Fascinated Journeys into Blue Light

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CONTENTS

1. Introduction
2. Creation of GaN single crystal with excellent quality
3. Development of GaN p-n junction Blue LEDs and Laser diodes
4. Summary
Blue Light-Emitting Devices (LED, Laser diode)

[A] Energy bandgap $E_g$: 
$>2.6 \text{ eV} (< 480 \text{ nm})$ (Wide bandgap semiconductors)

[B] Energy band structure: 
Direct-transition type for conservation of electron momentum

Conservation of energy

(Internal) photo-electric effect

spontaneous emission

1. Introduction
High-performance Blue LED and Laser diode

[1] High-quality single crystal
[2] p-n junction

Depletion layer

Electron energy

Electric current

Light emission

Eg

(~3V) Applied forward voltage

p-n junction LED

1. Introduction
## Candidate materials for Blue Light-Emitters in 1960s-'70s

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<th>GaN</th>
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**Chose GaN in 1973 at Matsushita Research Institute Tokyo (MRIT) because of toughness, wider direct Eg, and non-toxicity**
GaN MIS Blue LED by HVPE

First as-grown highly n-type cathode

sapphire

Epoxy dome

n-GaN (30 μm)
i-GaN (~1 μm)

MIS Blue LED, not p-n junction LED

The brightest Blue LED at that time, however, still weak and high operating voltage

at MRIT
1. Introduction

Potential of GaN

Surface of GaN grown on sapphire by HVPE (1975-78)

- Tiny but high-quality crystallites embedded in HVPE-grown crystals
- Recognized the great potential of GaN
- Made up my mind to go back to the beginning; i.e. Crystal Growth in 1978
# Crystal growth methods for GaN

## Hydride Vapor Phase Epitaxy (HVPE)


\[
\text{GaCl} (g) + \text{NH}_3 (g) = \text{GaN} (s) + \text{HCl} (g) + \text{H}_2 (g)
\]

**Issues**: Susceptible to reverse reactions, Too fast growth rate

## Molecular Beam Epitaxy (MBE)


\[
\text{Ga} (g) + \text{NH}_3 (g) = \text{GaN} (s) + \frac{3}{2} \text{H}_2 (g)
\]

**Issues**: Prone to nitrogen deficiency, Slow growth rate (at that time)

## Metalorganic Vapor Phase Epitaxy (MOVPE), (MOCVD)


\[
\text{Ga(CH}_3)_3 (g) + \text{NH}_3 (g) \rightarrow \text{GaN} (s) + 3\text{CH}_4 (g)
\]

**Advantages**:

- No reverse reactions
- Easy to control growth rate, alloy (AlGaN, GaInN) composition, and impurity-doping

---

Decided to adopt MOVPE (1979) at MRIT
Mixing TMG (TMA) with NH$_3$ just before the reactor inlet, and
(1) High speed gas flow (2) Substrate inclined at a 45-degree angle

- Suppressed the convective gas stream, and the adduct formation
- Uniform growth, but not specular surface, still poor material quality

Started anew to MOVPE since 1981 at Nagoya University

First MOVPE system (Handmade)

Y. Koide (1985)

Exhaust

NH$_3$ + H$_2$, TMG + TMA + H$_2$

Guide

Inclined substrate (2)

0.7~20 cm/sec

Sapphire

Reactor design changed

TMG + (TMA) + H$_2$

delivery tube

110 cm/sec (1)
For epitaxial growth, it is considered to be gospel to have a lattice matching:
(e.g. Si on Si, GaAs on GaAs)
2. Creation of GaN single crystal with excellent quality

(3) Innovation in MOVPE growth method (1985)

**Low-temperature (LT-) buffer layer**

Key technologies:
1. Much higher-speed gas flow (425 cm/sec)
2. Substrate inclined at a 45-degree angle
3. Deposition of thin AlN buffer layer at about 500 °C, before the growth of GaN single crystal at about 1000 °C
2. Creation of GaN single crystal with excellent quality

**Creation of high-quality GaN (1985)**

**Until 1985**
- GaN grown by HVPE
- Many cracks, pits
- Rough surface
- Dislocations: $> 10^{11} \text{ cm}^{-2}$
- Free electron conc. $> 10^{19} \text{ cm}^{-3}$
- Electron mobility: $\sim 20 \text{ cm}^2/\text{V} \cdot \text{s}$
- Weak luminescence

**Since the late 1985**
- GaN grown by MOVPE using LT-buffer
- Crack-free, pit-free
- Specular surface
- Dislocations: $10^8 - 10^9 \text{ cm}^{-2}$
- Free electron conc. $< 10^{16} \text{ cm}^{-3}$
- Electron mobility: $\sim 700 \text{ cm}^2/\text{V} \cdot \text{s}$
- Intense luminescence

Crystal quality, electrical property, and luminescence property were dramatically improved at the same time.
2. Creation of GaN single crystal with excellent quality

Growth model of GaN using LT-buffer layer

Surface (SEM) images

Growth model

(1) As-deposited LT-AlN buffer layer

Mixture both amorphous & fine crystallites of AlN

LT-buffer layer

Sapphire

(2) 5 min GaN growth

Lateral growth of GaN dominates

GaN island

K. Hiramatsu

Direct growth for 60 min.
(No LT-buffer)

Surface (SEM) images

Growth model

(3) 10 min GaN growth

(4) 20 min GaN growth

(5) 60 min GaN growth

GaN layer of excellent quality

GaN island

Sapphire

1 μm
Realization of **p-type** GaN, AlGaN, and GaInN

**1986 Basic Technology**

- **High-quality GaN** using LT-buffer layer (Low residual impurities)

**1988**

- Found greatly enhanced blue emission of Zn doped GaN by electron irradiation (LEEBI)

**1989**

- Doped Mg using CP$_2$Mg and electron irradiation

**Achieved the first p-type GaN**

**1991**

- p-type AlGaN

**1995**

- p-type GaInN
The world’s first GaN p-n junction blue LED (1989)

GaN p-n junction Blue LED

I-V curves

0.5mA/div.

V 5V/div.

Current

M. Kito  H. Amano
3. Development of GaN p-n junction Blue LEDs and Laser diodes

Conductivity control of n-type GaN, AlGaN

1986 Basic Technology

High-quality GaN using LT-buffer layer (Low residual impurities)

1989 Doped Si into high-quality GaN using SiH$_4$
Achieved conductivity control of n-type GaN

1991 n-type AlGaN

Allowed the use of heterostructure and quantum well in the design of more efficient p-n junction light-emitting structures
On the basis of the technologies of LT-buffer layer and p-n junction heterostructures, GaN-based lasers were achieved.
Number of Papers Related to Nitrides (1965-2012)

Distinguished Important Achievements

- 1969  Single crystal GaN (H. P. Maruska et al.)
- 1971  MIS-type Blue LED (J. I. Pankove et al.)
- 1986  High-quality GaN single crystal grown with LT-buffer layer by MOVPE
- 1989  GaN p-n junction Blue LED
- 1989  Conductivity control of p- and n-type GaN
- 1990  Room temperature UV stimulated emission from GaN by optical pumping
- 1990  Growth of GaInN (T. Matsuoka et al.)
- 1991  p-type GaN by thermal annealing (S. Nakamura et al.)
- 1993  GaInN double hetero-junction Blue LED (S. Nakamura et al.)
- 1995  Stimulated emission from GaInN/GaN quantum wells by current injection
- 1996  Violet laser diode (S. Nakamura et al.)
- 1996  UV laser diode

Red characters: Akasaki and Amano group
While many researchers abandoned the development of GaN Blue LED, I have been fascinated with the research on GaN-based semiconductors, since 1973.

Through persistent efforts, with the collaboration of Hiroshi Amano, Yasuo Koide, and many students/coresearchers over many years, we invented high-quality GaN single crystal in 1986, and GaN p-n junction Blue LED in 1989.

GaN-based photonic & electronic devices are environmentally-sound, robust, and energy-saving, which benefit humanity.
Acknowledgements

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