

GaN Buffer: 600 cm^2/V s

Hall Mobility vs. GaN Thickness

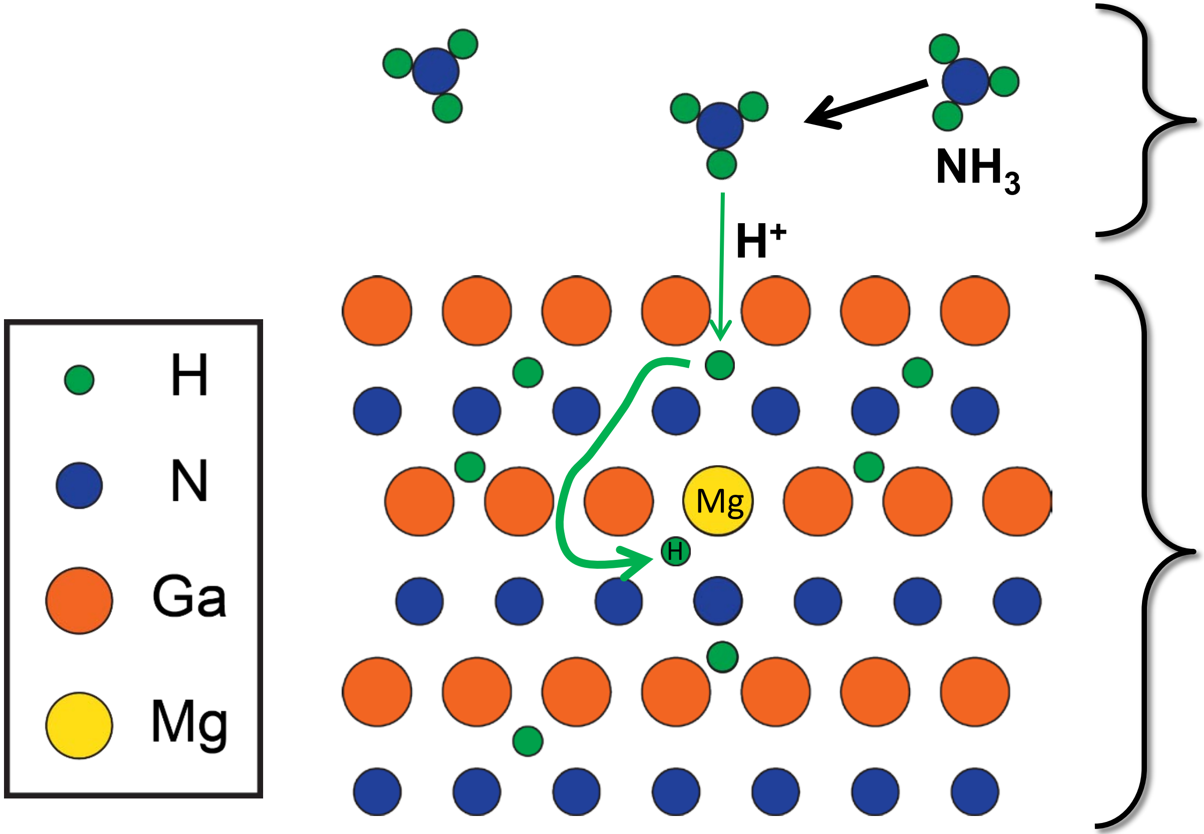


Passivation of *p*-type GaN

1992: S. Nakamura *et al.*, *Jpn. J. Appl. Phys.*, **31** (1992) L139—L142
1992: S. Nakamura *et al.*, *Jpn. J. Appl. Phys.*, **31** (1992) 1258—1266

Discovery: ***Hydrogen (H^+)*** is source of passivation of *p*-type GaN

As grown MOCVD GaN contains significant hydrogen concentrations:



MOCVD Growth Gases
contains NH_3

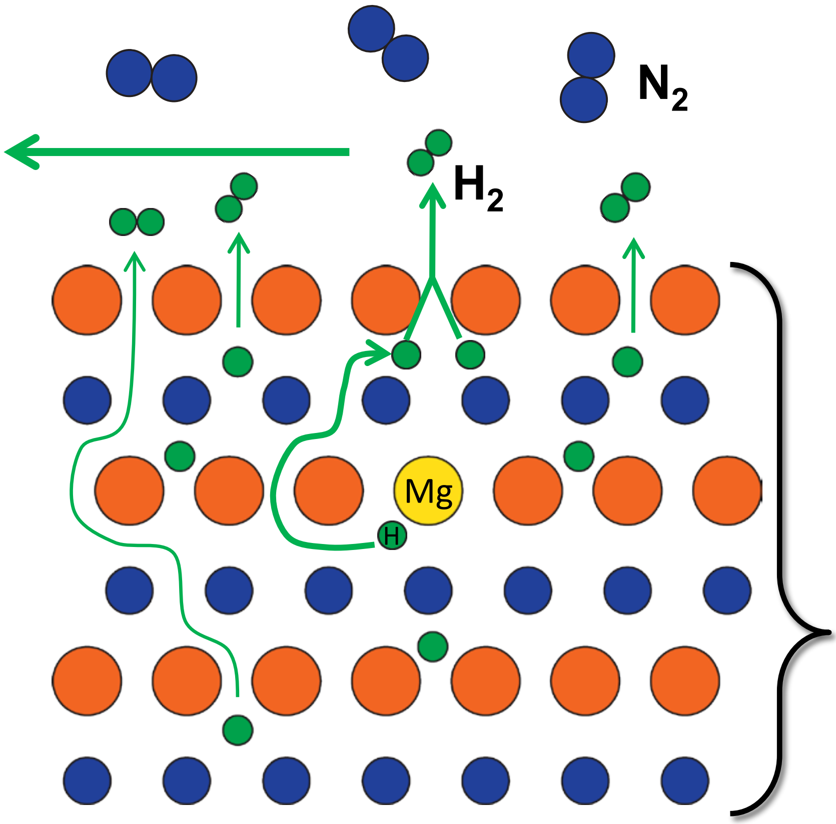
GaN:Mg
with Mg-H Complex
(not p-type, highly resistive)

Thermal Annealing of *p*-type GaN

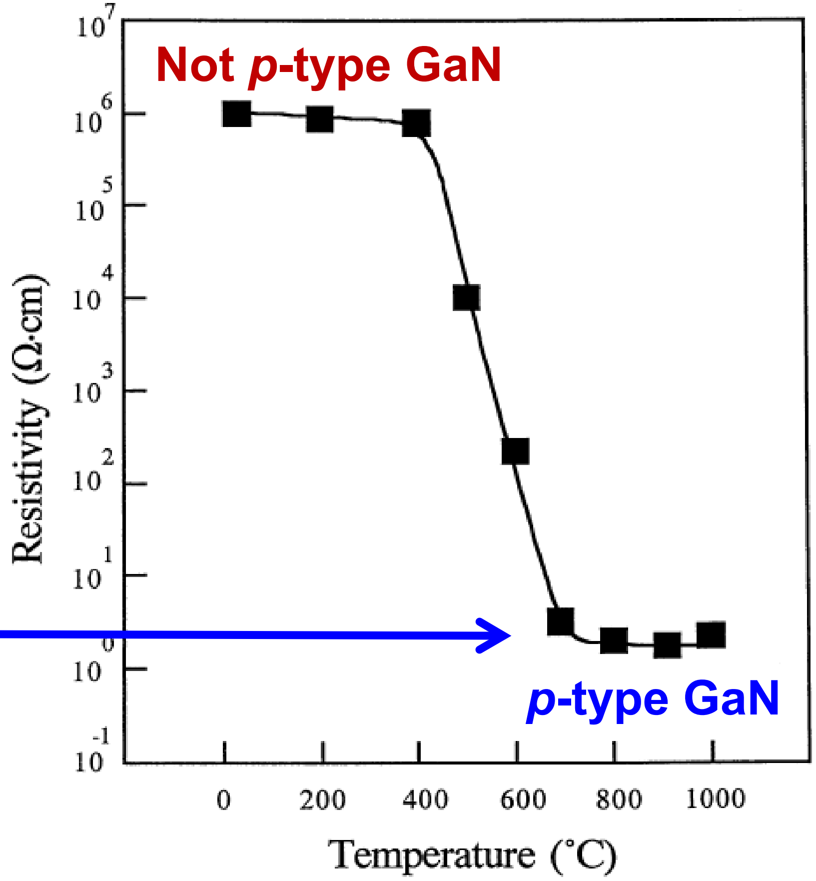
Prior: Everyone annealed in **H^+ containing** environment: **no *p*-type GaN**

Thermal Annealing in **H^+ free** environment: ***p*-type GaN, Industrial Process Compatible**

Thermal Annealing in N_2



Resistivity of MOCVD GaN:Mg vs. T


Not *p*-type GaN

p-type GaN

GaN Based Diodes

p-n GaN Homojunction

p-n GaN Homojunction

(as developed by Akasaki & Amano)

- **Good Crystal Quality**
- **Very Dim** Light Production
- Very **Inefficient**
- Output power **<< mW**
- Cannot tune color

Not Suitable for LEDs

Needed

- **Tunable** Colors
- **Efficient** Device Structure
- Output Power **> mW**

⇩

Double Heterostructure

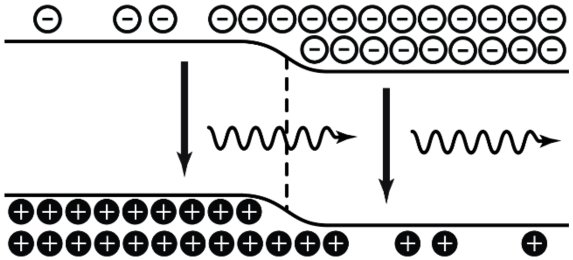
(Z.I. Alferov & **H. Kroemer**,
2000 Nobel Prize in Physics)

Confines carriers, yielding higher Quantum Efficiencies

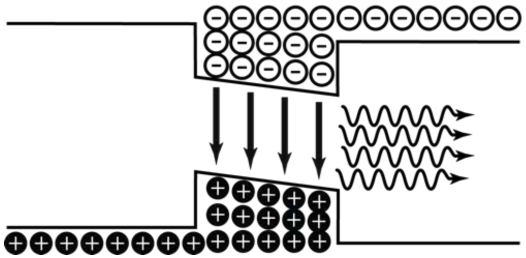
Homojunction vs. Double Heterostructure

Energy Band Diagrams

Homojunction LED



Double **Hetero**structure LED



Internal Quantum Efficiency

$$\eta_{IQE} = \frac{\text{Light generated}}{\text{Electrons injected}} = \frac{R_{radiative}}{R_{radiative} + R_{non-radiative}} = \frac{Bn^2}{An + Bn^2 + Cn^3}$$

Auger

Shockley-Read-Hall (SRH) ***Spontaneous Emission***

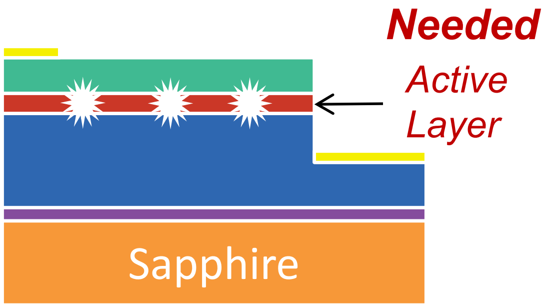
Double heterostructures **increase carrier concentrations (*n*)** in the active layer and **enhance radiative recombination** rates (more light generated).

Development of InGaN

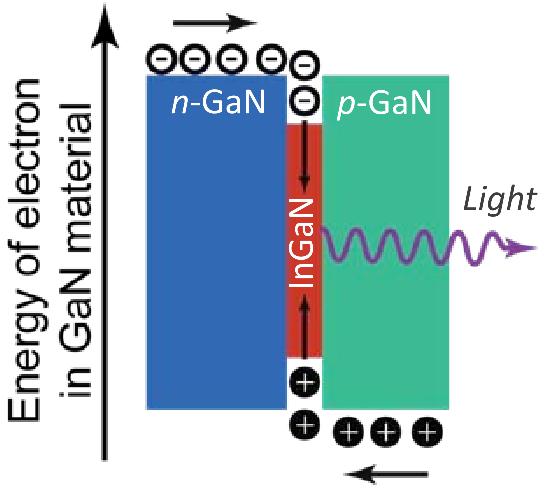
ENABLING THE HIGH-EFFICIENCY LED

InGaN: At the Heart of the LED

GaN Double Heterojunction (DH)



GaN DH-LED: Band Diagram



InGaN meets DH requirements

Smaller, Tunable Band Gap / Color by changing **Indium** in $\mathbf{In}_{\mathbf{x}}\mathrm{Ga}_{1-x}\mathrm{N}$ Alloy

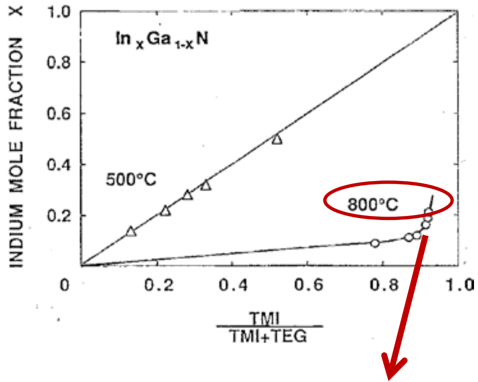
Significant Challenges though …

- Hard to **incorporate Indium** as high vapor pressure (Indium boils off)
  - Growth at substantially **lower T**:
    - Poor Crystal Quality
    - More Defects, Impurities
- Grow ***thin*** Layer (“***Quantum*** Well”)
  - Need fine Control over Growth Conditions
  - High quality interfaces / surface morphology
- Introduces **Strain** in Crystal
  - Indium **~ 20 % bigger** than Gallium

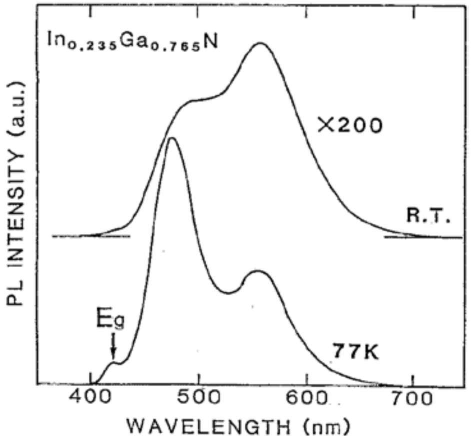
InGaN growth in 1991

Despite numerous attempts by researchers in the 1970s—1980s, high quality InGaN films with **room temperature band-to-band emission had not been achieved**.

Indium Incorporation



Photoluminescence



N. Yoshimoto, T. Matsuoka, T. Sasaki, A. Katsui, *Appl. Phys. Lett.*, **59** (1991) 2251—2253

InGaN Growth:

- **Poor quality** at low T
- Low incorporation at high T
- **Hard to control In concentration**
- High impurity incorporation
- Heavily defected

InGaN Luminescence:

- **No band-to-band light emission at room temperature** (fundamental for any LED device)
- **Significant defect emission**

High Quality InGaN Layers

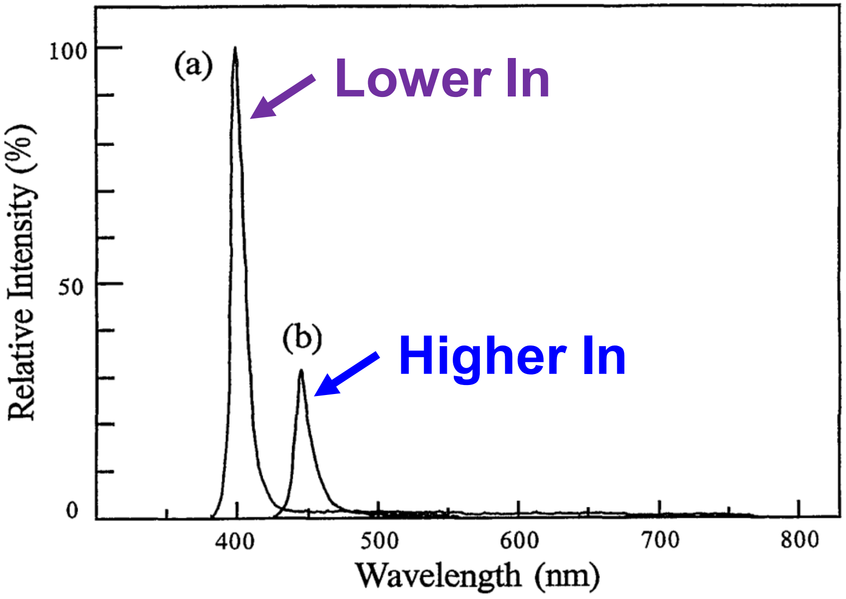
1992: S. Nakamura *et al.*, *Jpn. J. Appl. Phys.*, **31** (1992) L1457—L1459

Enabling Technology: **Two-Flow MOCVD**

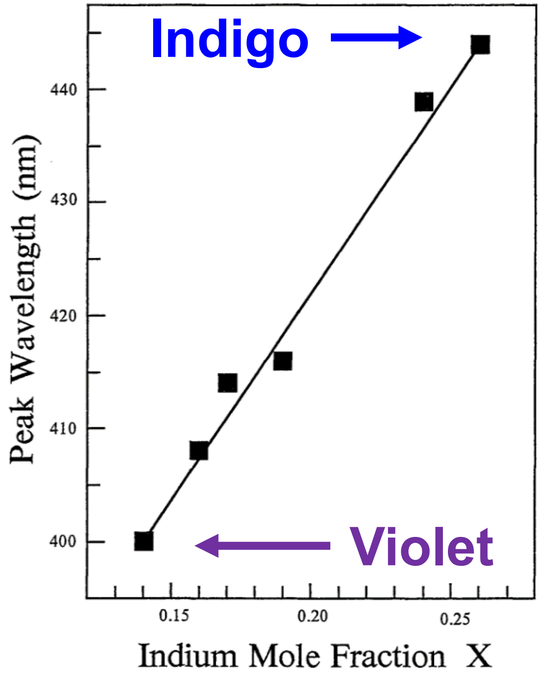
High Quality InGaN Growth with **Band-to-Band Emission**

Controllably vary Indium Concentration and hence color

Photoluminescence Spectra of InGaN



Wavelength vs. Indium Fraction



First High Brightness InGaN LED

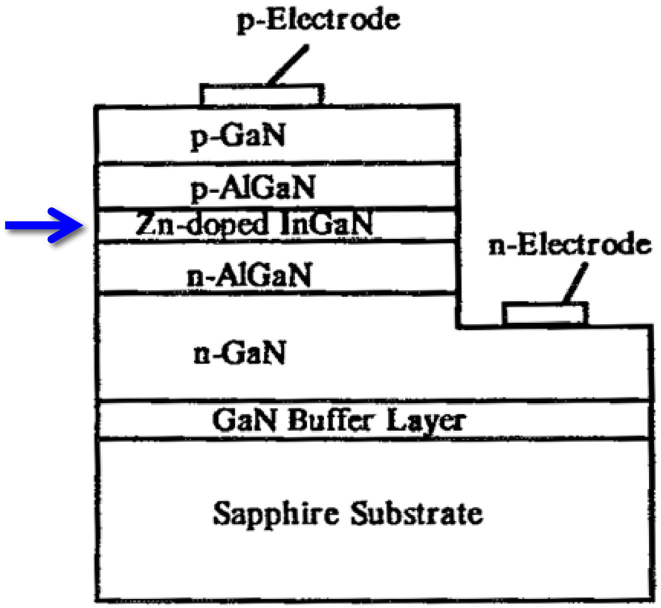
1994: S. Nakamura *et al.*, *Appl. Phys. Lett.*, **64** (1994) 1687—1689

Breakthrough Device with Exceptional Brightness

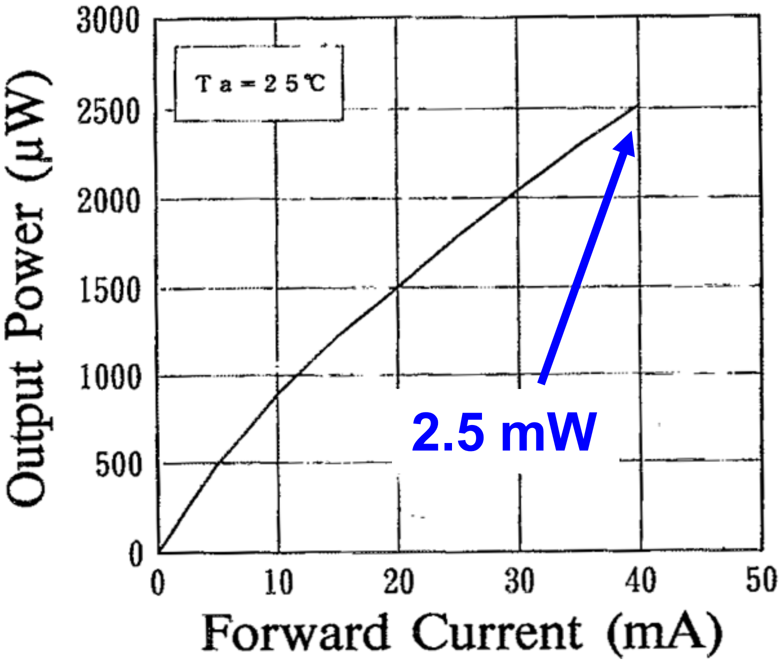
(2.5 mW Output Power @ 450 nm (Blue))

Optimization of **thin InGaN Active Layer**

InGaN/AlGaN **Double Heterostructure** LED



Output Power vs. Current



The Blue LED is born

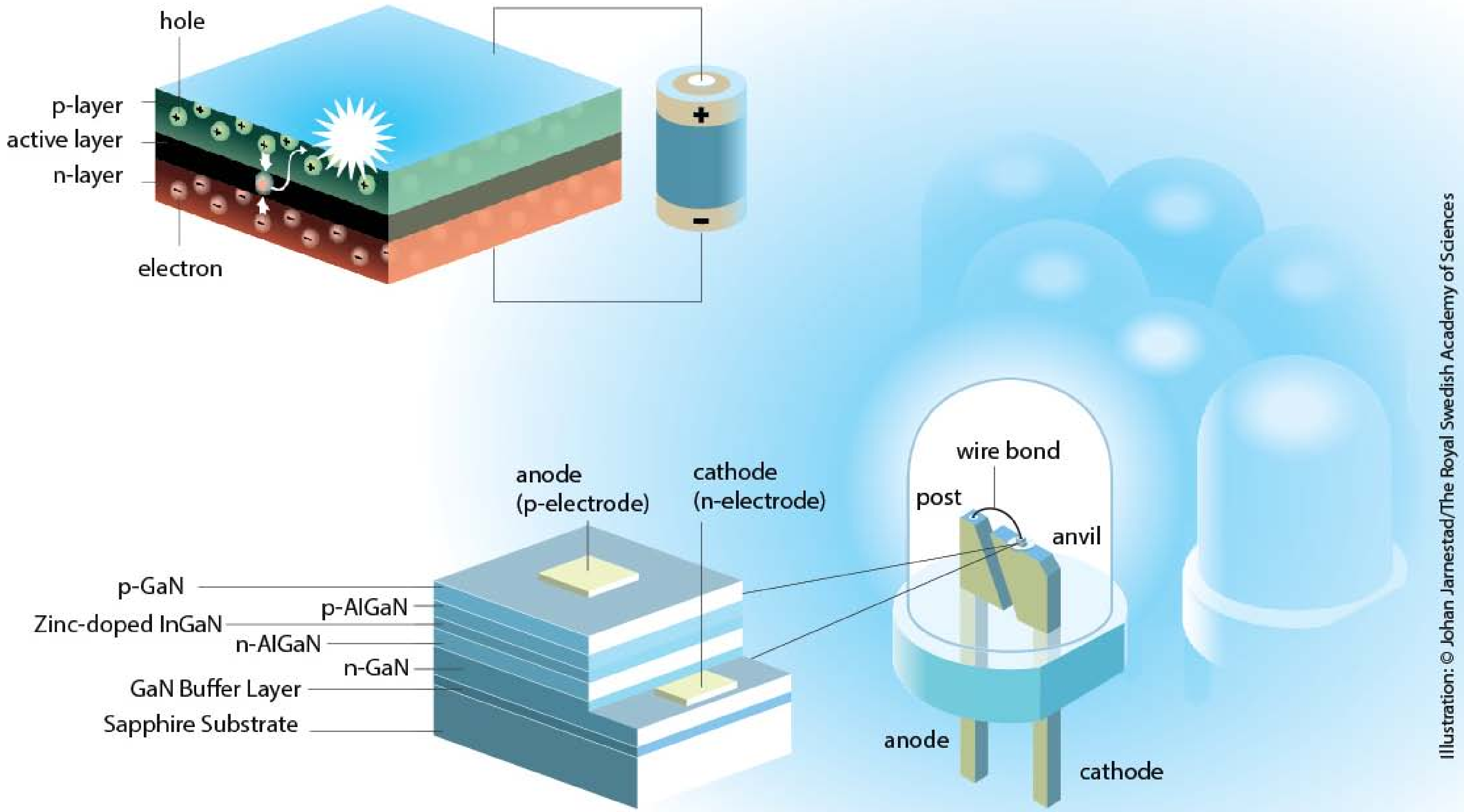


Illustration: © Johan Jarnestad/The Royal Swedish Academy of Sciences

Source: www.nobelprize.org

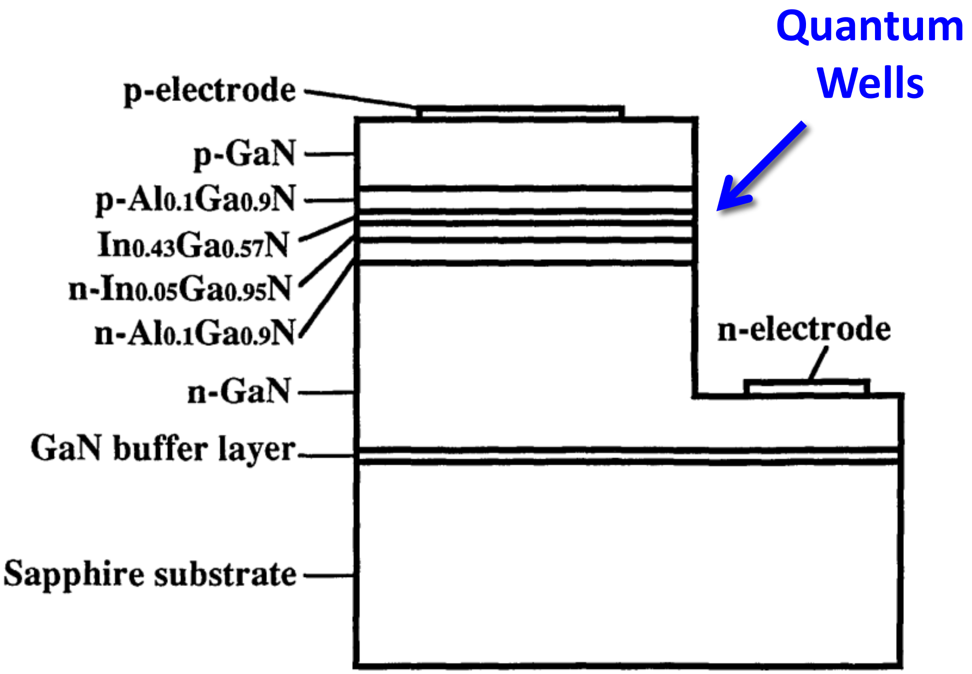
1st InGaN QW Blue/Green/Yellow LEDs

1995: S. Nakamura *et al.*, *Jpn. J. Appl. Phys.*, **34** (1995) L797—L799

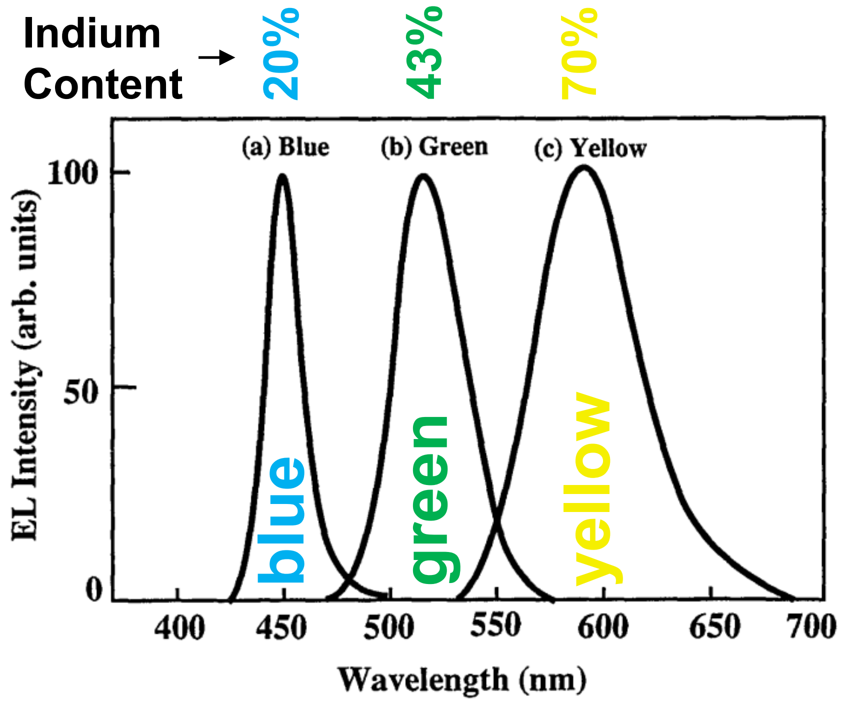
High Brightness LEDs of **varying colors** by increasing Indium content.

Demonstration of **Quantum Wells** (QWs).

Green SQW LED



Electroluminescence

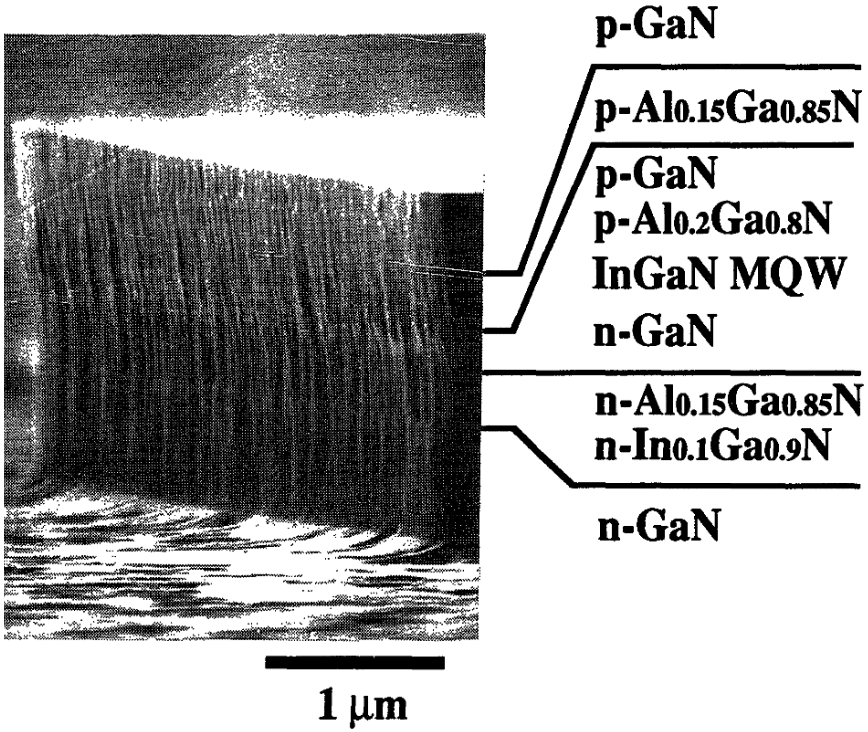


1st Violet InGaN MQW Laser Diode

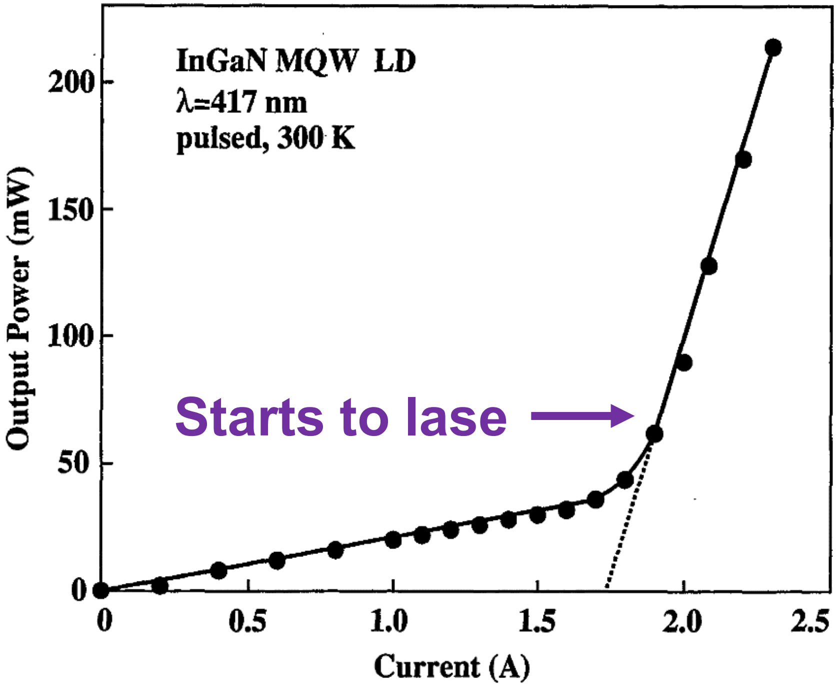
1996: S. Nakamura *et al.*, *Jpn. J. Appl. Phys.*, **35** (1996) L74—L76

First Demonstration of a **Violet Laser** using multiple QWs.

Laser Structure using InGaN

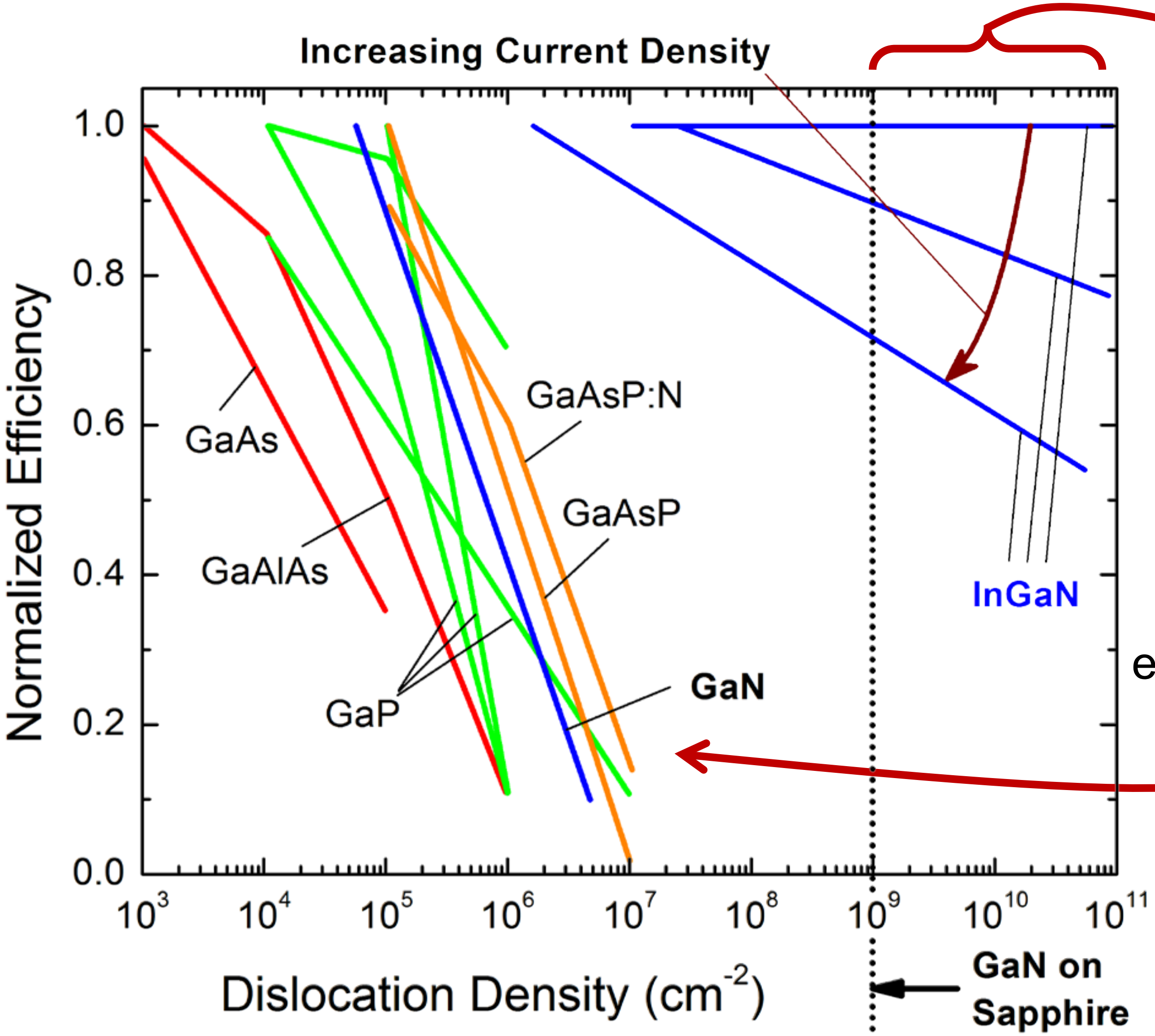


Light Output vs. Current



Starts to lase →

Comparison InGaN vs. other LEDs



Inhomogeneous: (InGaN)
Bright (!) despite high defects

Higher currents mask inhomogeneity effects (valleys fill up)

Homogeneous: *(GaN,AlGaN)*
Dim as defects "swallow" electrons **without** producing light

After: Lester *et al.*, *Appl. Phys. Lett.*, **66**, (1995) 1249

Possible Origins of High Efficiency

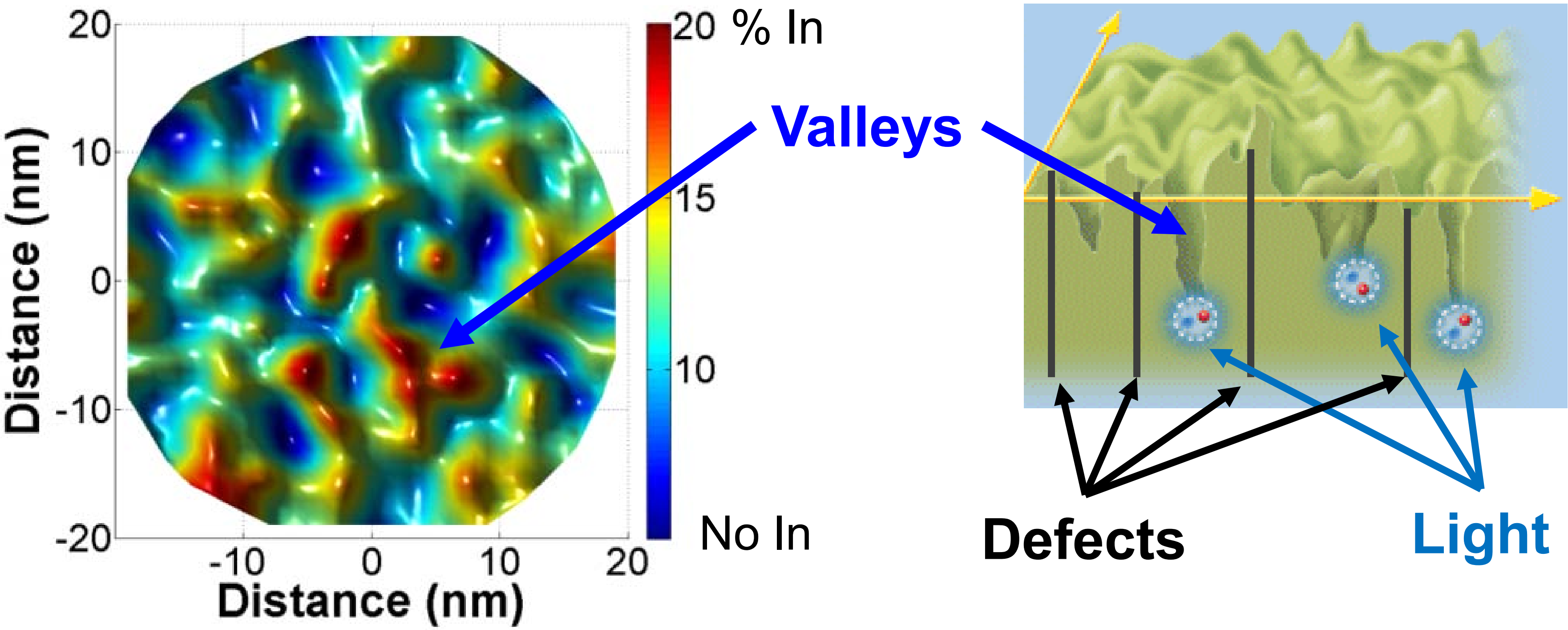
Indium Fluctuations form localized states:

Separate electrons from defects

Indium in Active Layer

Random Binomial Distribution

Side View in Energy Landscape



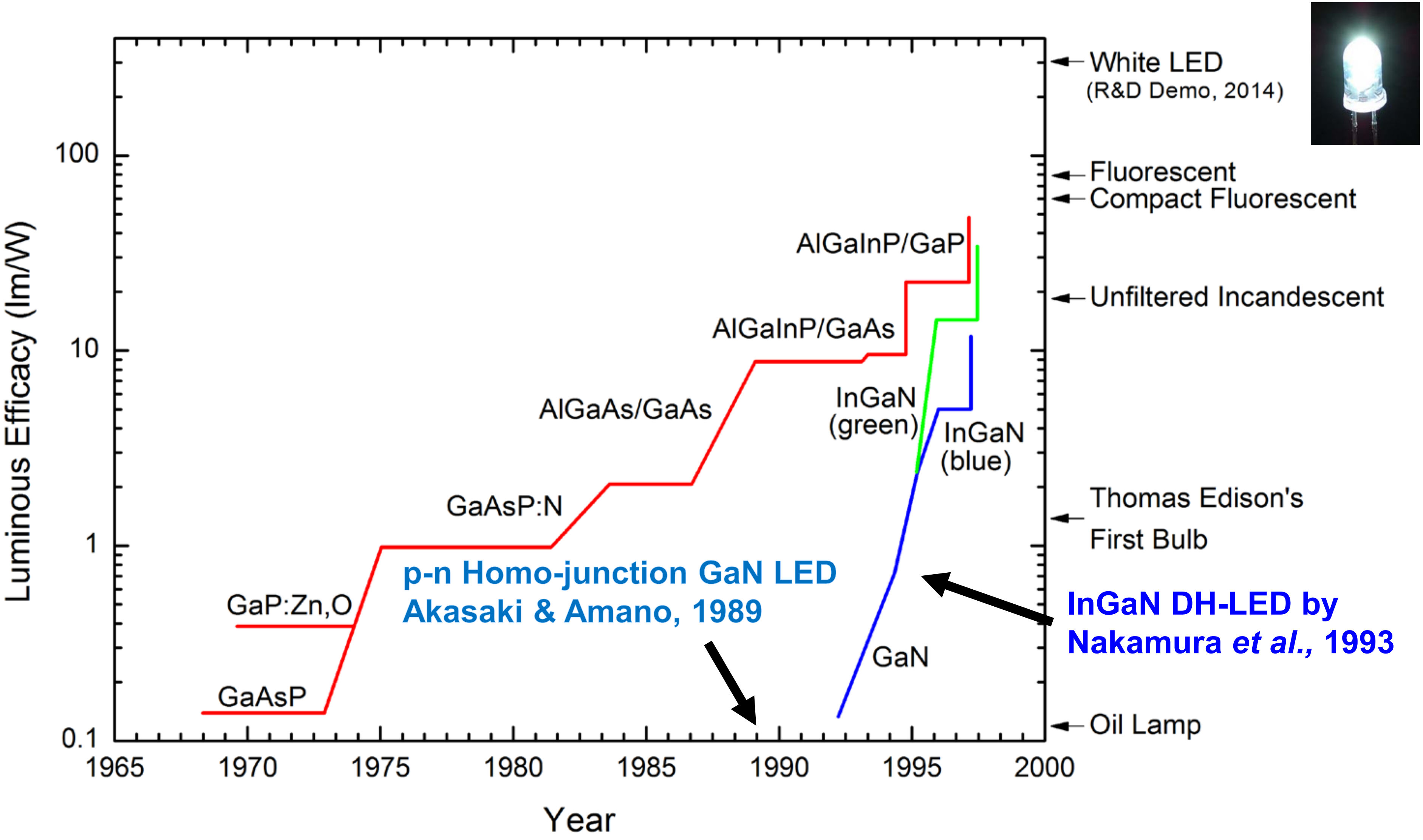
Atom Probe Tomography, D. Browne *et al.*, UCSB

Chichibu, Nakamura *et al.*, *Appl. Phys. Lett.*, **69** (1996) 4188; Nakamura, *Science*, **281** (1998) 956.

Historical Perspective

PAST, PRESENT, FUTURE

Historical: LED Efficiency

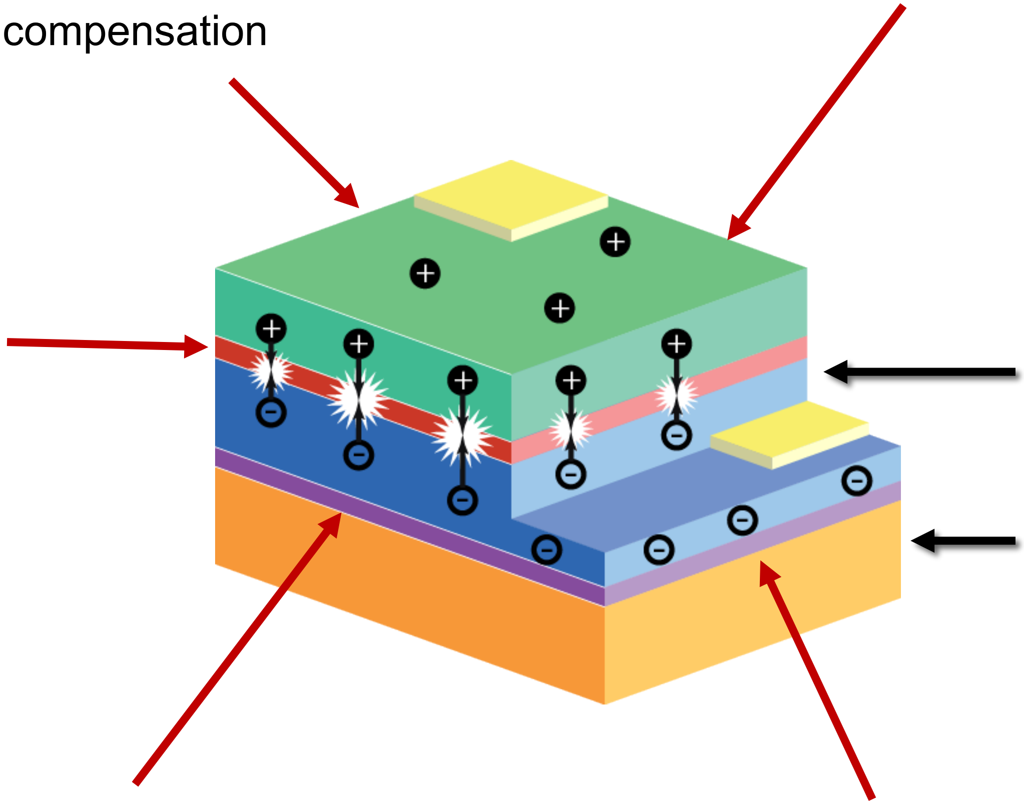


p-n Homo-junction GaN LED
Akasaki & Amano, 1989

InGaN DH-LED by
Nakamura *et al.*, 1993

After: G. Craford, Philips Lumileds Lighting Company

Contributions towards efficient blue LED



***p*-type GaN** **activated by thermal annealing** by *Nakamura*, **1991**

Hydrogen passivation was clarified as an origin of hole compensation

***p*-type GaN** **activated by Electron Beam Irradiation** by *Akasaki & Amano*, **1989**

InGaN Emitting (Active) Layer by *Nakamura*, **1992**

n-type GaN

Sapphire substrate

GaN Buffer by *Nakamura*, **1991**

AlN Buffer by *Akasaki & Amano*, **1985**

GaN/InGaN on Sapphire Research

	Year	Researcher(s)	Achievement
GaN	1969	Maruska & Tietjen	GaN epitaxial layer by HVPE
	1973	Maruska *et al.*	1st blue Mg-doped GaN MIS LED
	1983	Yoshida *et al.*	High quality GaN using AlN buffer by MBE
	1985	Akasaki & Amano *et al.*	**High quality GaN using AlN buffer by MOCVD**
	1989	Akasaki & Amano *et al.*	**p-type GaN using LEEBI** (p is too low to fabricate devices)
	1991	Nakamura	**Invention of Two-Flow MOCVD**
	1991	Moustakas *et al.*	High quality GaN using GaN buffer by MBE
	1991	Nakamura	**High quality GaN using GaN buffer by MOCVD**
	1992	Nakamura *et al.*	**p-type GaN using thermal annealing**, **Discovery hydrogen passivation** (p is high enough for devices)
InGaN	1992	Nakamura *et al.*	**InGaN layers with RT Band to Band emission**
	1994	Nakamura *et al.*	**InGaN Double Heterostructure (DH) Bright Blue LED (1 Candela)**
	1995	Nakamura *et al.*	InGaN DH Bright Green LED
	1996	Nakamura *et al.*	1st Pulsed Violet InGaN DH MQW LDs
	1996	Nakamura *et al.*	1st CW Violet InGaN DH MQW LDs
	1996	Nichia Corp.	Commercialization **White LED using InGaN DH blue LED**

UCSB's Vision

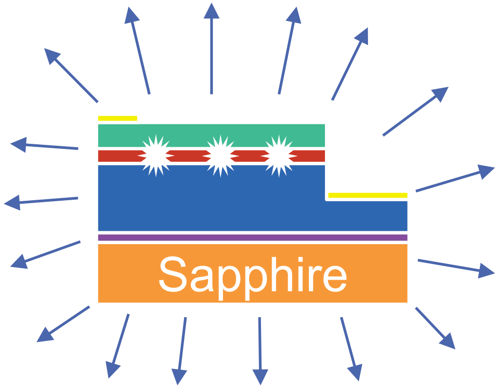
LED based White Light is great, **Laser based** is even better!

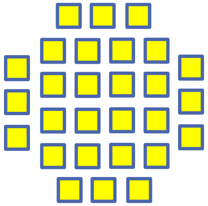
Device

60 W Incandescent Equivalent

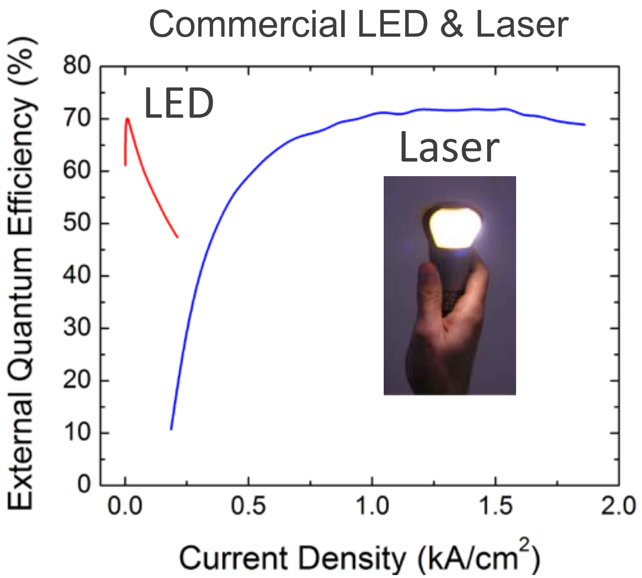
External Quantum Efficiency LED/Laser vs. Current Density

LED





$28\ mm^2$



M. Cantore *et al.*, UCSB

Laser

$0.3\ mm^2$

Acknowledgements

Nichia:

Nobuo Ogawa, Founder of Nichia Chemical Corp.

Eiji Ogawa, President

Colleagues of R&D Departments in 1989—1999

All employees of Nichia Chemical Corporation

NICHIA

UCSB:

Chancellor **Henry Yang**

Dean **Rod Alferness, Matthew Tirrell**

Profs. **Steve DenBaars, Jim Speck, Umesh Mishra**

UC SANTA BARBARA
engineering

SSLEEC
Solid State Lighting & Energy Electronics Center