Fascinated Journeys into Blue Light

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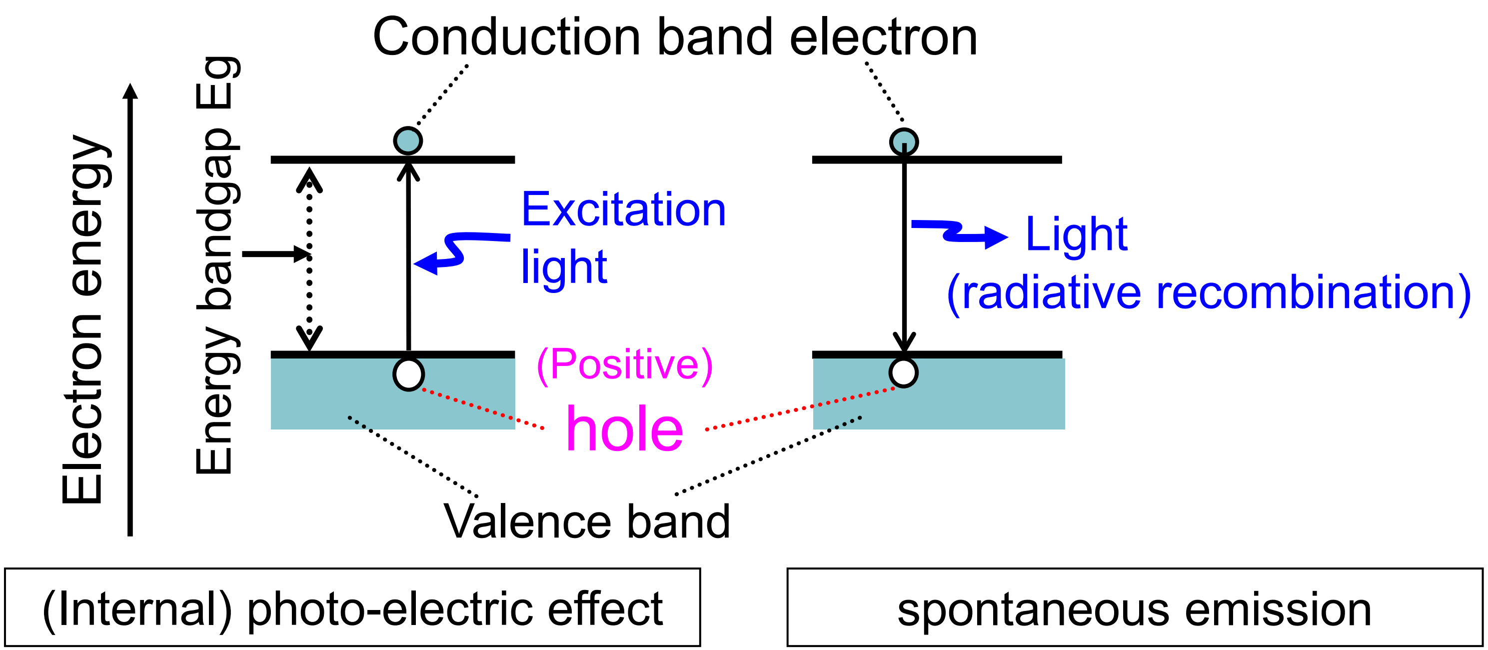
1. Introduction
2. Creation of GaN single crystal with excellent quality
3. Development of GaN p-n junction Blue LEDs and Laser diodes
4. Summary

Blue Light-Emitting Devices (LED, Laser diode)

[A] Energy bandgap Eg:
>2.6 eV (< 480 nm) (Wide bandgap semiconductors)

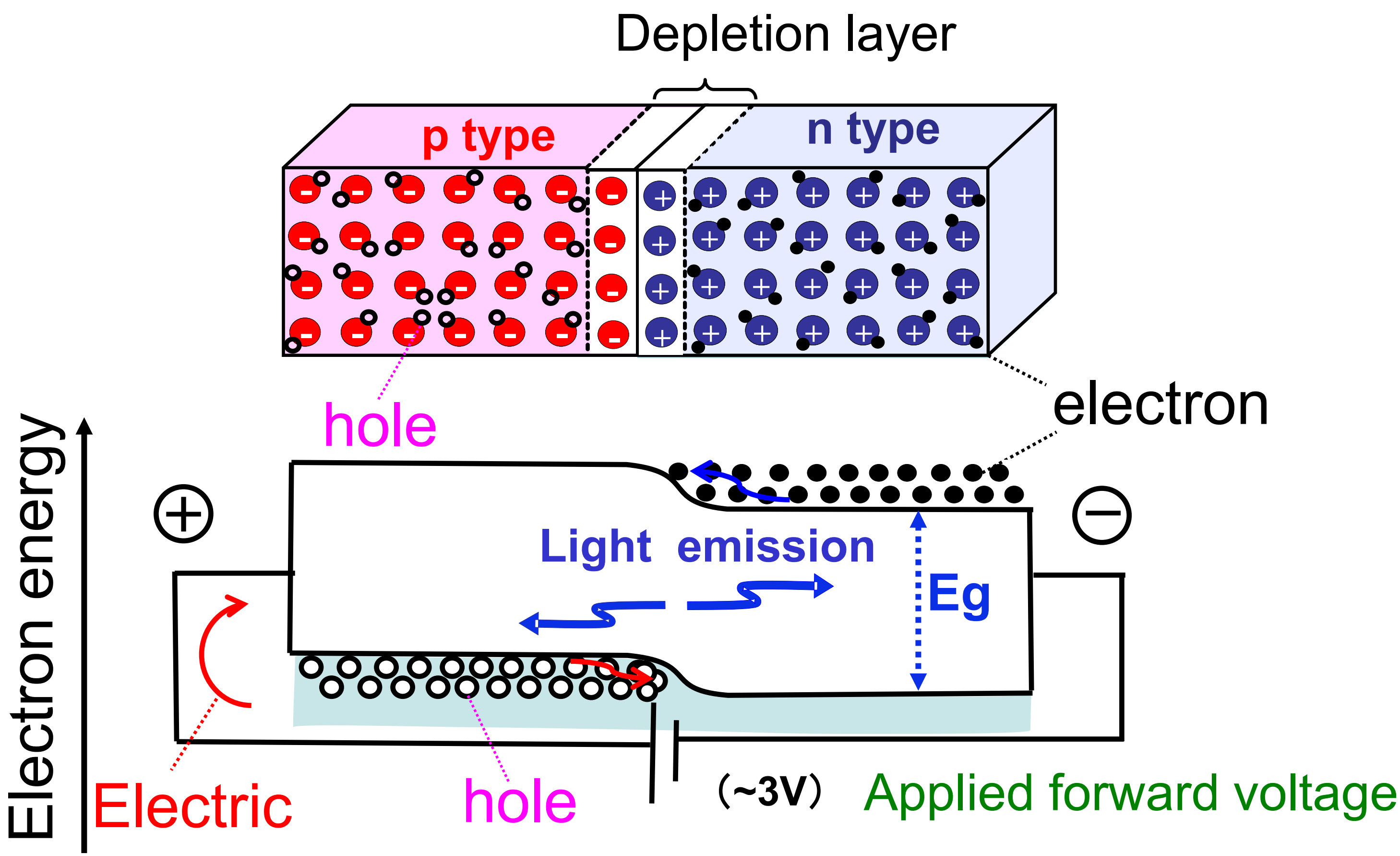
[B] Energy band structure:
Direct-transition type for conservation of electron momentum



Conservation of energy

High-performance Blue LED and Laser diode

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



p-n junction LED

Candidate materials for Blue Light-Emitters
in 1960s-’70s

	ZnSe	GaN
[A] Energy gap (Eg)	**2.7 eV**	**3.4 eV**
[B] Energy band structure	**direct**	**direct**
[1] Crystal growth	straightforward	**too difficult**
Substrate	GaAs	sapphire
Lattice mismatch	**0.26 %**	**16 %**
[2] p-n junction	**not realized at that time**	
Number of researchers	many	few
Physical & chemical stability	**low**	**high**

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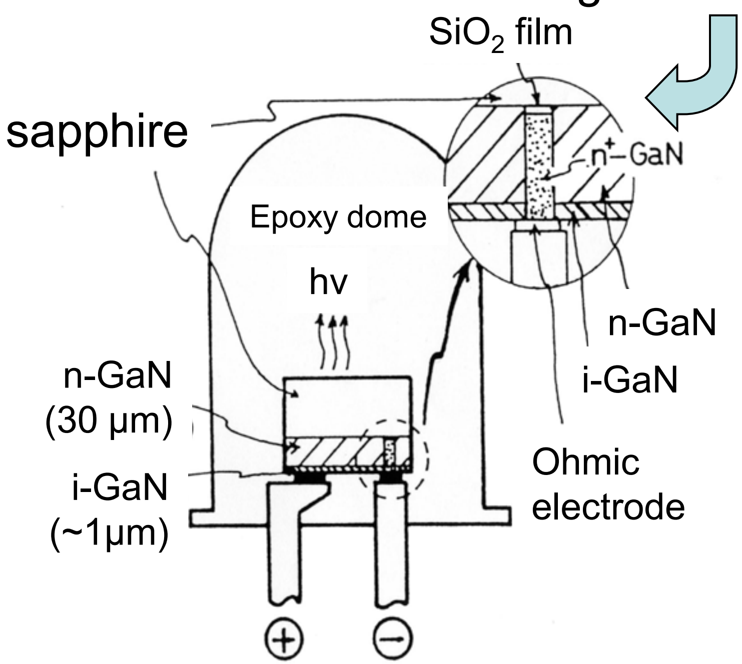
Chose GaN in 1973 at Matsushita Research Institute Tokyo (**MRIT**)

because of toughness, wider direct Eg, and non-toxicity

Started growth of GaN by MBE in 1973, and by HVPE in 1975

GaN MIS Blue LED by HVPE

First as-grown highly n-type cathode

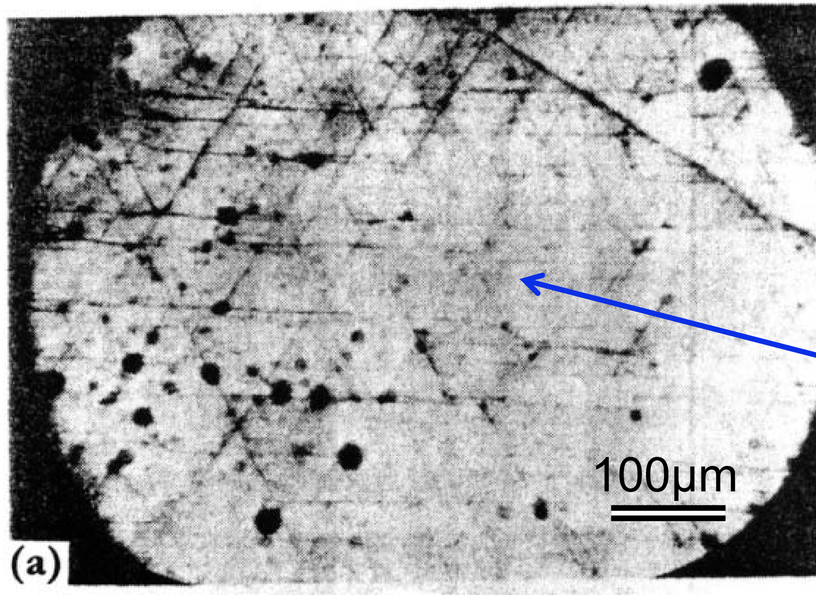


MIS Blue LED,
not p-n junction LED

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

at **MRIT**

Potential of GaN at MRIT



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) H. P. Maruska and J. J. Tietjen: (1969).

$$GaCl\ (g) + NH_3\ (g) = GaN\ (s) + HCl\ (g) + H_2\ (g)$$

Issues: Susceptible to reverse reactions, Too fast growth rate

Molecular Beam Epitaxy (MBE) I. Akasaki: (1974) (unpublished).

$$Ga\ (g) + NH_3\ (g) = GaN\ (s) + \frac{3}{2} H_2\ (g)$$

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

Metalorganic Vapor Phase Epitaxy (MOVPE), (MOCVD) H. M. Manasevit et al: (1971).

$$Ga(CH_3)_3\ (g) + NH_3\ (g) \longrightarrow GaN\ (s) + 3CH_4\ (g)$$

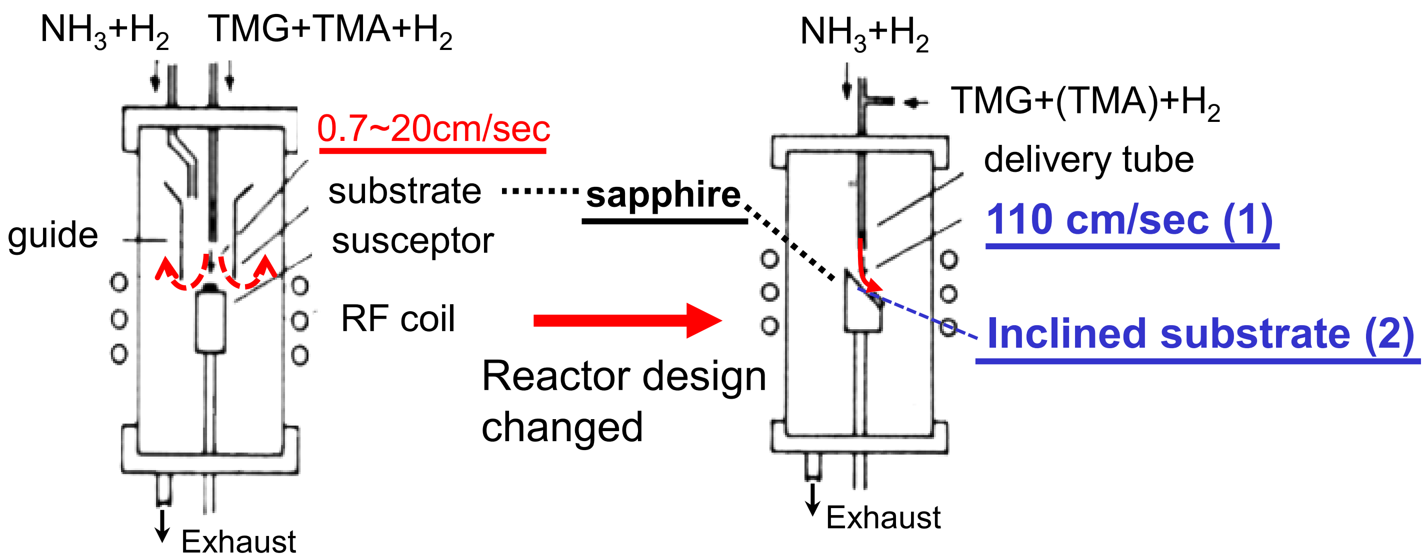
Advantages:

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

Decided to adopt MOVPE (1979) at MRIT

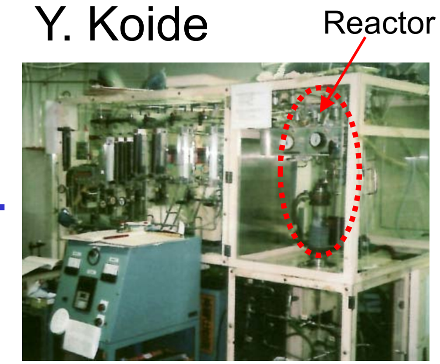
Started anew to MOVPE since 1981 at Nagoya University

Improvements in MOVPE reactor and growth condition (1) (2)



(1985)

Y. Koide



First MOVPE system (Handmade)

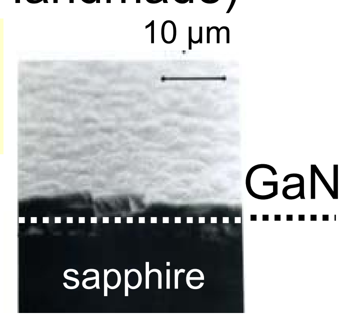
Mixing TMG (TMA) with NH_3 just before the reactor inlet, and (1) High speed gas flow (2) Substrate inclined at a 45-degree angle

↓

Suppressed the convective gas stream, and the adduct formation

↓

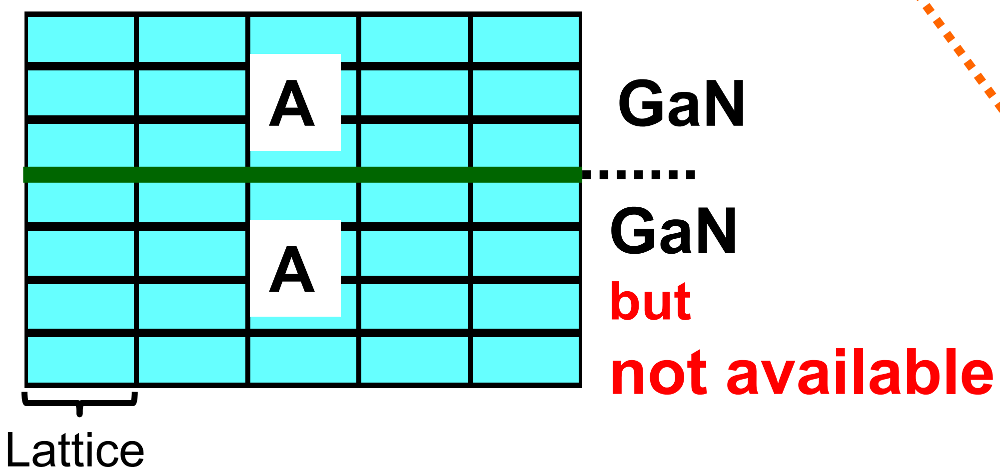
Uniform growth, but not specular surface, still poor material quality

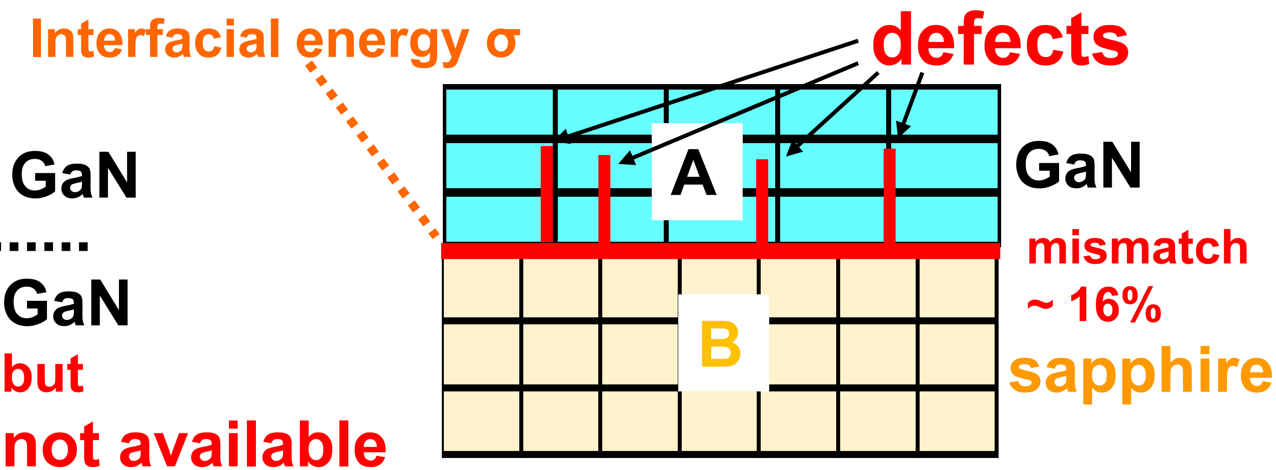


Bird-view SEM image by H. Amano

Growth on the same substrate

Growth on a highly-mismatched substrate





Homoepitaxy

Lattice matching

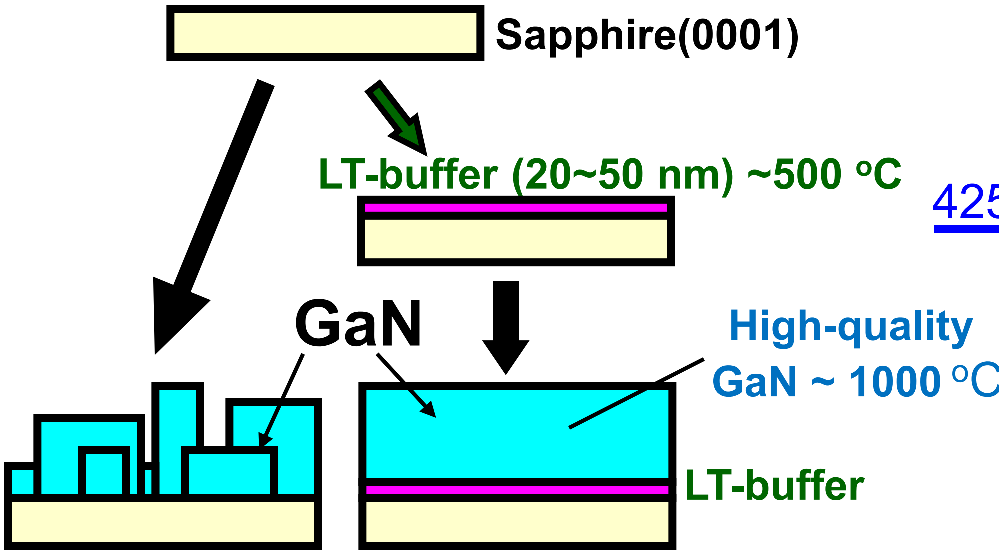
Heteroepitaxy

Huge lattice-mismatch

For epitaxial growth, it is considered to be gospel to have a lattice matching: (e. g. Si on Si, GaAs on GaAs)

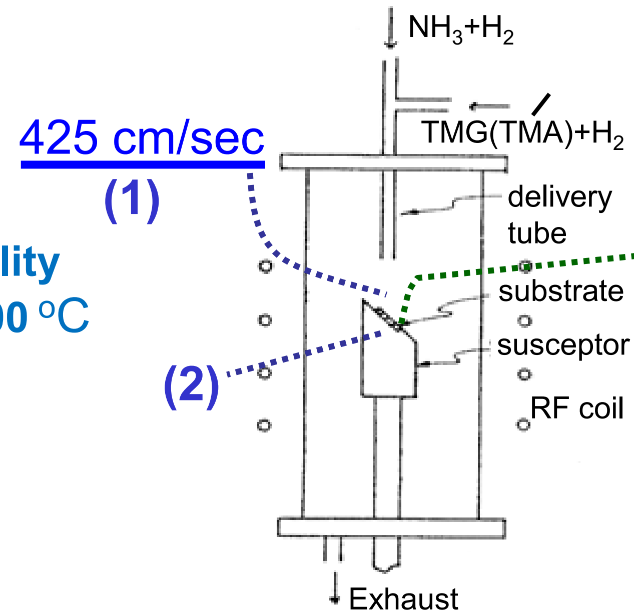
(3) Innovation in MOVPE growth method (1985)

Low-temperature (LT-) buffer layer



Direct growth
(Common method)

newly-developed



LT-buffer layer (3)

H. Amano

Key technologies:

(1) Much higher-speed gas flow (425 cm/sec)

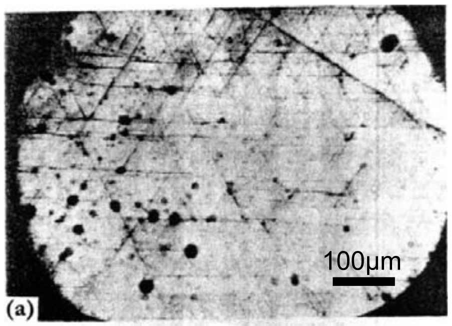
(2) Substrate inclined at a 45-degree angle

(3) Deposition of thin AlN buffer layer at about 500 °C, before the growth of GaN single crystal at about 1000 °C

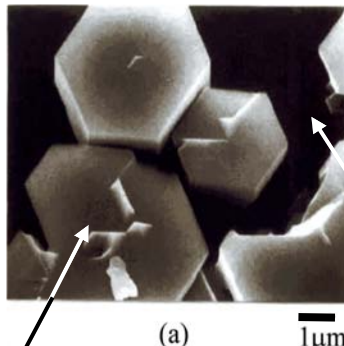
Creation of high-quality GaN (1985)

Until 1985

GaN grown by HVPE



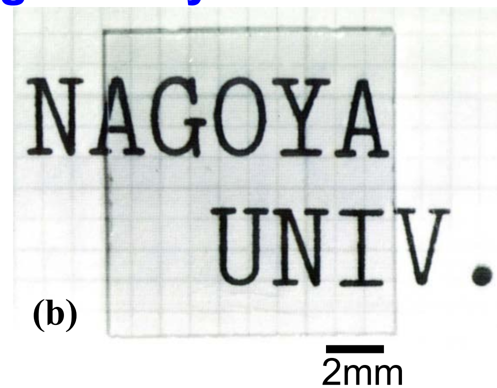
GaN grown by MOVPE



- Many cracks, pits
- Rough surface
- Dislocations: > 10^{11} cm^{-2}
- Free electron conc. >10^{19} cm^{-3}
- Electron mobility: ~20 $cm^2/V \cdot s$
- Weak luminescence

Since the late 1985

GaN grown by MOVPE using LT-buffer



- Crack-free, pit-free
- Specular surface
- Dislocations: 10^8-10^9 cm^{-2}
- Free electron conc. < 10^{16} cm^{-3}
- Electron mobility: ~700 $cm^2/V \cdot s$
- Intense luminescence

Crystal quality, electrical property, and luminescence property were dramatically improved at the same time

Growth model of GaN using LT-buffer layer

Surface (SEM) images | Growth model

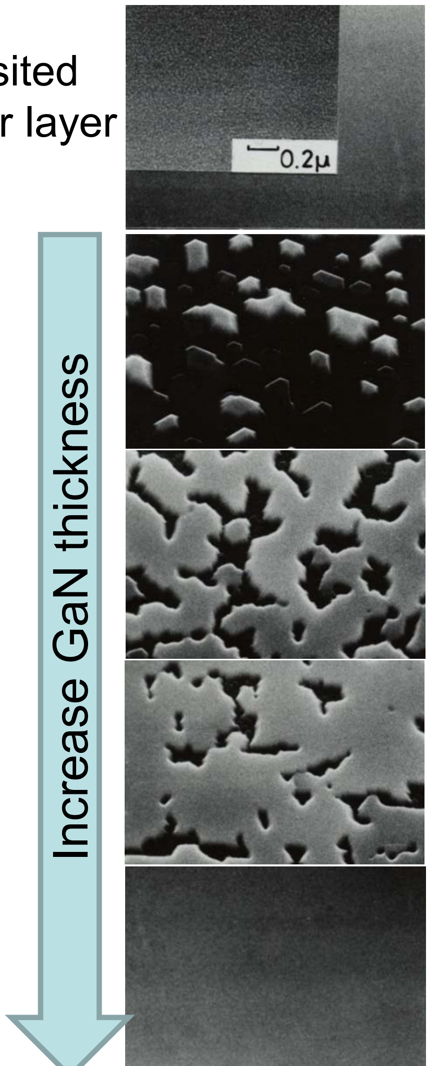
(1) As-deposited LT-AlN buffer layer

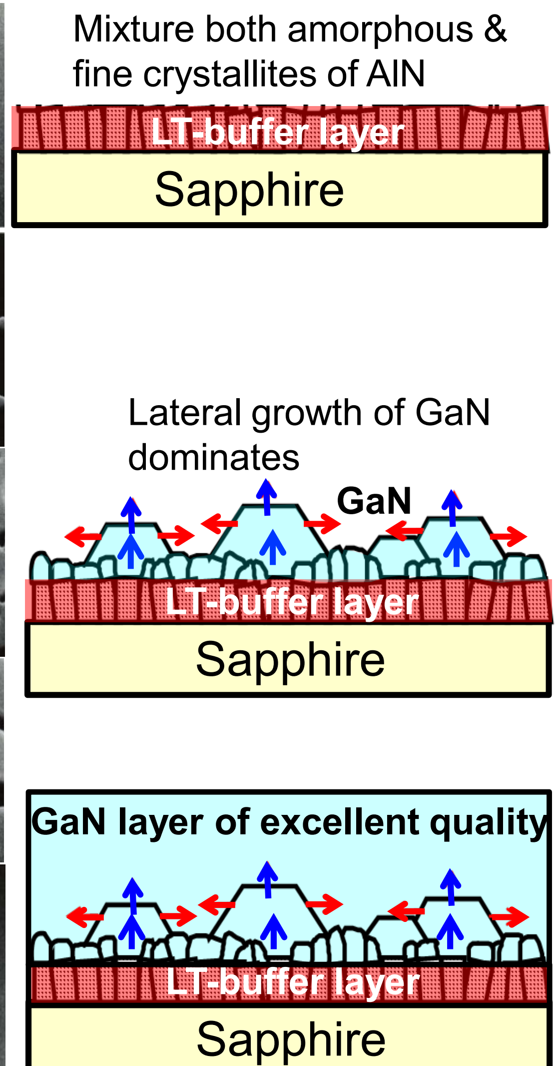
(2) 5 min GaN growth

(3) 10 min GaN growth

(4) 20 min GaN growth

(5) 60 min GaN growth

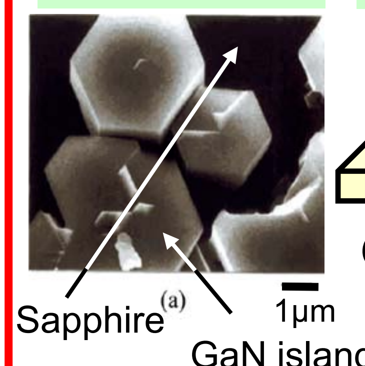


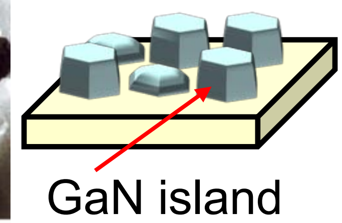


K. Hiramatsu

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

Surface (SEM) images | Growth model





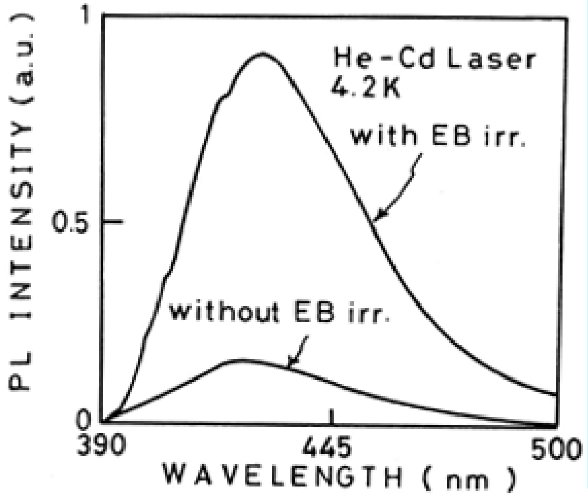
Realization of p-type GaN, AlGaN, and GaInN

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)

H. Amano



High-quality Mg-doped GaN subjected to LEEBI

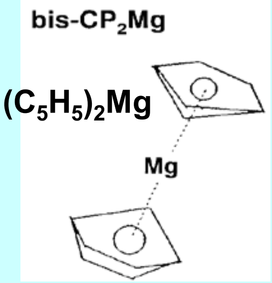
1989 Doped Mg using CP_2Mg and electron irradiation

Achieved the first p-type GaN

1991 p-type AlGaN

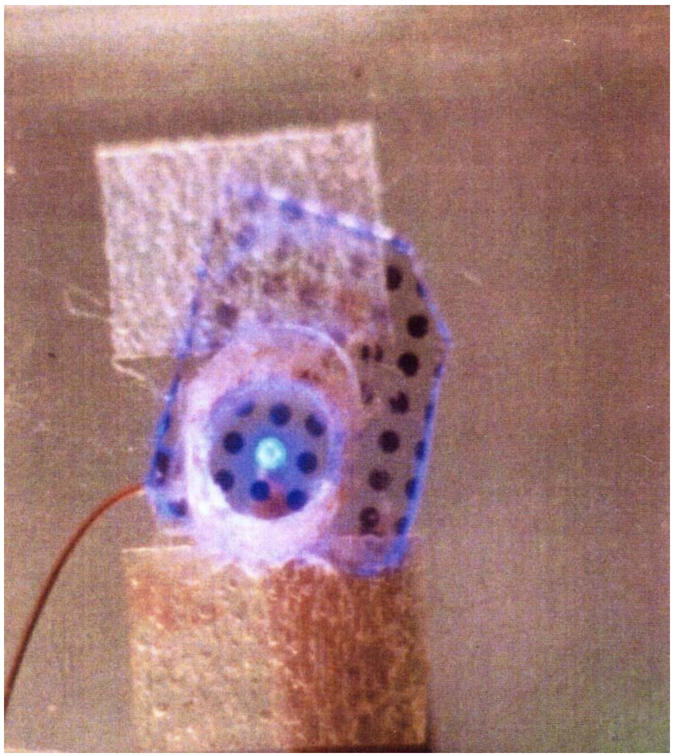
1995 p-type GaInN

M. Kito

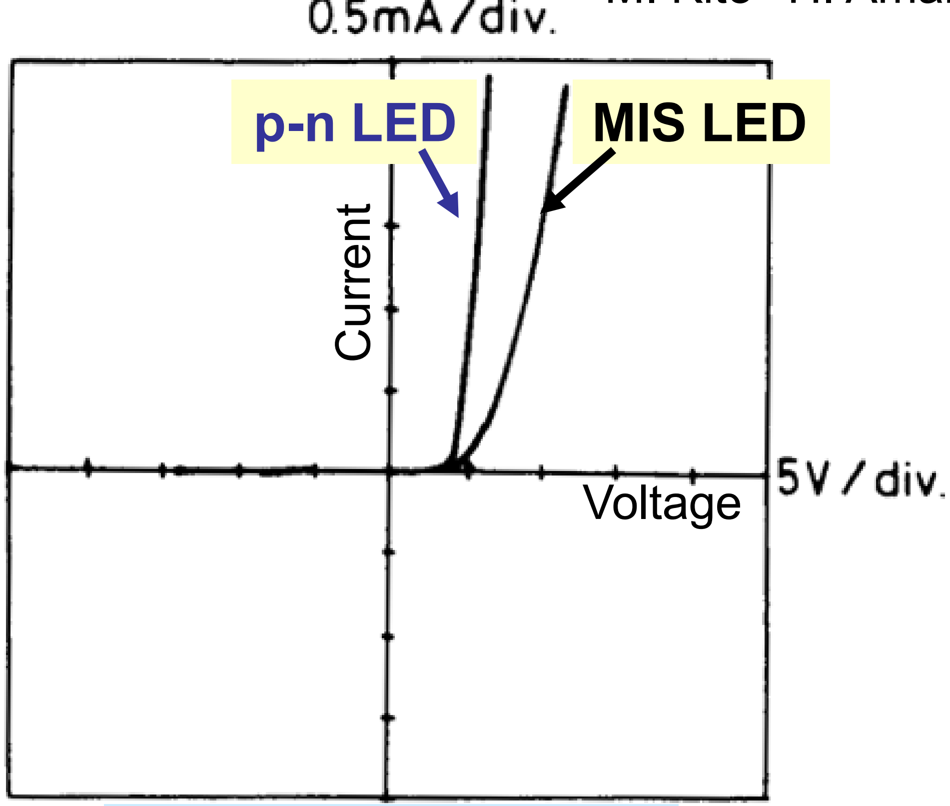


The world's first GaN p-n junction blue LED (1989)

M. Kito H. Amano



GaN p-n junction Blue LED



I-V curves

Conductivity control of n-type GaN, AlGaN

1986
Basic Technology

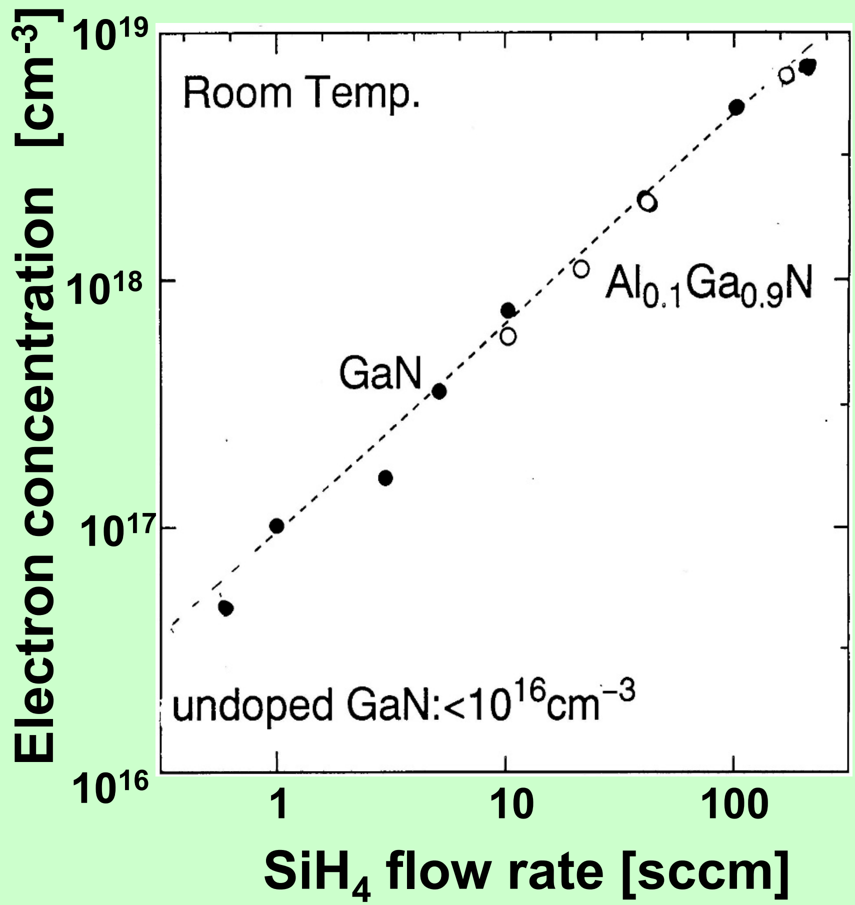
High-quality GaN using LT-buffer layer (Low residual impurities)

1989 Doped Si into high-quality GaN using SiH_4

Achieved conductivity control of n-type GaN

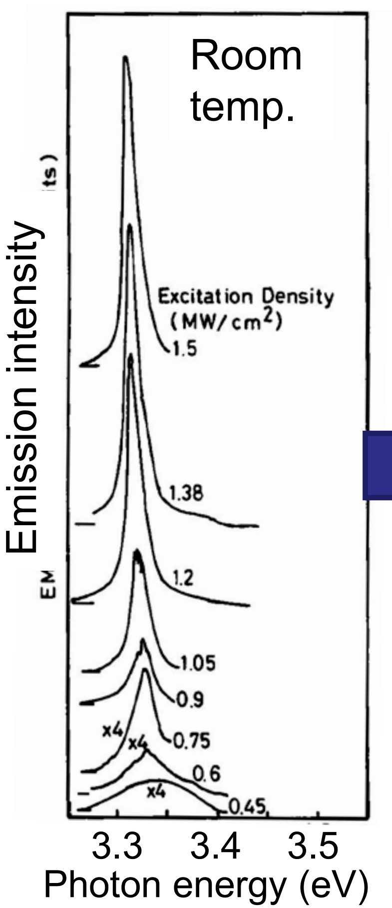
1991 n-type AlGaN

Allowed the use of heterostructure and quantum well in the design of more efficient p-n junction light-emitting structures

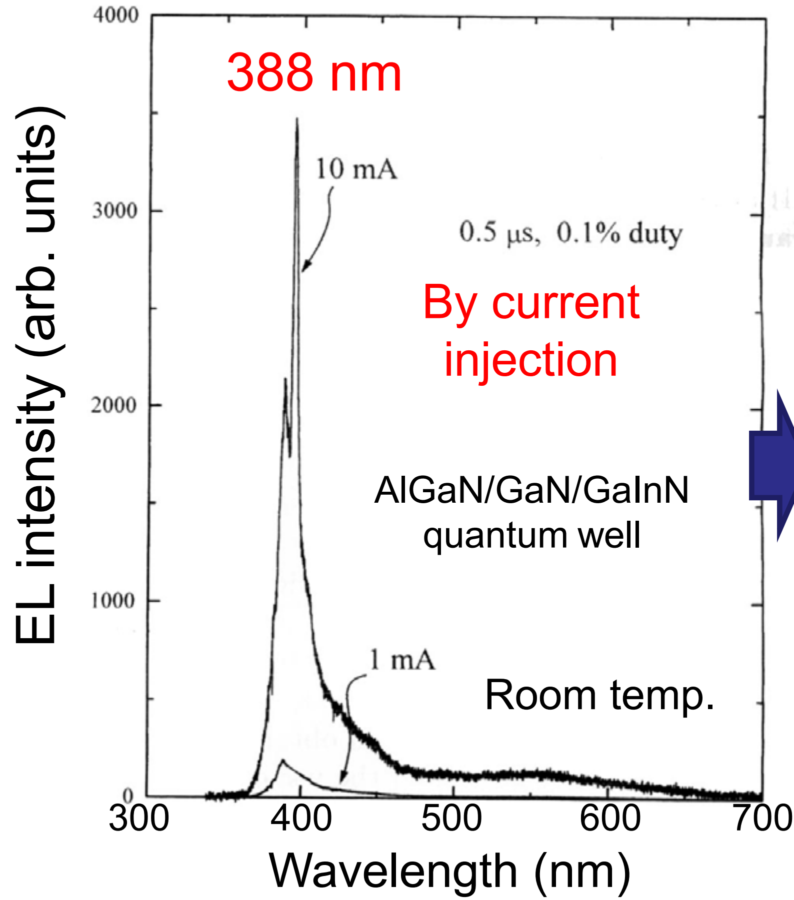


GaN-based laser

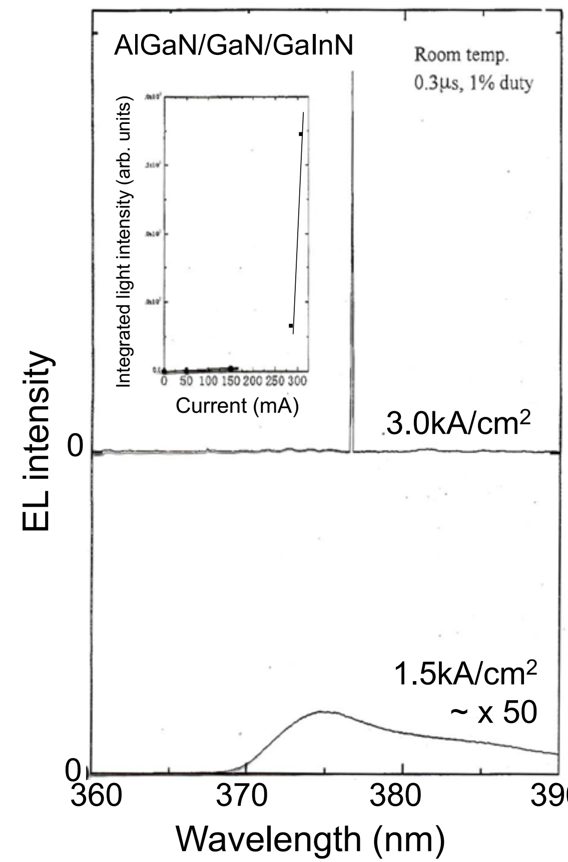
Stimulated emission by optical pumping (1990)



Stimulated emission by current injection (1995)

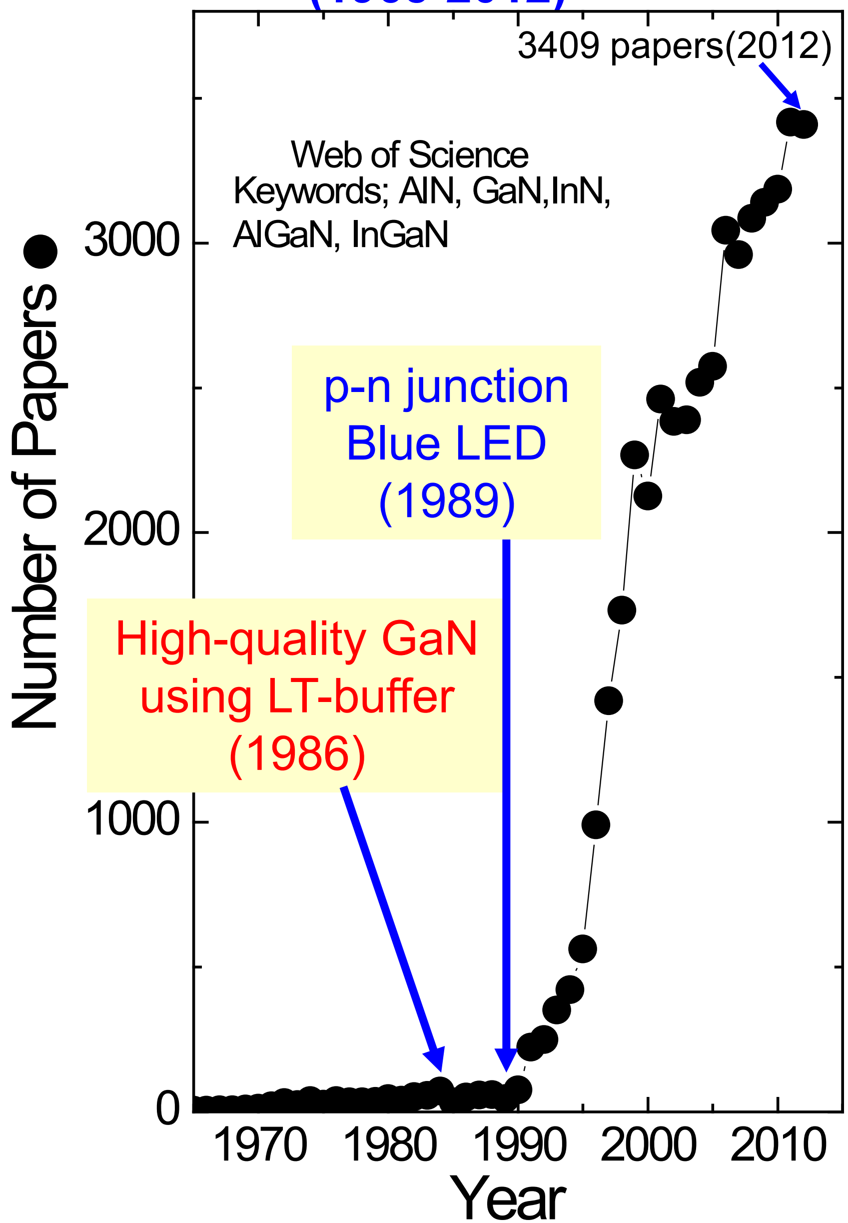


UV (376 nm) Laser diode (1996)



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.

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- B. Monemar

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- JST Project (Blue LED,1987−1990) (Violet laser diode,1993−1999)
- JSPS Research for the Future Program (1996−2001)
- MEXT High-Tech Research Center Project (1996−2004)