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

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2014 NOBEL LECTURE IN PHYSICS
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
A Light Emitting Diode (LED) produces light of a single color by combining holes and electrons in a semiconductor.
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 → White Light

- Blue LED
- Phosphor: Convert Blue to Yellow
- White Light: Blue + Yellow

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 CO₂
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:

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice Mismatch</th>
<th>Dislocations (Defects)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe</td>
<td>0 %</td>
<td>Few</td>
</tr>
<tr>
<td>GaAs</td>
<td>16 %</td>
<td>Significant</td>
</tr>
<tr>
<td>Al₂O₃ (Sapphire)</td>
<td></td>
<td></td>
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<tr>
<td>GaN</td>
<td></td>
<td></td>
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</tbody>
</table>

Dislocation / Defect
GaN on Sapphire: Heavily Defected

Too many Dislocations/Defects

GaN

Sapphire (Al₂O₃)

Cross section Transmission Electron Microscope (TEM) of GaN on Sapphire, F. Wu et al., UCSB
1989: ZnSe vs. GaN for Blue LED

ZnSe on GaAs Substrate

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

GaN on Sapphire Substrate

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

Interest at 1992 JSAP Conference:

- **ZnSe** – Great Interest: $\sim 500$ 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 $< 1 \times 10^3$ cm$^{-2}$

Never thought I could invent blue LED using GaN...
Development of GaN

GaN MATURES
MOCVD GaN before 1990s

MOCVD Reactor

MOCVD System:
- High carrier gas velocity: \( \sim 4.25 \text{ m/s} \)
- 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

H. Amano, N. Sawaki, I. Akasaki, Y. Toyoda, 
Invention: Two-Flow MOCVD


Invention of Two-Flow MOCVD System
(MOCVD: Metal-Organic Chemical Vapor Deposition)

Reproducible, uniform, high quality GaN growth possible
Low carrier gas velocity: \(~ 1 \text{ m/s}\)

Schematic of Two-Flow MOCVD

Main Breakthrough:
Subflow to gently “push” gases down
and improve thermal boundary layer
First MOCVD GaN Buffer Layer


**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 cm²/V s
- AlN Buffer: 450 cm²/V s
- **No Buffer**: 200 cm²/V s
- **GaN Buffer**: 600 cm²/V s

**Hall Mobility vs. GaN Thickness**

- •: 77 °K
- ■: 300 °K

Two-Flow
Passivation of $p$-type GaN

**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. \( T \)

![Graph showing Resistivity of MOCVD GaN:Mg vs. Temperature (°C)](image)

- **Not \( p \)-type GaN**
- **\( p \)-type GaN**
**GaN Based Diodes**

**p-n GaN Homojunction**

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

**Not Suitable for LEDs**

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

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

**InGaN** meets **DH requirements**

- Smaller, Tunable Band Gap / Color by changing **Indium** in $\text{In}_x\text{Ga}_{1-x}\text{N}$ 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 $\sim 20\%$ **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.

**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

N. Yoshimoto, T. Matsuoka, T. Sasaki, A. Katsui,
High Quality InGaN Layers

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

Wavelength (nm)

Indium Mole Fraction $X$

- Violet
- Indigo
First High Brightness InGaN LED


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

- **2.5 mW**
- Forward Current (mA)
- Output Power (μW)
- $T_a = 25 \degree C$
The Blue LED is born
1st InGaN QW Blue/Green/Yellow LEDs

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

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


**Green SQW LED**

**Electroluminescence**

![Diagram of Green SQW LED with Quantum Wells and Electroluminescence spectra showing blue, green, and yellow emissions at 20%, 43%, and 70% Indium content.](image-url)
1st Violet InGaN MQW Laser Diode

First Demonstration of a Violet Laser using multiple QWs.

Laser Structure using InGaN

p-GaN
p-Al_{0.15}Ga_{0.85}N
p-GaN
p-Al_{0.2}Ga_{0.8}N
InGaN MQW
n-GaN
n-Al_{0.15}Ga_{0.85}N
n-In_{0.1}Ga_{0.9}N
n-GaN

Light Output vs. Current

InGaN MQW LD
\( \lambda = 417 \text{ nm} \)
pulsed, 300 K

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

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**Possible Origins of High Efficiency**

**Indium Fluctuations** form localized states:

Separate electrons from defects

**Indium in Active Layer**

Random Binomial Distribution

![Image of Indium in Active Layer with Random Binomial Distribution](image)

Side View in Energy Landscape

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

Historical Perspective
PAST, PRESENT, FUTURE
Historical: LED Efficiency

After: G. Craford, Philips Lumileds Lighting Company

InGaN DH-LED by Nakamura et al., 1993

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
- **InGaN Emitting (Active) Layer** by Nakamura, 1992
- **p-type GaN** activated by Electron Beam Irradiation by Akasaki & Amano, 1989
- **GaN Buffer** by Nakamura, 1991
- **AlN Buffer** by Akasaki & Amano, 1985
- **n-type GaN**
- **Sapphire substrate**
## GaN/InGaN on Sapphire Research

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

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

### Device

**LED**
- Sapphire

**Laser**
- Bulk GaN
- Phosphor Strip

### 60 W Incandescent Equivalent

- **LED**: 28 mm²
- **Laser**: 0.3 mm²

### External Quantum Efficiency

LED/Laser vs. Current Density

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M. Cantore *et al.*, UCSB

Commercial LED & Laser

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External Quantum Efficiency (%)

- **LED**: High efficiency at lower current densities
- **Laser**: Constant high efficiency across a wide range of current densities

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Current Density (kA/cm²)

- **LED**: Peaks at lower densities
- **Laser**: Consistent performance across densities

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M. Cantore *et al.*, UCSB
Acknowledgements

Nichia:

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