

Breakthroughs in Improving Crystal Quality of GaN and Invention of the p–n Junction Blue-Light-Emitting Diode

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Marked improvements in the crystal-line quality of GaN enabled the production of GaN-based p–n junction blue-light-emitting and violet-laser diodes. These robust, energetically efficient devices have opened up a new frontier in optoelectronics. A new arena of wide-bandgap semiconductors has been developed due to marked improvements in the crystalline quality of nitrides. In this article, we review breakthroughs in the crystal growth and conductivity control of nitride semiconductors during the development of p–n junction blue-light-emitting devices. Recent progress mainly based on the present authors' work and future prospects of nitride semiconductors are also discussed.

KEYWORDS: group III nitride semiconductors, MOVPE, low-temperature buffer layer, conductivity control, p–n junction, blue-light-emitting diode, short-wavelength laser diode, high-speed and high-power transistor

1. Introduction

Group III nitride semiconductors are recognized as one of the most promising materials for fabricating optical devices in the visible short-wavelength and UV region. To develop such novel devices and clarify the intrinsic materials properties of nitrides, it is essential to grow high-quality single crystals and control their electrical conductivity. However, high-quality epitaxial GaN was impossible to grow and its conductivity was uncontrollable. These problems have prevented the development of GaN-based p–n junction blue-light-emitting devices for many years.¹⁾

In 1986, we achieved a marked improvement in the crystal quality of GaN which enabled us to realize p-type conduction in nitrides and to control the conductivity of n-type nitrides in 1989. In the same year, these achievements led to the invention of the world's first GaN p–n junction blue/UV-light-emitting diode (LED). In 1990, stimulated emission in the UV region at room-temperature (RT), which is indispensable for laser action, was also achieved. These breakthroughs inspired nitride researchers around the world to exert great effort, which eventually led to the commercialization of high-performance blue LEDs and long-lifetime violet-laser diodes (LDs), and to the development of nitride-based devices such as UV detectors and high-speed field-effect transistors.

Furthermore, quantum size and quantum-confined Stark effects in the nitride system were first verified in 1991 and 1997, respectively, using high-quality multiple-quantum-

well structures grown with a low-temperature-deposited buffer layer.

Unique properties of nitrides, such as a large piezoelectric effect, are also well understood owing to the marked improvement in the crystal quality of nitrides.

Here, we review the breakthroughs during the development of nitride-based blue-light-emitting devices and describe recent advances in the crystal growth technology and UV-emitting devices of nitride semiconductors.

2. Research on Nitride Semiconductors in Early Days

Because of the difficulty in growing large bulk, single-crystal GaN, heteroepitaxial growth had to be adopted to grow GaN thin films. In 1969, Maruska and Tietjen succeeded in growing single-crystal GaN on a sapphire substrate by hydride vapor phase epitaxy (HVPE).²⁾ They found such GaN to have a direct-transition-type band-structure with a bandgap energy of about 3.39 eV at RT. This intensified research on blue LEDs based on GaN as shown in period (A) in Fig. 1,³⁾ which shows the number of publications related to nitrides and major topics in nitride research over the years. In 1971, Dingle *et al.* demonstrated optically pumped stimulated emission from a GaN at 2 K.⁴⁾ In the same year, the first blue LED with a metal–insulator–semiconductor (MIS) structure was announced by Pankove *et al.*⁵⁾ Then [period (B) in Fig. 1], Ejder reported the energy dispersion of the refractive index of GaN⁶⁾ and Monemar determined the fundamental energy gap of GaN.⁷⁾

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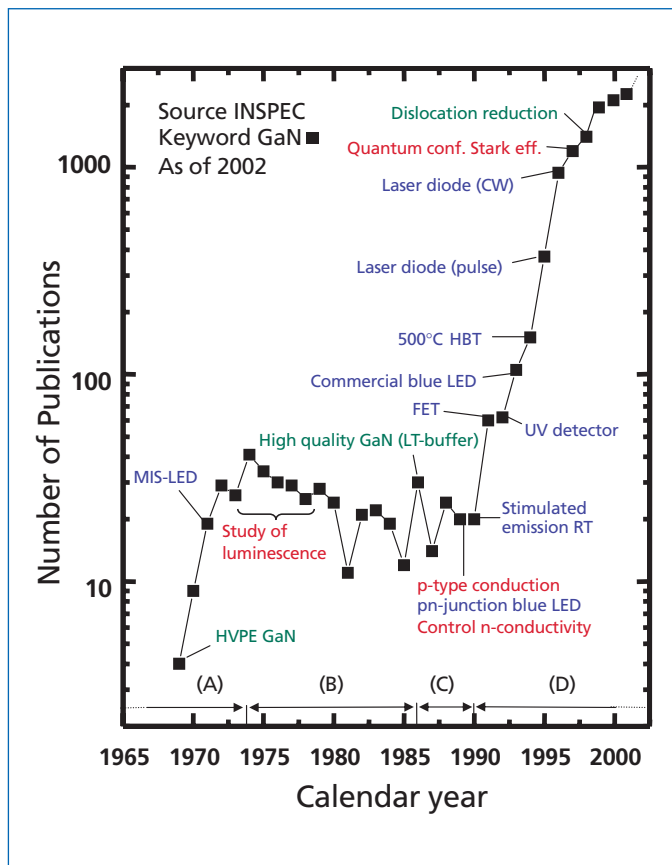


Fig.1. Number of publications (INSPEC) and activities related to nitrides over the years. All events are marked in the years, when they were first achieved. It is clear that the start of the steep increases in the numbers of publications and accomplishments is due to the key inventions in the late 1980s. Green: Crystal Growth, Red: Conductivity Control and Physics, Blue: Devices

The luminescence properties of GaN were also studied by many researchers during this period.

In contrast to traditional III-V compounds such as GaAs and InP, it is quite difficult to grow high-quality epitaxial GaN films, particularly layers with flat surfaces free of cracks. Moreover, residual donor concentrations higher than 10^{19}cm^{-3} in GaN made it impossible to achieve p-type conduction and control the conductivity of n-type nitrides. From the second half of the 1970s to the first half of the 1980s, there were no reports on significant improvements in the crystal quality of GaN. Thus, many groups withdrew from the

nitride field, activities in nitride research rapidly declined and the number of publications decreased, as seen in period (B) in Fig. 1.

3. Breakthrough in Crystal Growth of GaN

3.1 Choice of MOVPE as growth method

In the early 1970s, while I (Isamu Akasaki) was working at Matsushita Research Institute Tokyo, Inc. (MRIT), I decided to focus on the research and development of GaN-based blue-light-emitting devices using a p-n junction; something that no one had yet realized.

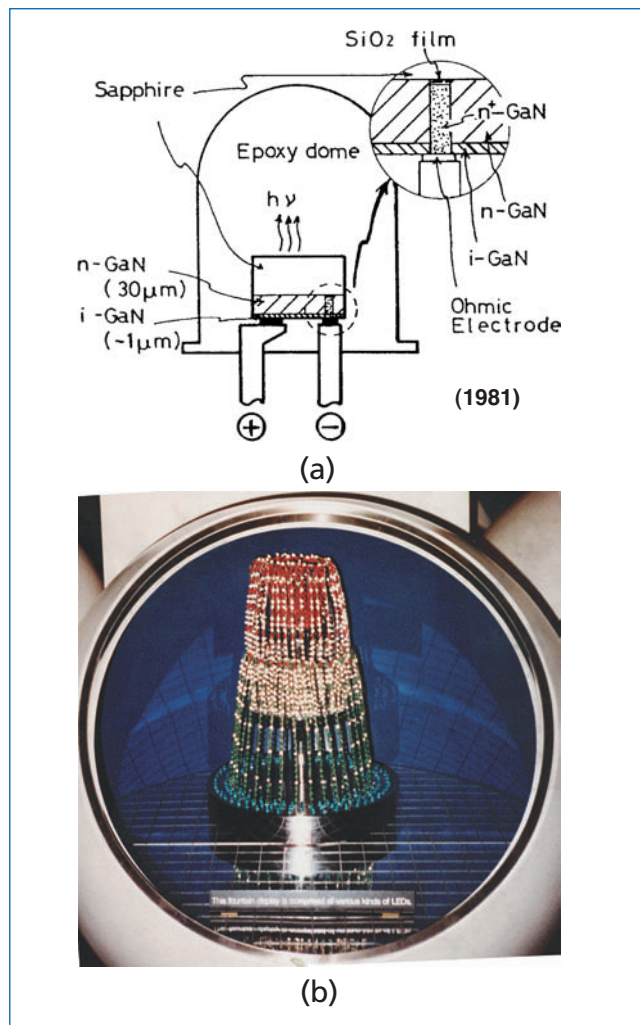


Fig.2. (a) Schematic of new structure of GaN blue LED developed in 1979. The n^+ GaN pillar reaching the chip surface through the n and i layers is shown in the inset. (b) Tricolor LED display using blue LEDs, which was later exhibited in Chicago in 1981 (by Matsushita Electric Industrial Co., Ltd.).

In 1974, I succeeded in growing single-crystal GaN by MBE for the first time, although with a poor surface uniformity. With this accomplishment, in 1975, I was awarded a three-year research grant by the Ministry of International Trade and Industry (MITI) of Japan for the "Development of a Blue-Light-Emitting Devices based on GaN."⁸⁾ In 1978, my team at MRIT developed a blue LED with an external efficiency of 0.12%; the highest ever reported at that time. Figure 2(a)^{9,10)} shows a schematic of the MIS-type blue LED with a unique device structure with selective n^+ -GaN pillars buried in the top insulating GaN layer and underlying n-GaN film. The n^+ pillars can be used as n^+ cathodes. This structure was

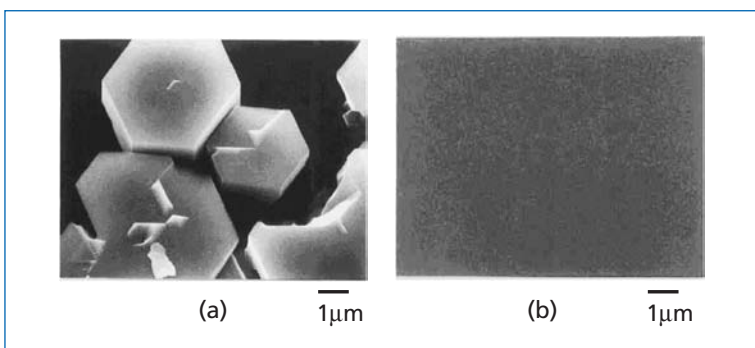


Fig.3. SEM photographs of surfaces of GaN films grown on sapphire substrate by MOVPE (a) without and (b) with LT-AlN buffer layer.

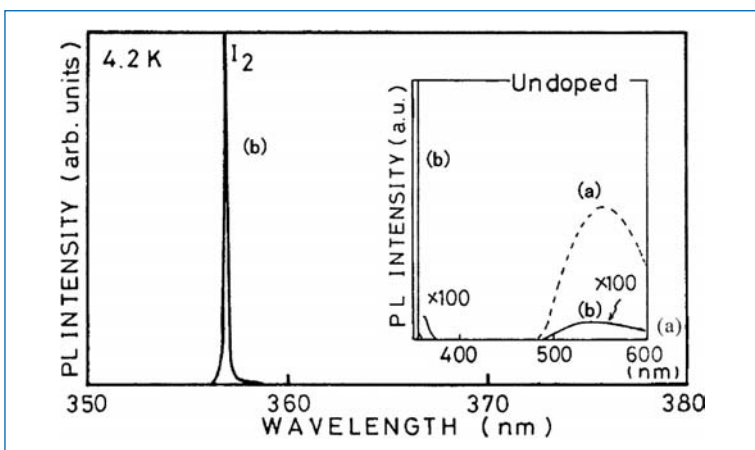


Fig.4. Photoluminescence spectra of undoped GaN films grown on sapphire substrate by MOVPE (a) without (dashed line in the inset) and (b) with (solid line) LT-AlN buffer layer.

formed by single-step HVPE growth over SiO_2 patterned substrates. Approximately 10,000 GaN blue LED test devices with such as-grown cathodes, which simplified the fabrication of LEDs, were manufactured. Figure 2(b) shows a tricolor LED display produced using such blue LEDs, which was exhibited in 1981 in Chicago by Matsushita Electric Industrial Co., Ltd. However, blue LEDs were not commercialized because the yield of devices was low as a result of the poor controllability of the thickness of the i-layer and the poor surface uniformity.

However, owing to my extensive experience in handling GaN crystals, fluorescent microscopy was able to show the existence of high-quality microcrystals in tiny parts of larger crystals containing cracks and pits. Also, my team found that clusters of needle like crystals, which looked like “GaN fungus,” left

inside the growth reactor exhibited highly efficient light emission.

From these experiments, I reconfirmed the great potential of GaN as a blue luminescent material and believed that p-type GaN could indeed be produced if a whole wafer could be made with the same quality as high-quality microcrystals. Thus, in 1978, I decided to go back to the basic, i.e., crystal growth, hoping to remedy the stagnant situation mentioned above.^{11,12)} It has been known that crystal quality is greatly affected by the method of growth and conditions, hence, the choice of the growth method is critical in determining the future of the research. Epitaxial GaN can be grown by MBE, HVPE, and metalorganic vapor phase epitaxy (MOVPE). MBE is prone to nitrogen deficiency and the growth rate was slow at that time. In the case of HVPE, the growth rate is too fast to fabricate devices

with nanometer thick layers and the reactions are reversible. Thus, these methods were not suitable for producing well-controlled devices based on high-quality GaN crystals. However, MOVPE seemed to be more suitable for the growth of nitrides on highly mismatched substrates, because this method had negligible reverse reactions and the growth rate was between of those using the other two methods. Another advantage of this method was that alloy composition and impurity doping could be readily controlled by varying the flow rates of the source gases.

Thus, in 1979, I decided to adopt MOVPE as the preferred growth method for GaN, although it was rarely employed at the time. It was a crucial decision.^{11,12)} As for the substrate, sapphire was provisionally chosen, which was widely used because it was stable under MOVPE growth conditions (above 1000°C and in NH_3 atmosphere) and was similar to GaN in terms of crystal symmetry.^{11,12)}

3.2 Development of low-temperature (LT) buffer layer method for MOVPE

In 1981, we started the MOVPE growth of GaN at Nagoya University (N.U.) using a handmade MOVPE reactor, which was constructed by Koide and Amano, graduate students in the department at that time. In spite of the eager effort of my team at N.U., the MOVPE growth did not yield favorable results. This was mainly due to the large lattice and thermal mismatches between GaN and sapphire. To reduce interfacial free energy, we developed “low-temperature (LT)-deposited buffer layer technology,” which overcame the problems mentioned in §2 and §3.1. This technology was based on the idea of making the growth conditions similar to those of homoepitaxy, in which there is no interfacial free energy in principle, by predepositing, at a low temperature, a very thin layer of material with physical properties similar to those of both GaN and sapphire. For the buffer layers, we thought of using AlN, GaN, ZnO, and SiC, because these materials had similar physical properties to GaN and sapphire. Among them, we first chose AlN, which had been familiar to us since 1966.¹³⁾ After many trials, we even-

tually succeeded in growing the world's first extremely high quality GaN single crystals in 1985.¹⁴⁾

As shown in Fig. 3, scanning electron micrographs (SEM) of the surfaces of GaN films grown on a sapphire substrate show the surface morphology of the films to be markedly improved by the LT-AlN buffer layer. X-ray diffraction profiles also showed that the crystal quality of GaN was significantly improved by this method.^{14,15)} Near-band-edge emission predominates the photoluminescence (PL) spectrum of the undoped GaN grown with the LT-AlN buffer layer, whereas deep-level-related yellow emission is the major emission from GaN grown without the LT-AlN buffer layer, as shown in Fig. 4.¹⁶⁾ In the spectrum shown in Fig. 5, which is from another GaN grown with the LT-AlN buffer layer, free exciton lines FE^A and FE^B and the impurity-bound excitons DBE and ABE are clearly observed showing that crystalline quality is drastically improved.¹⁷⁾ The residual electron concentration of GaN grown with an LT-AlN buffer layer decreased to the order of 10^{17} cm^{-3} which is more than two orders of magnitude lower than that of GaN grown without the LT-AlN buffer layer.^{16,18)} Soon after, electron concentration decreased to less than 10^{15} cm^{-3} . Simultaneously, electron mobility markedly increased to around several hundreds of $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^{16,18)} Cross-sectional transmission electron microscopy (TEM) showed that crystal defects such as dislocations markedly decreased with the use of the LT-AlN buffer layer.¹⁹⁾

These results clearly show that not only the crystal quality but also the electrical and luminescence properties of GaN could be markedly improved at the same time. The effect of the LT-AlN buffer layer is summarized in Fig. 6. The essential role of the LT-AlN buffer layer was found to be related to both the supply of high-density nucleation centers having the same orientation as the substrate and the promotion of the lateral growth of the epitaxial film due to the decrease in interfacial free energy between the epitaxial film and the substrate.^{16,19)}

Later, in 1990, we achieved stimulated emission in the UV region at RT, which is

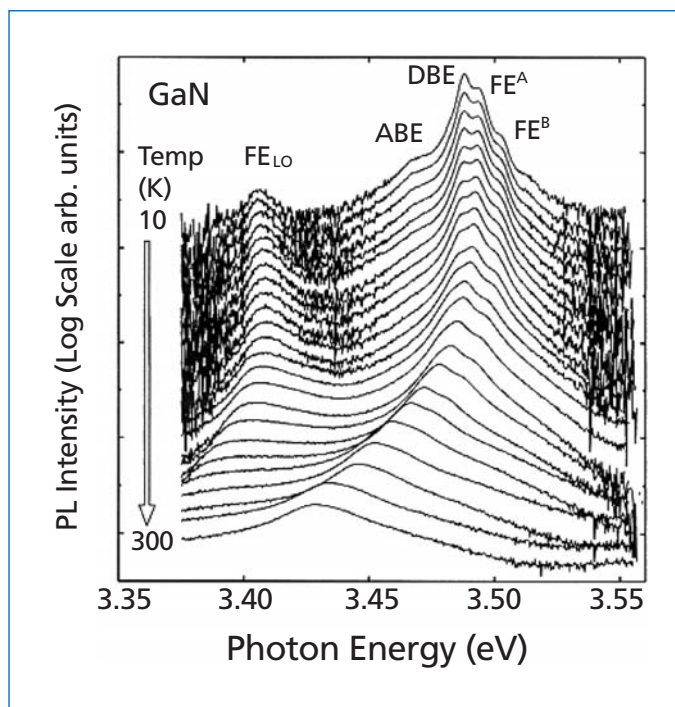


Fig.5. Photoluminescence spectra from cryogenic temperature to room temperature of GaN layer grown on sapphire by MOVPE with LT-AlN buffer layer.

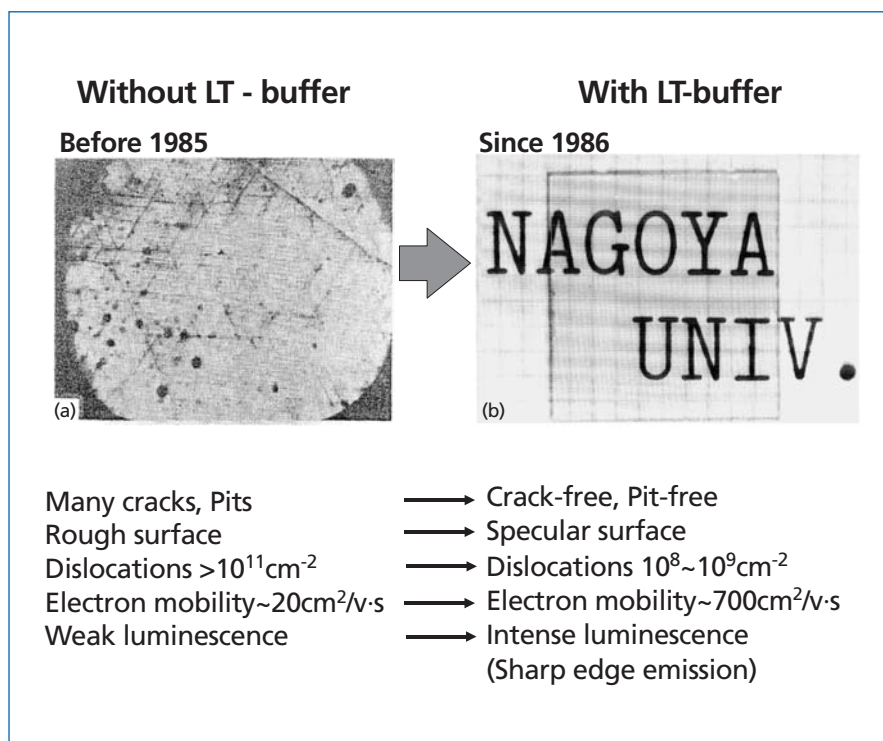


Fig.6. Photographs of GaN films grown on sapphire substrate by MOVPE (a) without and (b) with LT-buffer layer. The latter is quite transparent and colorless.

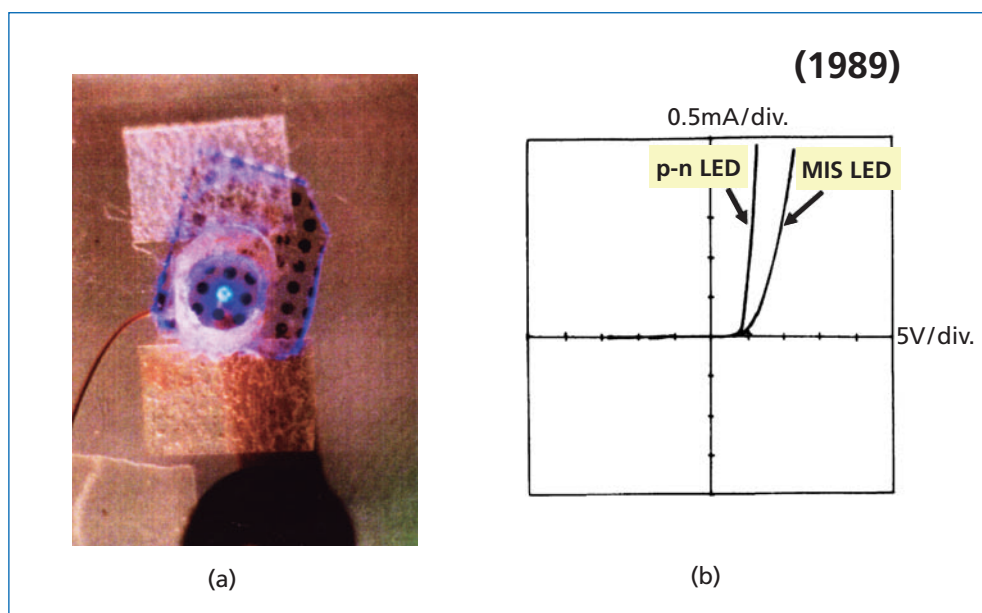


Fig.7. (a) World's first GaN p-n junction blue LEDs on sapphire substrate. Only one LED is lighting. (b) I - V characteristics of p-n junction LED (left) and MIS-LED (right).

indispensable for laser action, from GaN crystals for the first time.²⁰⁾ This showed that the crystal quality of GaN was drastically improved by the insertion of the LT-AlN buffer layer. In 1991, the LT-buffer method was implemented using an LT-GaN buffer layer instead of an LT-AlN buffer layer.²¹⁾ Today, these LT-AlN and LT-GaN buffer layer methods are indispensable and standard in the growth of GaN and nitride alloys on dissimilar substrates such as sapphire by MOVPE.

4. Conductivity Control of Nitride Semiconductors

4.1 Realization of p-type conduction in GaN and GaN p-n junction blue LEDs

Many groups have attempted to produce p-type GaN, but without success. With the successful control of the crystal quality of GaN, we could start to work on p-type doping. By using LT-AlN buffer layers, the residual donor density in GaN also drastically decreased as mentioned above. But in spite of repeated efforts on Zn doping, no p-type GaN production succeeded. In 1987, we found that the intensity of Zn-related luminescence greatly

increases when high-quality Zn-doped GaN grown with an LT-AlN buffer layer is irradiated with electron beams during cathodoluminescence (CL) measurement.²²⁾ It was thought that this phenomenon named the LEEBI effect²²⁾ is closely related with the activation of Zn acceptors and hence with p-type conduction. However, the crystals did not show p-type conduction. In 1988, we noticed that Mg can be an acceptor shallower than Zn, since its electronegativity is between Zn and Ga.²³⁾ In 1989, we succeeded in doping Mg in high-quality GaN using bis-Cp₂Mg or bis-MCp₂Mg as a Mg dopant, while maintaining a high crystal quality using LT-AlN buffer layer technology.^{24,25)} Then, Mg-doped GaN samples were irradiated with electron beams in the same way as Zn-doped samples. We found that the samples became low resistivity p-type GaN.²⁶⁾ Immediately, we realized the world's first GaN p-n junction blue/UV LED with encouraging current-voltage (I - V) characteristics in 1989, as shown in Figs. 7(a) and 7(b).²⁶⁾

The detailed mechanism of the effects of LEEBI on the electrical and luminescence properties of Mg-doped or Zn-doped GaN is not yet clear. As one possible mechanism, we proposed the Coulombic explosion²⁷⁾ model.

Electrons having energies of 6kV can generate many Auger electrons. As a result, the electronic configuration in an irradiated part of GaN may change (so-called Coulombic explosion), so that weakly bonded atoms, particularly light atoms like hydrogen may move. This results in the dissociation of Mg-H bonds and the activation of Mg as an acceptor. This hypothesis was supported by experiment results which showed that the electron beam activation effect occurs even at low temperatures.^{22,28)}

We achieved p-type AlGaIn in 1991²⁹⁾ and p-type GaInN in 1995³⁰⁾ in the same manner. In 1992, p-type GaN was also produced by the thermal annealing of Mg-doped GaN grown with an LT-GaN buffer layer.³¹⁾ Afterwards, p-type GaN was obtained by UV³²⁾ or electromagnetic wave irradiation^{33,34)} at elevated temperatures below 400°C.

To realize p-type nitrides, it is essential to activate Mg acceptors by releasing hydrogen.^{35,36)} However, it should be noted that residual donors should be reduced before solving problems related to the hydrogen passivation of acceptors. This clearly demonstrates the importance of crystal growth.

4.2 Conductivity control of n-type nitrides

Regarding n-type doping, researchers previously attempted doping Si using SiH_4 ,³⁷⁾ but it was difficult to control the conductivity due to the high density of residual donors in GaN grown without the LT-buffer layer. We also achieved, for the first time, the conductivity control of n-type nitrides (GaN in 1989³⁸⁾ and AlGaIn in 1991³⁹⁾ by doping Si using SiH_4 as a Si dopant, while maintaining the high crystalline quality of nitrides using the LT-AlN buffer layer. The conductivity control of n-type nitrides is practically important as well as the realization of p-type conduction. Today, this method for controlling the conductivity of n-type nitrides is used worldwide.

These breakthroughs, namely, the growth of extremely high-quality GaN, the conductivity control of nitrides and the invention of p-n junction blue LEDs in period (C) in Fig. 1, inspired nitride researchers around the world to exert great effort, which eventually led to the marked increase in the number of publications on nitride materials and devices, the commercialization of high-brightness blue LEDs and long-lifetime violet LEDs and the development of nitride-based electronic devices such as high-speed transistors,⁴⁰⁾ as seen in period (D) in Fig. 1.

5. Progress in Nitride-Based Blue LEDs and Violet LEDs

Chronological developments in the external quantum efficiency, η_{ext} of nitride-based blue LEDs are shown in Fig. 8.^{1,3)} η_{ext} saturated at about 0.1%, before the breakthroughs mentioned above. It began to increase steeply soon after the success in growing high-quality nitride crystals, which resulted in the GaN p-n junction LED. In 1992, a high η_{ext} of 1.5% was achieved⁴¹⁾ and, in 1993, a nitride-based blue LED with η_{ext} of 2.7% was first commercialized.⁴²⁾

To improve the emission efficiency of blue LEDs and violet LED performance, the use of GaInN alloy as an active layer is essential. The first successful growth of single-crystal GaInN alloy was reported in 1989–

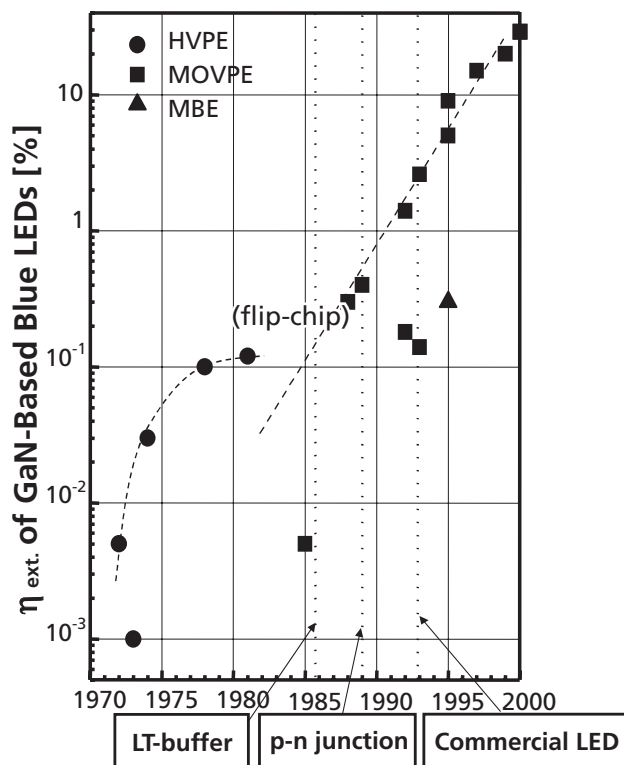


Fig.8. Chronological change in external quantum efficiency η_{ext} of nitride-based blue LEDs.

- ▲ Stimulated emission (low temperature)
- Stimulated emission (room temperature)
- Laser action (room temperature)
- (S) Surface mode

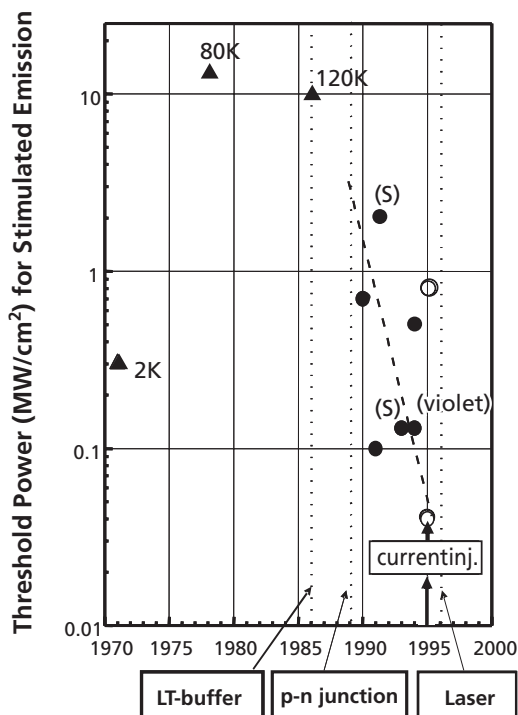


Fig.9. Change in threshold power P_{th} for stimulated emission by optical pumping (before 1995) and current injection (after late 1995) from nitrides.

1991.^{43,44)} Although GaInN alloy was soon used as an active layer of double-heterostructure (DH) blue LEDs, the devices functioned via donor-and-acceptor-pair emission instead of band-edge emission because of its insufficient quality. The growth of high-quality GaInN/GaN quantum wells (QWs)⁴⁵⁾ and multiple QWs (MQWs)^{46,47)} exhibiting distinct band-edge emission currently used as an active layer in blue LEDs, was first reported in 1995. At present, blue LEDs using such high-quality GaInN/GaN MQWs have η_{ext} higher than 36 %⁴⁸⁾ and are much brighter than incandescent lamps. They have been used as an excitation source of yellow phosphors for white LEDs.

Figure 9^{1,3)} shows the threshold power, P_{th} for stimulated emission from nitrides over the years. Before 1986, stimulated emission with optical excitation was obtained only at

low temperatures and its P_{th} was very high. In 1990, our group realized stimulated emission at RT for the first time, from a GaN grown with an LT-AlN buffer layer, showing that GaN is of high-quality as shown previously.²⁰⁾ We also suggested that a significant reduction in P_{th} would be possible with the use of DH or separate-confinement heterostructures (SCHs). This is due to the fact that the refractive index of the nitride system decreases with increasing bandgap energy.⁴⁹⁾ Similar to the increase in blue LED efficiency shown in Fig. 8, P_{th} began to decrease exponentially immediately after the marked improvement in the crystal quality of nitrides, as mentioned in §3.

In 1995, we demonstrated that the band-edge emission intensity from GaInN/GaN MQWs increases greatly when the well width is smaller than about 3 nm, which roughly corresponds to the Bohr radius of GaN as

shown in Fig. 10.^{46,47)} These structures are widely used as the active layer in blue LEDs and violet LDs at present. This strong enhancement in emission intensity was later (1997) qualitatively attributed to the suppression of the quantum-confined Stark effect (QCSE)^{50,51)} caused by the presence of a large piezoelectric field⁵⁰⁾ in the GaInN well, which was found to be about 1 MV/cm for an InN fraction of 0.1. In 1995, we achieved the first lasing operation with pulsed current injection from a GaInN/GaN QW device, although the lifetime was very short.⁵²⁾ An LD with continuous-wave (CW) operation was announced in 1996.⁵³⁾

In 1997, we found that AlGaIn and GaInN grow coherently on a GaN film grown with LT-AlN buffer layers, even though each alloy layer thickness exceeds the critical layer thickness.⁵⁴⁾ As a result, AlGaIn and GaInN grown on GaN are under tensile and compressive stresses, respectively. These stresses generate large piezoelectric fields in the strained AlGaIn and GaInN layers, as mentioned above.

Note that GaN grown on sapphire with LT-buffer layers still contains a threading dislocation density of approximately 10^8 – 10^{10} cm^{-2} . Although these threading dislocations do not severely affect the lifetime of QW-based blue LEDs, they do however accelerate the degradation of LDs. Therefore the reduction in threading dislocation density in the active layer is indispensable for achieving long-lifetime nitride-based LDs. Various technologies have been developed for reducing the threading dislocation density. One is the application of micro-channel epitaxy (MCE), which was proposed in 1988.⁵⁵⁾ An epitaxial lateral overgrowth (ELO) method derived from MCE has been reported for the reduction in threading dislocation density in nitrides. A thick GaN layer with a threading dislocation density as low as 10^7 cm^{-2} was grown by HVPE using ELO.⁵⁶⁾ Another approach to the reduction in threading dislocation density to as low as 10^7 cm^{-2} over the whole wafer using an LT interlayer (LT-IL) was reported by us in 1998.⁵⁷⁾ Technologies using mass transport⁵⁸⁾ and growth on a grooved substrate covered by an LT-AlN buffer layer⁵⁹⁾ were also proposed for the reduction in threading dislocation density in nitrides. These three methods

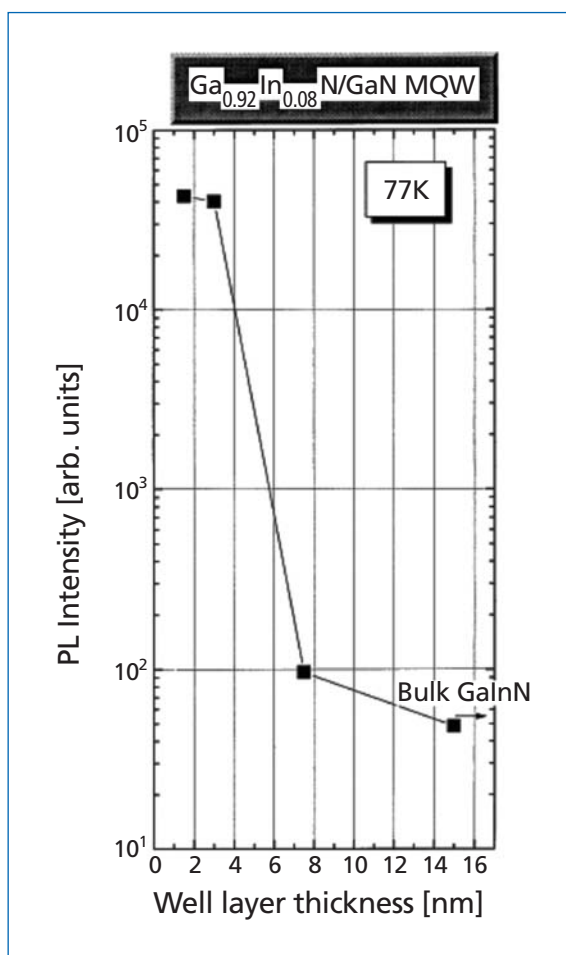


Fig.10. Dependence of band-edge photoluminescence intensity of GaInN/GaN MQWs on GaInN well width.

do not require SiO_x masks, which may diffuse into the crystal and act as obstacles. These methods enabled us to reduce the threading dislocation density to the order of 10^7 cm^{-2} .

Today, long-lifetime violet LDs are commercially available. In 1997, reliable violet LDs with lifetimes longer than 10,000 h at RT with a 2 mW operating power were fabricated using ELO-grown GaN.⁶⁰⁾ Recently, the lifetime of LD has been improved to 15,000 h at 60°C with a 130 mW operating power, which is sufficiently reliable for practical use and is applicable to writing data on the optical disk system.⁶¹⁾

6. Recent Advances in UV-Emitting Devices with Emphasis on Our Research in This Field

Owing to the key inventions in the crystal growth and conductivity control of nitrides, nitride-based high-performance blue LEDs and violet LDs are now commercially available. One of the next challenges is the fabrication of AlGaIn-based UV-light-emitting devices, particularly UV LDs. They can be used as the light sources of super high-density optical data storage, biological sensing and medical treatment systems, and as an excitation source for photocatalysis. However,

there are some difficulties to be resolved to realize high-performance UV devices with wavelengths shorter than 360 nm. In addition, it is very difficult or impossible to fabricate UV devices on GaN substrates, because of the lattice mismatch between GaN and the overgrown AlGaIn layers with high AlN molar fractions. During AlGaIn growth on GaN substrates, tensile stress accumulates due to lattice mismatch. Then, cracks are generated to relax the stress when the thickness of AlGaIn layers exceeds a critical value. Therefore, the above-mentioned approach used for visible devices is not applicable to the fabrication of UV devices. Another serious problem is that threading dislocations act more seriously as non-radiative recombination centers in the GaN/AlGaIn system. Figure 11 shows the PL intensities of two types of MQWs as a function of threading dislocation density.⁶²⁾ As shown, the two types of MQW have different optical properties. The emission intensity of the GaInN/GaN-MQW used in violet LDs is not significantly dependent on the threading dislocation density. In contrast, emission from GaN/AlGaIn-MQW for UV devices depends greatly on the threading dislocation density. However, conventional ELO methods for reducing threading dislocation density in GaN are not effective for the growth of AlGaIn with a low threading dislocation density because of its low lateral growth rate and

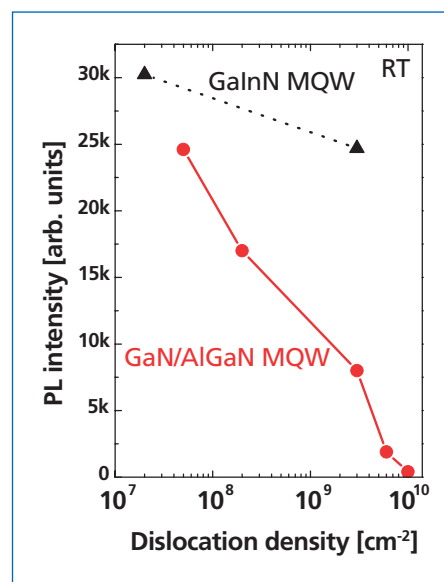


Fig.11. Band-edge photoluminescence intensity as function of dislocation density in GaInN/GaN and GaN/AlGaIn MQWs.

the adhesion of AlGaIn polycrystals to dielectric masks. To solve the above-mentioned problems, we developed a new growth method called hetero-ELO, which enables the growth of a crack-free AlGaIn template with a threading dislocation density as low as $2 \times 10^7 \text{ cm}^{-2}$.^{63,64)} This template was used to develop high-efficiency UV LEDs⁶⁵⁾ and UV LDs.⁶⁶⁾ Figure 12(a) shows the schematic of the UV LD structure grown on a high-quality

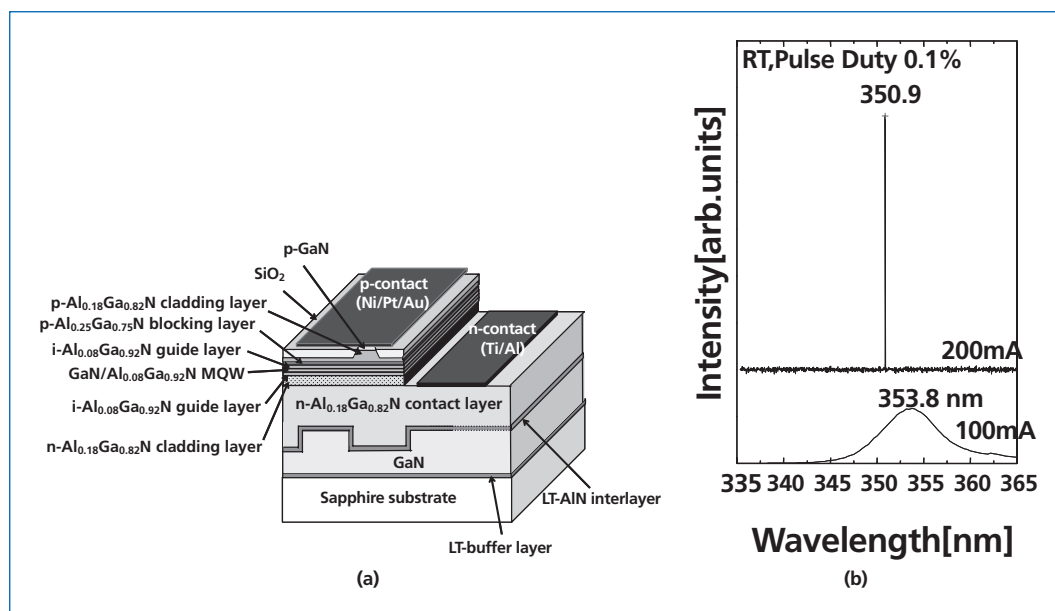


Fig.12. (a) Schematic of 350.9 nm UV LD fabricated by hetero-ELO, in which AlGaIn template was grown on grooved GaN film covered with LT-AlN interlayer. (b) Emission spectra of LD before and after threshold.

Al_{0.18}Ga_{0.82}N template.⁶⁶⁾ Hetero-ELO was used for the growth of the AlGaIn template, where the width, spacing and depth of the grooves were 10, 20, and 1.5 μm, respectively. The LT-AlIn interlayer with a thickness of 20 nm was deposited at 500 °C on a grooved GaN film grown on sapphire with the previously developed LT-AlIn buffer layer. **Figure 12(b)** shows the EL spectra of the device thus fabricated under a pulsed current injection at RT. At a current of 100 mA, band-edge spontaneous emission with a peak wavelength of 353.8 nm was observed. With increasing current up to 200 mA, the spectrum exhibited distinct lasing operation at 350.9 nm. Recently, 343 nm is the record for the shortest lasing wavelength in UV LDs.⁶⁷⁾ For the realization of even shorter-wavelength LDs, high-quality AlGaIn layers with much higher AlIn molar fractions and with higher electrical conductivities are necessary.

The importance of the LT-buffer layer should be emphasized, because in all cases even in ELO and hetero-ELO, the use of an

LT-buffer layer is essential. The development of single-crystal substrates such as GaN⁶⁸⁾ and ZrB₂⁶⁹⁾ lattice-matched to nitrides will be important for further reduction in dislocation density as well as strain.

7. Conclusions

The marked improvement in crystal quality of wide-bandgap nitride semiconductors by pioneering low-temperature buffer layer technology in MOVPE growth enabled us to control the electrical conductivity of nitrides. Unique properties such as large piezoelectric effects have been revealed owing to the marked improvement in the crystal quality of nitrides. These breakthroughs led to the invention of the world's first nitride-based p-n junction blue LED, and eventually to the commercialization of high-performance blue, green and white LEDs and long-lifetime violet LDs. High-speed transistors and high-sensitivity UV detectors have also been developed.⁷⁰⁾ All of these devices are robust and enable significant energy conservation. Today, the performance

of these devices is progressing, mainly owing to advances in the area of crystal growth. Further studies are still required for the expansion of device applications toward frontier regions, such as solid-state lighting, and high-speed and high-power electronics.

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