REVIEWS OF MODERN PHYSICS, VOLUME 87, OCTOBER–DECEMBER 2015

Nobel Lecture: Fascinated journeys into blue light[*]

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(published 5 October 2015)

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I. INTRODUCTION

"In the beginning there was light," emphasizes how closely light is tied to our lives. Light is indispensable for mankind and for many other creatures, and humans have pursued light sources since ancient times. Starting with flame, humans have developed the electric light bulbs, the fluorescent lamps, and then semiconductor light-emitting devices [the light-emitting diodes (LEDs) and the laser diodes (LDs)] in the second half of the last century. Although these light sources cover a wide wavelength range, the development of high-energy light sources has largely lagged behind. Development of an efficient blue LED had been a long-term dream for researchers worldwide, since it is indispensable for realizing LED-based full-color displays and general lighting applications.

Drastic improvements in the crystal quality of gallium nitride (GaN) (Amano *et al.*, 1986) and the ability to control the conductivity in both *p*- and *n*-type nitride semiconductors (Amano *et al.*, 1989; Amano and Akasaki, 1990) in the late 1980s have enabled the production of high-brightness GaN-based *p*-*n* junction blue/ultraviolet (UV) LEDs (Amano *et al.*, 1989), high-performance blue-violet LDs (Nakamura *et al.*, 1996a), and many other novel devices. These successes triggered the opening of an entirely new field of electronics.

In this paper, I would like to describe the historical progress that led to the invention of the first *p*-*n* junction blue/UV LED and related optical devices.

II. LED RESEARCH IN THE EARLY DAYS

In 1962, a red LED based on gallium arsenide phosphide (GaAsP) alloys was developed by Holonyak, Jr. and Bevacqua (1962). This was the first LED in the world to emit visible light. In 1968, a green LED was produced by Logan, White, and Wiegman (1968) based on nitrogen-doped gallium phosphide (GaP:N). At that time, however, there was no prospect of developing practical blue-light-emitting devices, which operate at the shortest wavelength in the visible spectrum and produce the highest energy.

The energy of photons from light-emitting semiconductor devices, such as LEDs, is approximately equal to the band-gap energy (E_g) for the semiconductor that is being used. The wavelength of blue light is in the range 445–480 nanometers (nm), which is equivalent to a band-gap energy of 2.6–2.8 eV. There were therefore two requirements for creating blue-light-emitting devices.

Requirement [A]: It is essential to use semiconductors with an E_g of approximately 2.6 eV or larger, equivalent to a wavelength of 480 nm or shorter (blue light). Semiconductors that have such a large E_g are referred to as "wide bandgap semiconductors." In contrast, the E_g for the most commonly used semiconductor silicon is 1.1 eV.

Requirement [B]: It is advantageous to use direct band-gap semiconductors in which the momentum of electrons at the bottom of the conduction band is almost equal to that of holes at the top of the ground state valance band, as shown in Fig. 1, yielding a high radiative recombination probability. In

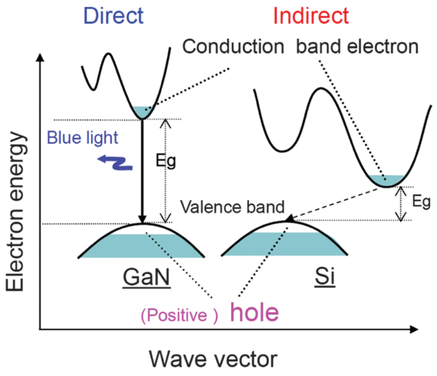

FIG. 1 (color). Band structures of GaN (direct transition type) and Si (indirect transition type).

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[*] The 2014 Nobel Prize for Physics was shared by Isamu Akasaki, Hiroshi Amano, and Shuji Nakamura. These papers are the text of the address given in conjunction with the award.

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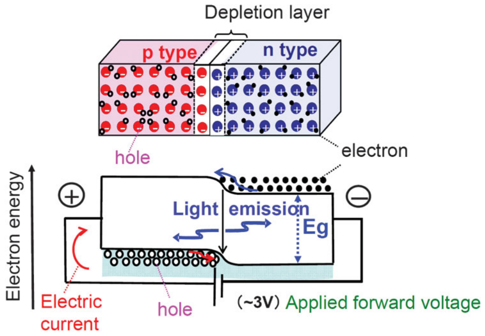


FIG. 2 (color). A schematic structure of a *p*-*n* junction LED.

contrast, indirect band-gap semiconductors exhibit a lower radiative recombination probability, because the momentum of these electrons and holes is different.

However, requirements [A] and [B] are not always sufficient conditions. To realize high-performance LEDs, it is essential to (1) grow high-quality single crystals and (2) successfully produce *p*-*n* junctions (Fig. 2). Semiconductors that have more holes (electron deficiency) than electrons are referred to as *p*-type semiconductors, whereas those with more electrons than holes are referred to as *n*-type semiconductors. A *p*-*n* junction is an atomically continuous boundary between a *p*- and *n*-type semiconductor, and is necessary for the fabrication of devices such as highly efficient light emitters, solar cells, and transistors.

It is, however, extremely difficult to achieve (1) and (2) in wide bandgap semiconductors, and this prevented the development of high-performance blue-light-emitting devices for many years.

In the late 1960s and 1970s, candidate materials for blue-light-emitting devices included silicon carbide (6H-SiC) with an E_g of 3.0 eV, zinc selenide (ZnSe) with an E_g of 2.7 eV, and GaN with an E_g of 3.4 eV. Of those, SiC was the only wide bandgap semiconductor for which *p*-*n* junctions could be created in those days, and some researchers attempted to develop blue LEDs based on this material (Matsunami *et al.*, 1977). I had, however, absolutely no interest in this material for photonic device applications because of its indirect band structure which prevented efficient light emission. Meanwhile, although ZnSe and GaN as summarized in Table I were known to be direct band-gap semiconductors, it was difficult to grow large bulk crystals of these materials, and no *p*-type crystals had been realized at that time. When it is difficult to produce large bulk crystals, epitaxial growth of single-crystal thin films is generally used. In vapor-phase epitaxial growth, source materials for a crystal growth are provided to the substrate in the form of a gas. Growth then takes place such that there is general alignment between the crystallographic axes of the grown crystals and the substrate. This method has been widely used in the growth of a high-quality semiconductor with nanostructures. The term “homoepitaxy” or “heteroepitaxy” is used when the grown crystal is the same as or different to the substrate crystal, respectively. In the latter case, it is necessary for the lattice constants of the two crystals to be the same as possible to each other.

TABLE I. A comparison between ZnSe and GaN.

	ZnSe	GaN
[A] Energy gap (E_g)	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 and chemical stability	Low	High

ZnSe emits bright light under excitation by an electron beam. Good-quality single-crystal ZnSe film can be grown using vapor-phase epitaxial growth on GaAs single-crystal substrates because the lattice constants are very similar. Thus, many researchers had been working on ZnSe, aiming to develop blue-light-emitting devices.

I myself, however, worried about the instability of ZnSe due to its low cohesive energy (bonding energy), and its poor crystallinity because of the low growth temperature required. In fact a technique for *p*-type doping of ZnSe was developed later in 1988 (Park *et al.*, 1990), and a lasing operation in a zinc cadmium selenide (ZnCdSe)/ZnSe heterostructure was demonstrated in 1991 (Hasse *et al.*, 1991). However, the lifetime of ZnSe-based optical devices was found to be very short, and the researchers gave up attempting to develop this material further.

III. BRIEF HISTORY OF RESEARCH ON GaN-BASED MATERIALS AND DEVICES

A. Early attempts at development of GaN blue LED

During the early stages of group-III nitride semiconductor research, I had insight into the great potential of this material for blue-light-emitting devices, and yearned to pioneer a new field founded on the unique properties of nitrides, such as their toughness, wider direct energy gaps, and nontoxicity, while I was working from 1964 to 1981 at Matsushita Research Institute Tokyo, Inc. (MRIT).

In 1967, I and Masafumi Hashimoto at MRIT grew aluminum nitride (AlN) crystals by vapor-phase reaction and determined the angular frequencies of longitudinal and transverse optical phonons by fitting the calculated reflectivity to Reststrahlen (residual ray) (Akasaki and Hashimoto, 1967). It was very difficult, however, to use AlN as an electroluminescent material, because of its excessively large E_g of about 6.2 eV.

In the meantime (in 1969), H. P. Maruska and J. J. Tietjen successfully grew single-crystal GaN films on sapphire substrates using hydride vapor-phase epitaxy (HVPE) and found that GaN is a direct band-gap semiconductor with an E_g of 3.34 eV at room temperature (RT) (Maruska and Tietjen, 1969). Then, in 1971, J. I. Pankove *et al.* developed GaN-based metal-insulator-semiconductor (MIS) type blue LEDs (Pankove, Miller, and Berkeyheiser, 1972). R. Dingle *et al.* observed stimulated emission and laser action in single-crystal needles of GaN at 2–4 K (Dingle *et al.*, 1971). These achievements intensified research and development of blue-light emitters based on GaN [period (A) in Fig. 3].

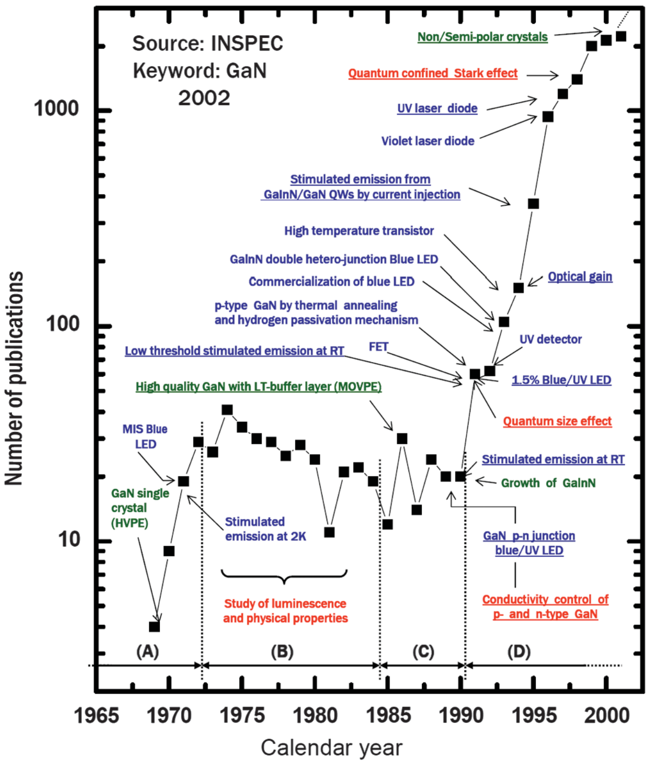


FIG. 3 (color). Number of publications (INSPEC) and activities related to nitrides from 1969 to 2002. All events are marked in the years when they were first achieved. Most of the important results were achieved by MOVPE using an LT-buffer layer after 1986. It is clear that the start of the steep increase in the number of publications and accomplishments is due to the key inventions (high-quality GaN, p- and n-type conductivity control, and p-n junction blue/UV LED) in the late 1980s and 1990. Achievements with underlines are works done by Akasaki's group. Green: crystal growth; blue: devices; red: conductivity control and physics.

In the mid-to-late 1970s, however, GaN researchers almost withdrew from the field, and activity on GaN-based devices declined [period (B) in Fig. 3], because they could not grow high-quality semiconductor-grade GaN single crystals nor control the electrical conductivity of the material (realize p-type conduction, in particular), both of which are indispensable for producing high-performance light emitters based on a semiconductor p-n junction, although some researchers had continued to work on the basic and physical properties of GaN (Ejder, 1971; Monemar, 1974).

Besides, at that time, theoretical studies indicated the impossibility of achieving p-type conduction in wide bandgap semiconductors such as GaN and ZnSe due to the "self-compensation effect" (Mandel, 1964).

Despite this stalemate, I started to work on the growth of GaN single-crystal film by molecular beam epitaxy (MBE) in 1973, and then by HVPE in 1975, aiming at the development of GaN-based p-n junction LEDs and LDs. In 1978, by utilizing HVPE, my group at MRIT developed a MIS-type GaN blue LED with a unique device structure of as-grown highly n-type (n^+) GaN pillars buried in a thick n-GaN/a thin insulating GaN structure as shown in Fig. 4. The n^+ pillars could be used as cathodes, which greatly simplified the fabrication of MIS-type LEDs (Ohki et al., 1981; Akasaki and Amano, 2006). The external efficiency was 0.12%, which was the highest ever reported at that time. However, due to the use of a MIS structure, the operating voltage was high and the brightness was low, in contrast to p-n junction LEDs that we invented later (Amano et al., 1989).

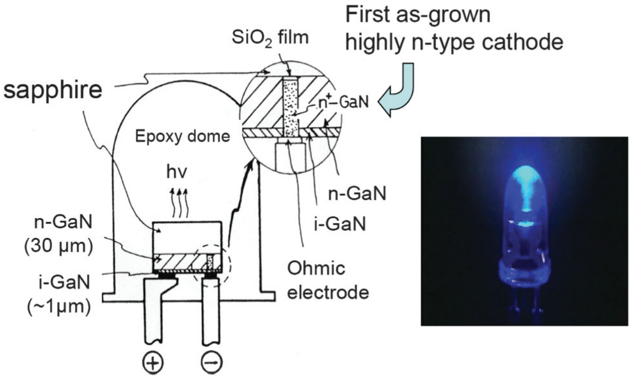


FIG. 4 (color). A schematic and a photograph of a MIS-type GaN blue LED developed in 1978.

B. Reconsideration of growth technology

In parallel with the work described previously (Akasaki and Amano, 2006), I also recognized the great potential of GaN as a blue luminescent material, when I found tiny but high-quality crystallites embedded in HVPE-grown crystals containing many cracks and pits in the field of view of microscopes. I was intuitively convinced that it would be possible to achieve conductivity control (even p-type GaN) if this kind of quality could be obtained over an entire wafer.

Thus, in 1978, I made up my mind to go back one more time to the beginning, i.e., "crystal growth," which is an interdisciplinary science and essential for the realization of quantum devices with nanostructure.

This decision, I think of, as a major turning point in not only my own GaN research, but also GaN research and development throughout the world, which had been stagnating at that time [period (B) in Fig. 3].

It is known that the quality of crystal is greatly affected by the nature of the chemical reactions involved in their production, in other words, the growth method and condition. Hence, the choice of growth method was critical for determining the future of the research. Epitaxial GaN can be grown by MBE, HVPE, or metalorganic vapor-phase epitaxy (MOVPE), the latter of which is also known as metalorganic chemical vapor deposition (MOCVD), as described in Table II.

On the basis of my crystal growth experience, I realized that MBE was prone to introducing a nitrogen deficiency and the growth rate was very slow at that time. In the case of HVPE, the crystal quality was degraded by appreciable reverse reactions, and the growth rate was too high to fabricate devices with layer thicknesses on the order of nanometers. Therefore, these methods were not suitable for producing well-controlled devices based on high-quality GaN crystals.

On the other hand, MOVPE, which was first applied to the growth of GaN by H. M. Manasevit et al. in 1971 (Manasevit, Erdmann, and Simpson, 1971), but almost never employed for this purpose, thereafter, seemed to be more suitable, because

TABLE II. Crystal growth methods for GaN.

Molecular beam epitaxy (MBE) $Ga(g) + NH_3(g) = GaN(s) + \frac{3}{2}H_2(g)$ Issues: Prone to nitrogen deficiency Slow growth rate (at that time)	
Hydride vapor-phase epitaxy (HVPE) $GaCl\,(g) + NH_3(g) = GaN\,(s) + HCl\,(g) + H_2(g)$ Issues: Susceptible to reverse reactions Too fast growth rate	Maruska and Tietjen (1969)
Metalorganic vapor-phase epitaxy (MOVPE) $Ga(CH_3)_3\,(g) + NH_3\,(g) \rightarrow GaN\,(s) + 3CH_4\,(g)$ Advantages: No reverse reactions Easy to control growth rate, alloy composition, and impurity doping	Manasevit, Erdmann, and Simpson (1971)

of the absence of reverse reactions. Furthermore, the composition of alloys such as aluminum gallium nitride (AlGaN) and gallium indium nitride (GaInN) and the level of impurity doping could be readily controlled by varying the flow rates of the source gases in MOVPE. Thus, in 1979, I decided to adopt MOVPE as the optimal crystal growth method for GaN. It was a crucial decision. As for the substrate for GaN growth, I tentatively (until a more suitable substrate would become available) chose the *c* face of sapphire as before, because it was stable even under the harsh MOVPE conditions, namely, a temperature above 1000° C and an ammonia (NH_3) atmosphere, and is similar to GaN in terms of crystallographic symmetry.

The fact that, even today, GaN-based crystals and devices are mainly grown on sapphire substrates by MOVPE is a clear indication that my choices were not wrong.

IV. CREATION OF GaN SINGLE CRYSTAL WITH EXCELLENT QUALITY

A. Development of low-temperature buffer layer technology in MOVPE

After making these crucial decisions, I returned to my old nest, Nagoya University, where I started anew to drastically improve the crystal quality of GaN grown by MOVPE in collaboration with my graduate students, Yasuo Koide and Hiroshi Amano, who put a lot of effort into crystal growth. Even with the MOVPE method, however, it was not easy for us to develop homogeneous GaN films. After many trials and errors, we made drastic innovations and improvements to the reactor tube and growth conditions.

The first improvement was that Koide mixed organometallic compounds such as trimethylgallium (TMGa) [and trimethylaluminum (TMAl) in the case of AlGaN growth] with NH_3 and hydrogen (H_2) gas as a carrier right in front of the opening of the reactor tube and blew this mixture through a gas delivery tube onto a substrate that was inclined at a 45° angle rather than being placed horizontally as in previous attempts as shown in Fig. 5. We also drastically increased the flow velocity of the gases in the reactor tube from only 2 cm per second to approximately 110 cm per second. We were thus able to reduce the formation of adducts of NH_3 and the organometallic sources and to suppress convective gas flows on the high-temperature substrate, which resulted in a uniform gas flow and the production of homogeneous GaN films.

Even though the film thickness was fairly constant over the entire wafer, this did not mean that there were no pits or cracks. There was also no substantial improvement in the electrical or optical properties, which suggested the presence of lattice defects and unintentionally incorporated impurities.

I suspected that, for the most part, this was due to the large interfacial free energy between GaN and sapphire caused by the huge lattice mismatch of 16% between the two crystals as in Fig. 6. In fact, for epitaxial growth of semiconductor crystals, it was considered to be “gospel” to have complete lattice matching as in the case of GaAs growth on a GaAs substrate. For heteroepitaxial growth, even a mismatch of about 1% would make it difficult to grow good-quality crystals.

To overcome this issue, we developed the low-temperature (LT) buffer layer technology in 1985 (Amano *et al.*, 1986; Akasaki and Sawaki, 1989; Manabe *et al.*, 1992; Akasaki and Amano, 2006). Specifically, this is a method for producing a thin buffer layer from a material with physical properties similar to those of GaN and sapphire with a thickness of 20–50 nm, which is thin enough not to interfere with the transmission of crystallographic information from the substrate to the epitaxial layer as shown in Fig. 7. The temperature for the deposition of the buffer layer might be

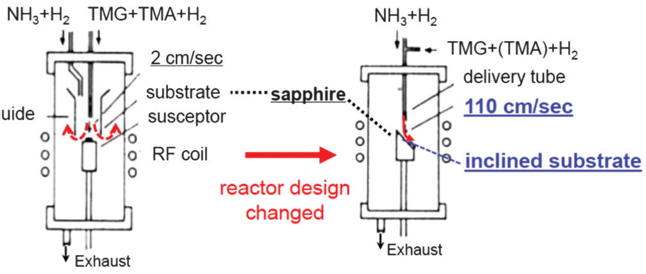


FIG. 5 (color). Schematic drawings of the reactor part of the MOVPE system before and after the reactor design was changed.

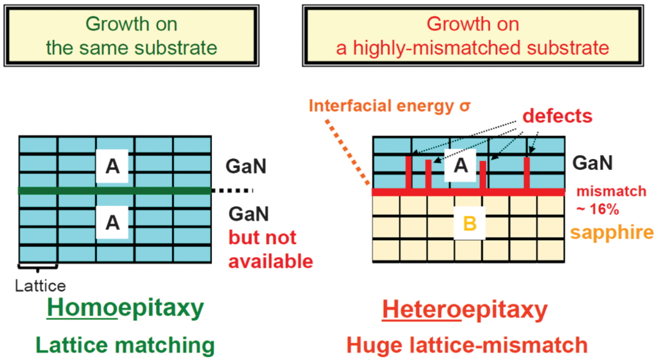


FIG. 6 (color). Schematics of homoepitaxy (e.g., GaN on the GaN case) and heteroepitaxy (e.g., GaN on the sapphire case).

suitable to be several hundred °C, which is considerably lower than the typical growth temperature for single-crystal GaN. The temperature would then be raised to that required for epitaxy growth of GaN single crystal, which is approximately 1000°C.

This is based on the idea of having a soft or flexible thin layer without a rigid structure like that of a single crystal, inserted between the substrate and the GaN film. The purpose of the buffer layer is to create conditions as close as possible to those for homoepitaxy, where no interfacial free energy exists in principle. For the buffer layer materials, I considered AlN, GaN, zinc oxide (ZnO), and SiC. First, we tried AlN, with which I was already familiar (Akasaki and Hashimoto, 1967).

In addition to the first improvement by Koide, Amano used the LT-AlN buffer layer technology combined with a further accelerated gas flow velocity of about 430 cm per second. By using this approach, in 1985, we eventually succeeded in growing the world's first extremely high-quality (semiconductor-grade) epitaxial GaN film (Amano *et al.*, 1986), which has been the drastic innovation in the GaN research.

Scanning electron micrographs (SEM) of surfaces of GaN films grown on a sapphire substrate showed the surface morphology of the films to be markedly improved by the LT-AlN buffer layer (Amano *et al.*, 1986; Akasaki, Amano, Koide *et al.*, 1989) as shown in Fig. 8. The GaN film had a specular surface with no pits or cracks and was so transparent that letters written on the underlying paper could be clearly seen as shown in Fig. 8(c).

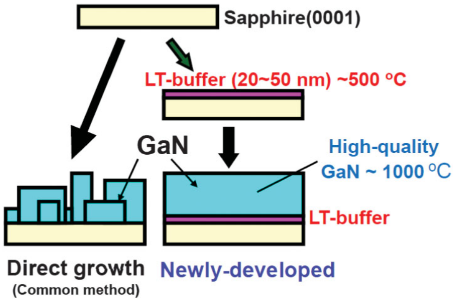


FIG. 7 (color). A procedure with newly developed low-temperature buffer layer technology for high-quality GaN.

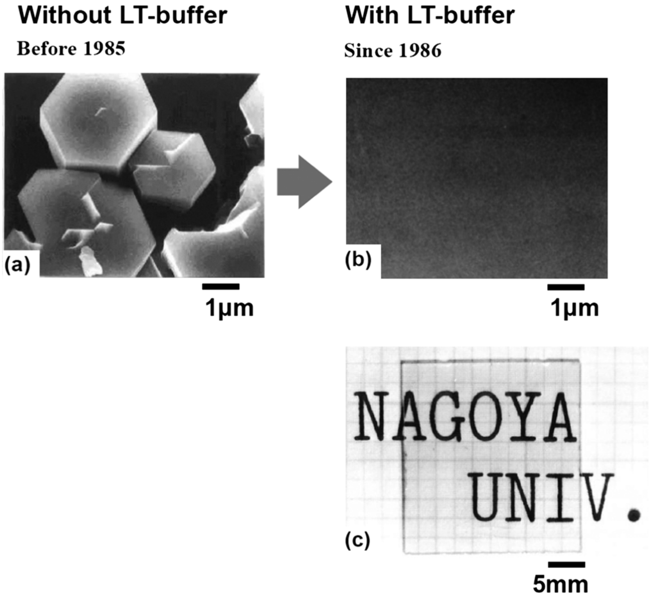


FIG. 8. Scanning electron micrographs of GaN on sapphire (a) without the LT-buffer layer and (b) with the LT-buffer layer. (c) A photograph of specular and transparent GaN film grown on sapphire with the LT-buffer layer.

Cross-sectional transmission electron microscopy (TEM) showed that the density of crystal defects such as dislocations markedly decreased with the use of the LT-AlN buffer layer (Hiramatsu *et al.*, 1991). X-ray diffraction profiles also showed that the crystal quality of GaN was significantly improved by this method (Amano *et al.*, 1986; Akasaki, Amano, Koide *et al.*, 1989). The residual donor (electron) concentration for GaN grown with the LT-AlN buffer layer decreased to the order of 10^{17} cm^{-3}, which is more than 2 orders of magnitude lower than that for GaN grown without the LT-AlN buffer layer (Akasaki, Amano, Koide *et al.*, 1989). Soon after, the electron concentration was further reduced to less than 10^{15} cm^{-3} (Akasaki and Amano, 2006). Simultaneously, the electron mobility markedly increased to several hundred cm^2 V^{-1} s^{-1} (Amano, Akasaki, Hiramatsu *et al.*, 1988; Akasaki, Amano, Koide *et al.*, 1989).

Figure 9 shows that near-band-edge emission predominated the photoluminescence (PL) spectrum of the undoped GaN grown with the LT-AlN buffer layer, whereas deep-level-related yellow emission was the major emission from GaN

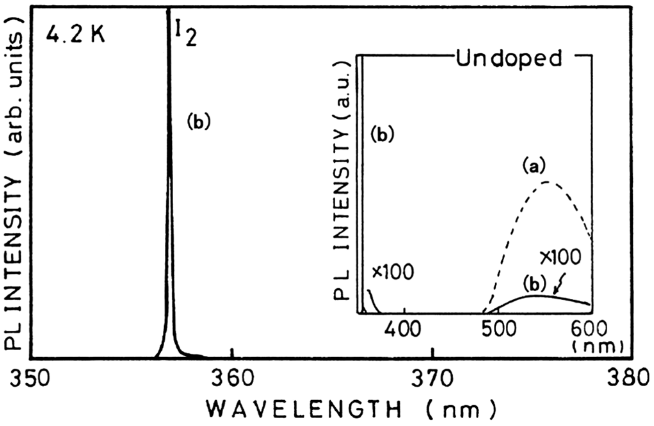


FIG. 9. 4.2 K photoluminescence spectra of undoped GaN films on sapphire substrates (a) without (dashed line in the inset) and (b) with (solid line) LT-buffer layers.

grown without the LT-AlN buffer layer (Akasaki, Amano, Koide *et al.*, 1989). In the spectrum from another GaN film grown with a LT-AlN buffer layer, free exciton lines (FE^A and FE^B) and impurity-bound excitons [donor-bound exciton (DBE) and acceptor-bound exciton (ABE)] were clearly observed showing that the crystal quality was drastically improved (Monemar *et al.*, 1996). By using the LT-AlN buffer layer deposited under optimum conditions, not only the crystal quality but also the electrical and luminescence properties of GaN were greatly improved (Amano *et al.*, 1986; Amano, Akasaki, Hiramatsu *et al.*, 1988; Akasaki, Amano, Koide *et al.*, 1989; Monemar *et al.*, 1996), as already seen in Figs. 8 and 9.

The thrill I felt when I finally saw transparent and specular GaN crystals is simply unforgettable. It was something that I had dreamt of realizing ever since the early 1970s.

This technology is an epochal concept that provides control over the growth of GaN, dramatically improving the quality of GaN and its alloys, which in turn has resulted in conductivity control for both *p*- and *n*-type nitrides, *p*-*n* junction blue-light-emitting device applications, and a revival in the materials science of nitrides.

In 1991, S. Nakamura reported that a LT-GaN buffer layer had the same effect as a LT-AlN buffer layer (Nakamura, 1991).

Today, this LT-buffer layer technology in MOVPE has become the standard approach to growing high-quality GaN and nitride alloys.

B. Model for the growth mode

In order to clarify the role of the LT-AlN buffer layer, different stages of GaN growth on the *c* face of sapphire were studied by SEM and reflection high-energy electron diffraction (RHEED) (Amano, Akasaki, Hiramatsu *et al.*, 1988; Akasaki, Amano, Koide *et al.*, 1989; Hiramatsu *et al.*, 1991). Figure 10 taken by Kazumasa Hiramatsu *et al.* shows (a) SEM images of the changes in surface morphologies during the growth and (b) the corresponding RHEED patterns from the same region. Image (1) in Fig. 10(a) was obtained for the deposited AIN buffer layer, whose thickness was about 50 nm; the layer appears uniform and featureless. However, the image in the inset, which was taken at high magnification, appears to show fine particles with sizes of several nanometers, which seem to be embedded in the futureless structure.

The corresponding RHEED pattern in Fig. 10(b) shows somewhat diffuse spots together with a halolike pattern, which is in agreement with the SEM results. The AIN buffer layer is thought to consist of fine crystallites in an amorphous-like matrix. After 5 min of growth, as seen in image (2) in Fig. 10(a), many truncated hexagonal pyramidal mesas (trapezoidal crystals) are seen to have formed. Two-dimensional lateral growth then occurs for a certain period, as shown in image (3). Subsequently, quasilateral growth dominates when the GaN film reaches a certain thickness, as seen in image (4). Finally, the entire substrate is covered by a flat GaN film, as seen in image (5). In Fig. 10(b), RHEED pattern (2), obtained after 5 min of growth, is spotlike, indicating that the GaN islands are three dimensional. Subsequently, the pattern becomes streaky, as the surface becomes flatter.

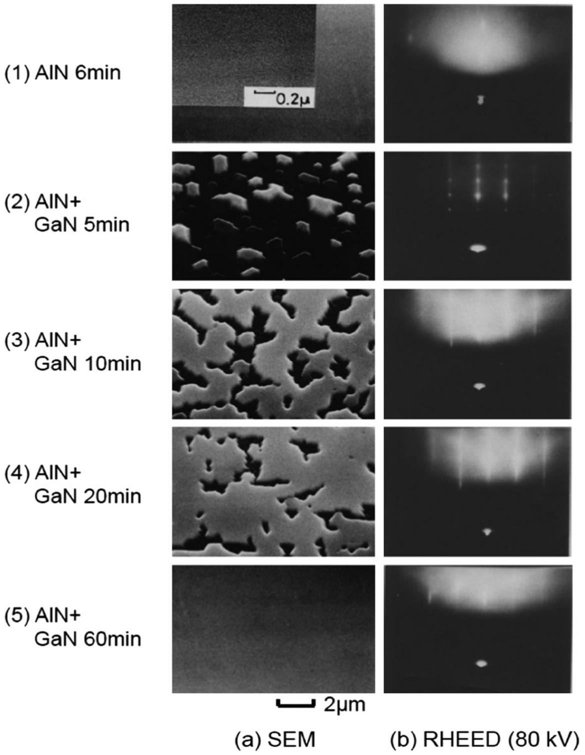


FIG. 10. (a) Scanning electron micrographs and (b) reflection high-energy electron diffraction patterns during the GaN growth on sapphire with a LT buffer.

Figure 11 shows a low-magnification cross-sectional bright-field TEM image of a wide region of a GaN film grown using a LT-AlN buffer layer (Hiramatsu *et al.*, 1991). It can be seen that three zones with different microstructures exist within the GaN layer. The zone nearest to the AlN buffer layer has fine image contrasts due to a number of defects. Consequently, this zone is referred to as the *faulted zone* (Z_F) and is about 50 nm thick. Above the faulted zone, there is another zone, which contains a number of trapezoid crystals, corresponding to the truncated hexagonal pyramidal GaN islands observed by SEM, as shown in image (3) in Fig. 10(a). Since the defect density in this zone is much lower than that in the faulted zone, it is called here the *semisound zone* (Z_{ss}) and is about 150 nm thick. The upper zone is referred to as the *sound zone* (Z_s), as it contains only a small number of defects.

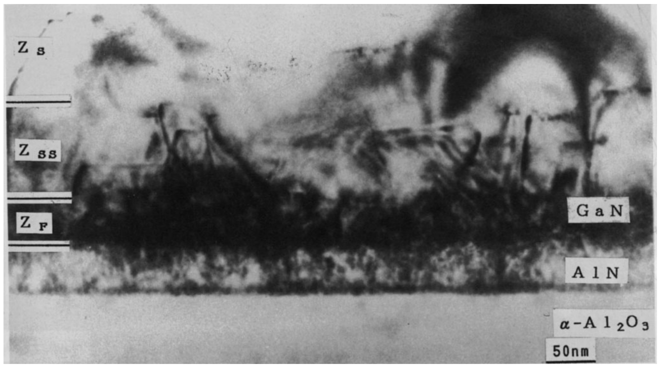


FIG. 11. A bright-field image of GaN on sapphire with a LT-AlN buffer by cross-sectional TEM.

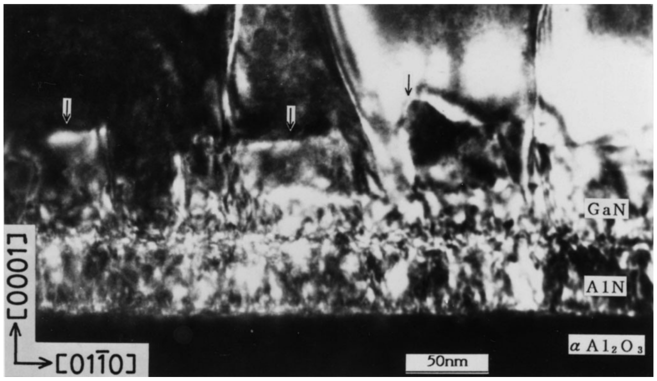


FIG. 12. A dark-field image of GaN on sapphire with a LT-AlN buffer by cross-sectional TEM.

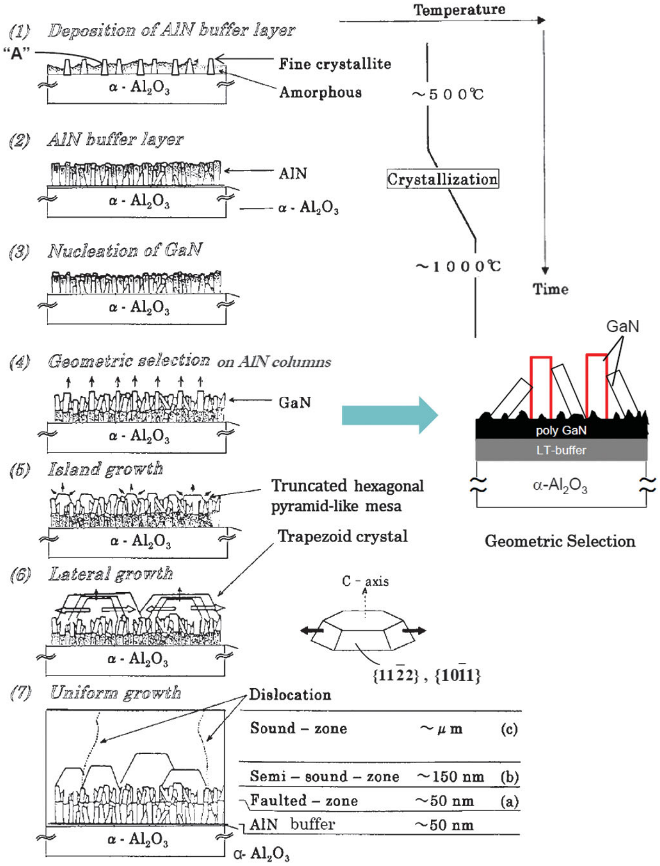


FIG. 13 (color). A growth model of GaN on sapphire with a LT-buffer layer. "Geometric selection" of the GaN fine crystals was suggested.

In the sound zone, the defect density decreases abruptly for GaN layers thicker than about 300 nm, resulting in high-quality uniform GaN.

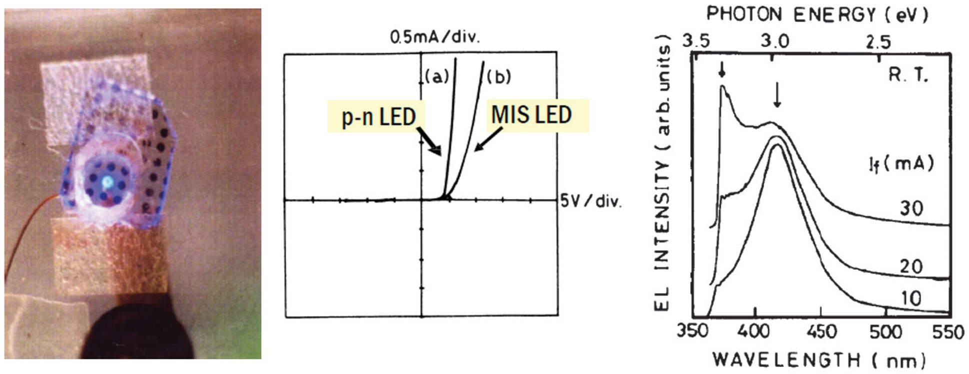
Figure 12 shows a dark-field cross-sectional TEM image with a little higher magnification in order to clarify the microstructure of the AlN layer and the different zones in the GaN layer. The image contrasts in the figure reveal that the AlN layer is composed of columnar fine crystals like frost columns. The diameter is of the order of 10 nm, which corresponds to the front of the columnar crystals. The AlN layer has an amorphouslike structure at the deposition temperature, as shown in Fig. 10 image (1). However, as the temperature is ramped from the low AlN deposition temperature to the GaN epitaxial temperature of about 1000° C, solid-phase regrowth occurs, and fine columnar structure forms in the AlN. A similar contrast is seen in the faulted zone of the GaN, which suggests that GaN in the faulted zone is also composed of columnar fine crystals. It is likely that each GaN column from a GaN nucleus has formed on top of a columnar AlN crystal. Therefore, it is thought that *high-density nucleation* of GaN occurs owing to the very higher density of AlN columns as described in Fig. 13 images (1)–(3), compared to the case where GaN is grown directly on a sapphire substrate as seen in Fig. 8(a).

Figure 13 shows the proposed growth model for a GaN film on a *c*-face sapphire substrate with a LT-AlN buffer layer. Each fine GaN crystal begins to grow along the *c* axis, forming a columnar structure. Each of the columns is slightly tilted or twisted at this stage, in order to absorb the strain due to the large lattice mismatch. This suggests that geometric selection (Chernov, 1984) of the GaN fine crystals occurs, and the columnar fine GaN crystals increase accordingly in size during the growth, as shown in Fig. 13 image (4). The number of columns emerging at the front gradually decrease with the front area of each column increasing accordingly. Because the only columns that survive are those that grow along the fastest growth directions, which is the *c* axis, all columns eventually have their *c* axis oriented normal to the substrate, as indicated by arrows in Fig. 13 image (4), which shows the growth model for GaN film on *c*-face sapphire with the LT-AlN buffer layer. In the faulted zone, trapezoidal islands are formed on top of the columnar crystals, as seen in Fig. 11. At this stage, all of the columnar crystals are *c* axis oriented, and this orientation is transferred to the trapezoidal islands, as shown in Fig. 13 image (5). These islands preferentially grow up to become larger trapezoid crystals, which cover the minor island nearby and form the semisound zone.

Subsequently, *lateral growth and coalescence* of the islands occur in the stages shown in SEM images (3) and (4) in Fig. 10(a). The trapezoid crystals grow at a higher rate in the lateral direction, as shown in image (6) in Fig. 13, because the growth rate of the *c* face is much lower. This lateral growth continues until the islands fully coalesce to form a continuous layer.

Since the crystallographic orientation of all of the islands is almost the same, a smooth well-oriented GaN layer with a low defect density is formed, as seen in Fig. 8(b). Thus, the uniform growth due to layer-by-layer growth occurs creating the sound zone.

On the other hand, in the case of direct growth without a LT-buffer layer, hexagonal GaN columns with many different sizes and heights are formed. These grow three dimensionally resulting in a rough surface, and many pits at their boundaries, exposing the bare sapphire substrate, as shown in Fig. 8(a). The optimum thickness of the deposited AlN layer was found to be around 50 nm. If it was too thick (for example, 150 nm), the GaN film became polycrystalline. Also, if the deposition temperature of the AlN buffer layer was close to the temperature at which AlN crystal could be grown, the surface of GaN showed many hexagonal hillocks (Amano, Akasaki, Hiramatsu *et al.*, 1988).



(a) (b) (c)

FIG. 14 (color). (a) GaN *p-n* junction blue/UV LEDs (black dots). An electric current is being passed only through the centered LED that is emitting blue light. (b) *I-V* characteristics of *p-n* junction LED (left) and MIS LED (right). (c) Electroluminescence spectra of GaN *p-n* junction blue/UV LED.

V. DISCOVERY OF *p*-TYPE GaN AND DEMONSTRATION OF *p-n* JUNCTION BLUE/UV LED

With the successful control of the quality of GaN, we could start working on *p*-type doping. Despite repeated efforts on Zn doping of high-quality GaN films grown with a LT-AlN buffer layer, no successful results were obtained (although the film resistivity was increased). In 1988, Amano found that the Zn-related luminescence intensity was greatly increased with no change in spectral shape, when a high-quality Zn-doped GaN film was irradiated with low-energy electron beam (LEEBI) at RT or lower (Amano, Akasaki, Kozawa *et al.*, 1988). We suspected that the Fermi level of the sample was changed, which potentially led to a shift toward the *p* type. However, the samples did not exhibit *p*-type conduction. We then realized that Mg was a potentially shallower acceptor than Zn, since the difference in electronegativity between Mg and Ga is smaller than that between Zn and Ga (Phillips, 1973). In early 1989, graduate student Masahiro Kito carried out Mg doping of high-quality GaN grown by the LT-buffer technology. For Mg doping, bis-cyclopentadienyl Mg (CP_2Mg) or methyl-CP_2Mg (MCP_2Mg) was used as a dopant precursor (Akasaki, Amano, Kito *et al.*, 1989; Amano *et al.*, 1990).

Then we applied the LEEBI treatment to the sample and found that the Mg-related blue-luminescence intensity was markedly enhanced, while the spectral shape remained unchanged, and that the sample had been converted to a low-resistivity *p*-type crystal, as confirmed by the Hall effect measurement (Amano *et al.*, 1989) and later by the electron-beam induced current measurement (Akasaki *et al.*, 1991).

We immediately produced a high-performance GaN p-n junction blue/UV LED with encouraging current-voltage (I–V) characteristic. This was demonstrated in 1989 and was the first such device in the world (Amano et al., 1989) [Figs. 14(a) and 14(b)]. This LED exhibited blue light emission with a low current injection (<20 mA*), and additional near UV light emission with a high current injection (Akasaki et al., 1991); see Fig. 14(c).*

As a possible mechanism for the LEEBI effect, we proposed the "Coulombic explosion" model (Carlson and White, 1966). In this model, electron-beam excitation generates many free electrons and holes (Coulombic explosion) which stimulate the breaking of Mg-H bonds and create active Mg as an acceptor impurity. The validity of this mechanism was later confirmed by researchers at the University of Illinois (Li and Coleman, 1996), and it was found to occur even at low temperatures (Amano, Akasaki, Kozawa *et al.*, 1988; Li and Coleman, 1996).

In 1992, S. Nakamura and his group obtained *p*-type GaN by thermal annealing above 400°C in a H_2-free atmosphere, rather than by electron irradiation of Mg-doped GaN using CP_2Mg. It was clarified that the Mg becomes passivated by forming a Mg-H complex (Nakamura *et al.*, 1992). To realize *p*-type nitrides, it is therefore essential to activate the Mg acceptor by releasing the hydrogen (Van Vechten, Horning, and Goldenberg, 1992). Indeed, there is a high concentration of hydrogen atoms in MOVPE-grown nitrides. It should be noted, however, that the concentration of residual donors should be drastically reduced before solving problems related to hydrogen passivation of acceptors (Nickel, 1999), which is also a well-known issue with regard to both III-V compounds and Si.

These results clearly show that improving crystal quality by the LT-buffer layer technology, Mg doping and its activation are the keys for the development of the p-type conduction in wide bandgap nitrides.

We later went on to develop *p*-type nitride alloys; *p*-AlGaN in 1991–1992 (Akasaki and Amano, 1992a) and *p*-GaInN in 1995 (Yamasaki *et al.*, 1995) for the first time.

VI. CONDUCTIVITY CONTROL OF *n*-TYPE GaN AND NITRIDE ALLOYS

Control of electric conductivity of *n*-type GaN grown without the LT-buffer layer had been quite difficult, because of the high residual donor concentration of greater than 10^{19} cm^{-3}. On the other hand, when a LT-AlN buffer layer was used, the conductivity of *n*-type GaN became extremely low due to the drastic reduction in the residual donor concentration. Control of *n*-type conductivity is extremely important for many types of nitride-based devices. In 1990, we succeeded in controlling the conductivity of *n*-type GaN (Amano and Akasaki, 1990) [and AlGaN in 1991 (Murakami

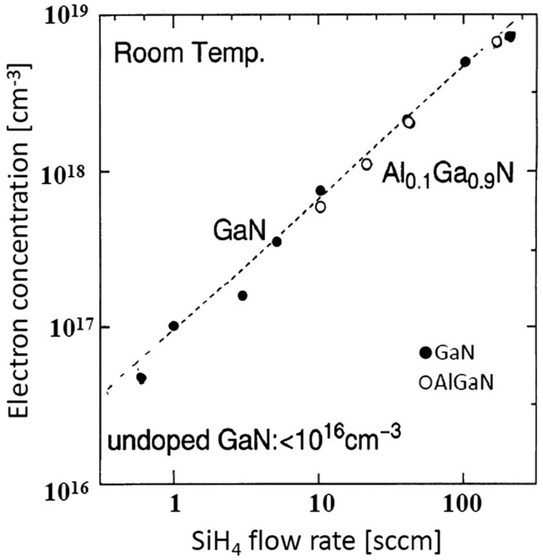


FIG. 15. Electron concentrations in GaN (●) and AlGaN (○) as a function of SiH_4 flow rate.

et al., 1991)], over a range of about 2 orders of magnitude, by Si doping using SiH_4, as shown in Fig. 15. High crystalline quality was again maintained by the use of the LT-buffer layer technology.

This conductivity-control method now enjoys widespread use around the world.

The conductivity control of high-quality p-type and n-type GaN and nitride alloys has allowed the use of heterostructure and multiple quantum wells (MQWs) for more efficient p-n junction light-emitting structures.

VII. BRIEF HISTORY OF NITRIDE-BASED BLUE LEDs

In 1992, we improved the external quantum efficiency of the blue/UV LED to 1.5% (power conversion efficiency of more than 1%) by employing an AlGaN/GaN double heterostructure (DH) (Akasaki *et al.*, 1993). And in 1994, the first commercial AlGaN/GaInN: Zn, Si DH blue LED with the external quantum efficiency of 2.7% was launched (Nakamura, Mukai, and Senoh, 1994). In 1992, we also developed the first UV LEDs based on *p*-AlGaN/GaN/*n*-AlGaN DH with an output power of several mW at RT (Akasaki and Amano, 1992b).

Chronological developments in the external quantum efficiency η_{ext} of nitride-based blue LEDs between 1971 and 2000 are shown in Fig. 16 (Akasaki and Amano, 1997). It can be seen that η_{ext} was relatively constant at about 0.1%, before the breakthroughs described in this paper. It began to increase steeply soon after success was achieved in growing high-quality nitride crystals, which resulted in the GaN *p-n* junction LED (Amano *et al.*, 1989). To improve the emission efficiency of blue LEDs and the performance of violet LD, the use of GaInN alloy as an active layer is essential. The first successful growth of single-crystal GaInN alloy was reported in 1989–1991 (Nagatomo *et al.*, 1989; Yoshimoto *et al.*, 1991). Although it was soon used as the active layer of blue DH LEDs, the devices functioned via donor-acceptor-pair emission rather than band-edge emission because of the low quality of GaInN. Growth of high-quality GaInN/GaN quantum wells (QWs) (Nakamura *et al.*, 1995) and multiple QWs (MQWs) (Amano and Akasaki, 1995) exhibiting distinct band-edge emission, which is currently used as an active layer in blue LEDs, was first reported in 1995. In 2002, M. Yamada *et al.* reported that blue LEDs using such high-quality GaInN/GaN MQWs exhibited a η_{ext} of higher than 36% (Yamada *et al.*, 2002). They have been used as an excitation source for yellow phosphors in white LEDs (Bando *et al.*, 1998; Shimizu and Banno, 1999).

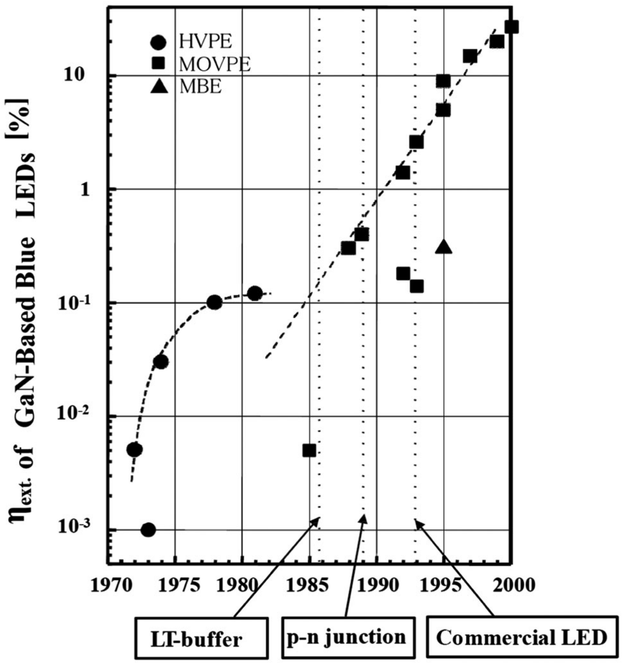


FIG. 16. Chronological developments in external quantum efficiency η_{ext} of nitride-based blue LEDs (1971–2000).

VIII. DEVELOPMENT OF NITRIDE-BASED LDs AND OTHER DEVICES

In 1990, we also succeeded for the first time in achieving RT stimulated emission in the UV range by optical excitation at a power that was 1 order of magnitude lower than before that previously required (Amano, Asahi, and Akasaki, 1990), showing that GaN is of high quality as shown previously. Figure 17 (Akasaki and Amano, 1992b, 1997) shows the threshold power P_{th} for stimulated emission from nitrides over the years. Before 1986, stimulated emission with optical excitation could be achieved only at low temperatures and P_{th} was very high. We proposed that a significant reduction in P_{th} would be possible with the use of DHs or separate-confinement heterostructures. This is due to the fact that the refractive index of the nitride system decreases with increasing band-gap energy (Akasaki and Amano, 1994). Similar to the increase in blue LED efficiency shown in Fig. 16, P_{th} began to decrease exponentially immediately after the marked improvement in the crystal quality of nitrides, described in the previous section. By optimizing the heterostructure, we obtained a new record of the lowest P_{th} almost every year between 1990 and 1995.

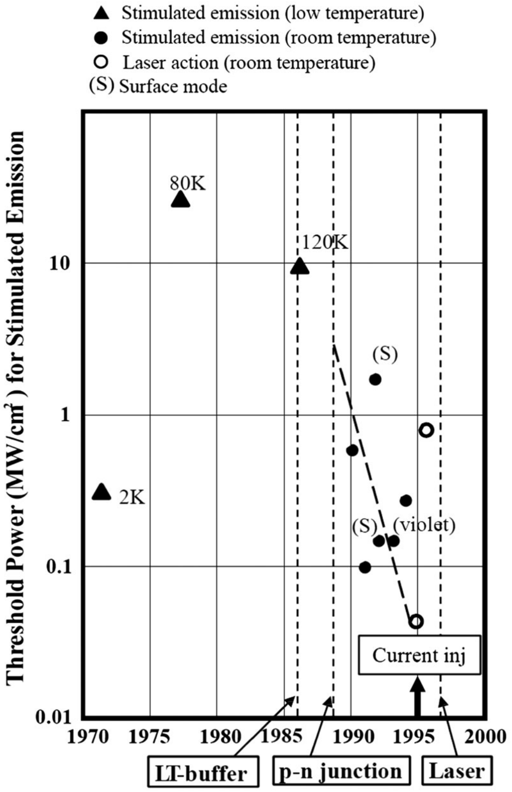


FIG. 17. Chronological developments in threshold power for stimulated emission by optical pumping (before 1995) and current injection (after late 1995) from nitrides (1971–2000).

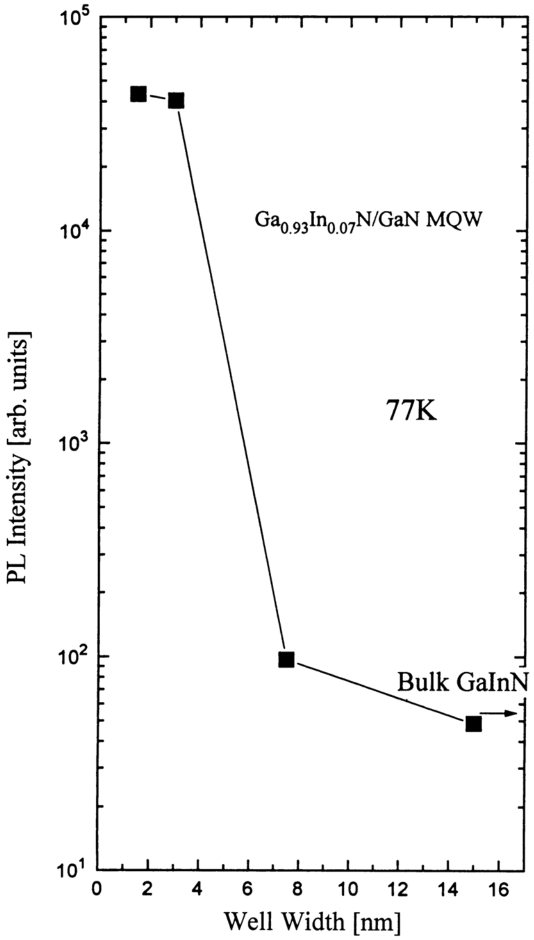


FIG. 18. 77 K PL intensities of GaInN/GaN QWs as a function of the GaInN well width.

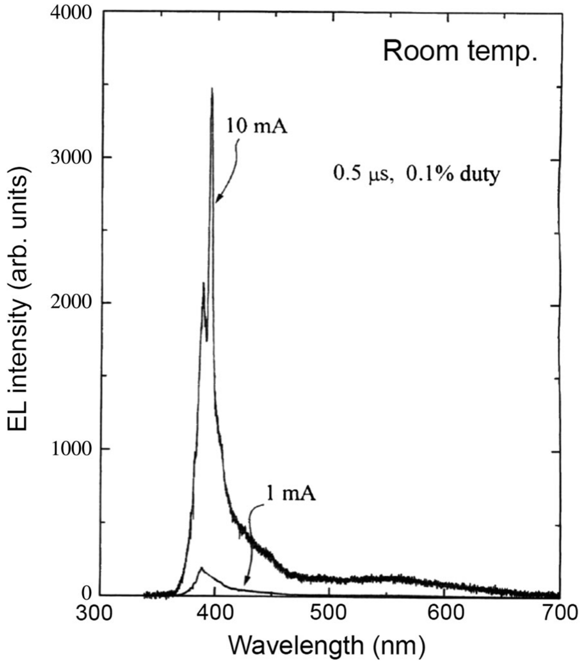


FIG. 19. A stimulated emission spectrum from a GaInN/GaN QW device under pulsed current injection at room temperature.

In 1995, we found that band-edge emission for GaInN/GaN MQWs with well widths of less than 3 nm, which roughly corresponds to the Bohr radius for excitons or electrons in GaN, was 3 orders of magnitude higher than that for a thick GaInN QW as shown in Fig. 18 (Akasaki, Amano, and Suemune, 1996). In 1997, this phenomenon was qualitatively attributed to suppression of the quantum confined Stark effect (QCSE) (Takeuchi *et al.*, 1997, 1998) in such narrow wells. The QCSE is caused by the presence of a large piezoelectric field (Takeuchi *et al.*, 1997) in the GaInN well, which was found to be about 1 MV/cm for an InN molar fraction of 0.1. By adopting such thin QWs as the active layer, we succeeded in demonstrating the first stimulated emission at 388 nm from a GaInN/GaN QW device with well width of 2.5 nm under pulsed current injection at RT as shown in Fig. 19 Akasaki *et al.* (1995).

Shortly after that, a group at Nichia Corporation reported a distinct pulsed lasing operation at 405 nm using an active layer composed of thin QWs (Nakamura *et al.*, 1996b). We achieved pulsed laser oscillations from a diode with a single quantum well at 376 nm in 1996 (Akasaki *et al.*, 1996) and at 350.9 nm in 2004 (Iida *et al.*, 2004), which were the shortest wavelengths at the time. The first RT continuous-wave operation of a 405 nm blue-violet LD was reported in 1996 (Nakamura *et al.*, 1996b), and such devices were later adapted as the light source for high-density digital disk systems. In 2000, we developed a high-sensitivity solar-blind UV sensor with low dark current (Pernot *et al.*, 2000), and in 2006 a high on-off ratio, low on-resistance, and normally off mode

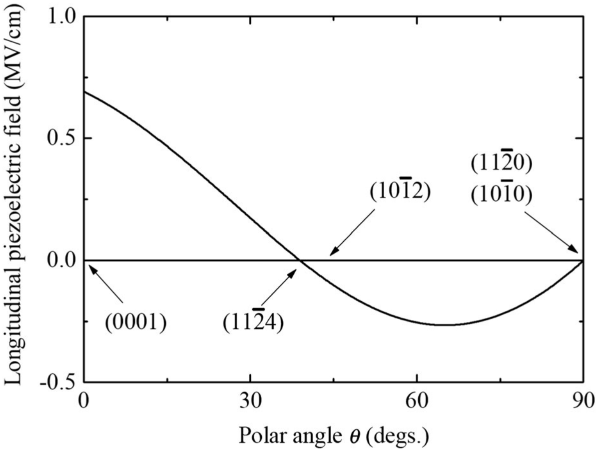


FIG. 20. Calculated longitudinal piezoelectric field in strained $Ga_{0.9}In_{0.1}N$ on GaN as a function of the polar angle from (0001).

AlGaN/GaN heterostructure field effect transistors (Fujii *et al.*, 2006).

With regard to quantum effects in the nitride system, we verified quantum size effect in 1991 (Itoh *et al.*, 1991), and the piezoelectric and quantum confined Stark effects in 1997 (Takeuchi *et al.*, 1997) as described above. In 2000 (Takeuchi, Amano, and Akasaki, 2000), Tetsuya Takeuchi *et al.* theoretically determined the orientation dependence of the piezoelectric field and showed the existence of nonpolar and semipolar nitride crystal planes (see Fig. 20). This has triggered worldwide efforts to grow such crystals in order to produce more efficient light emitters such as high-efficiency green/yellow-green LEDs (Yamamoto *et al.*, 2010), high-power blue-violet LEDs (Zhao *et al.*, 2011), and high-power green LDs (Takagi *et al.*, 2012).

IX. SUMMARY AND FUTURE EXPECTATIONS

The creation of high-quality semiconductor-grade single crystals of GaN and related alloys, realization of low-resistivity *p*-type GaN, and conductivity control in *n*-type nitrides are all of great practical importance, and, by 1991, these final pieces of the puzzle were in place. Stretching back to the late 1980s to the early 1990s, the remarkable achievements in GaN-based materials and devices have caught the eye of many scientists around the world, who become engaged in research in this field. Many topics relating to GaN-based LEDs and LDs have been published in scientific journals and presented at international conferences. Nitride research has become one of the most exciting themes in the world.

Going back to Fig. 3, it shows the number of publications per year referred from INSPEC using the keywords GaN; major events in the history of nitride research are indicated. Events are labeled by the year when they were first achieved, anywhere in the world. As can be seen, the number of papers in 1969 is only 4 but it increased to 34 in 1975, inspired by the first GaN single crystal (Maruska and Tietjen, 1969), the MIS LED (Pankove, Miller, and Berkeyheiser, 1972), and stimulated emission from GaN at 2 K [Dingle *et al.*, 1971) (period (A)].

The number then decreases until the year 1985, indicating that GaN research activity declined [period (B)], since the difficulty in achieving high-quality GaN and *p*-type conduction had come to be realized. However, after we succeeded in creating a GaN single crystal with excellent quality (1986) and creating a GaN *p*-*n* junction blue/UV LED (1989), the number of published papers began to increase. The increase was exponential to 60 in 1991 after a short incubation period [period (C)], to 370 in 1995, to 1200 in 1997, and to 2040 in 2000 [period (D)].

At present, the aforementioned innovations of blue LEDs allow us to complete the set of three primary colors using semiconductors. Coupled with existing high-brightness red LEDs, blue/green LEDs are leading to the development of completely solid-state full-color displays, traffic lights, signals, signage, and specialized lighting applications. White LEDs composed of nitride-based blue/UV LEDs and yellow phosphor are 2 times more efficient than fluorescent lamps, and as such white LEDs are now being used in TVs, mobile phones, computer displays, and general lighting equipment. The white and UV LEDs are expected to be used for biomedical applications, such as sterilization, microscopic level diagnoses, and medical treatments. Blue LEDs combined with existing red LEDs are also being used for agricultural lighting sources. GaN-based LED lamps can operate for many hours on electricity produced by a solar battery and can be used in places on Earth where there is no electrical power supply.

Long-lifetime nitride-based violet LDs are being used to read and write data in optical disk systems. Coupled with existing red LDs, GaN-based blue and green LDs are expected to be used in miniprojectors.

GaN-based group-III nitride semiconductors are also promising for high-speed/high-power electronic devices, due to their high electron saturation velocities and high breakdown voltages. Such devices are important in the mobile telecommunications industry, for energy savings in vehicles such as trains and automobiles, and also for home electrical appliances such as air conditioners and refrigerators.

All of these nitride-based devices are robust in harsh environments, allow a significant amount of energy to be saved, and provide a route to avoid the use of hazardous materials. The use of nitride-based devices will be one of our most powerful tools in the fight against global warming.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to many collaborators: M. Hashimoto, Y. Ohki, Y. Toyoda, M. Ohshima, N Mazda, H. Kobayasi, and M. Matsuki at Matsushita Research Institute Tokyo, Inc., numerous students and coresearchers: N. Sawaki, K. Hiramatsu, Y. Koide, H. Amano, M. Kito, and H. Murakami at Nagoya University and S. Kamiyama, T. Takeuchi, and M. Iwaya at Meijo University, and B. Monemar at Linköping/Lund Universities, for their great contributions throughout this research. His special thanks are extended to Toyoda Gosei Company Ltd., Toyota Central Research Laboratory, and Japan Science and Technology Agency for their co-operation in the development and production of GaN-based blue LEDs and related materials. This work received financial support from the Ministry of Economy, Trade and Industry, Japan (formerly Ministry of International Trade and Industry), the Ministry of Education, Culture, Sports, Science and Technology, Japan (formerly Ministry of Education, Science and Culture), and Japan Society for the Promotion of Science. Finally, the author would like to thank the Nobel Foundation and members of the Royal Swedish Academy of Sciences for honoring our "invention of efficient blue LEDs which has enabled bright and energy-saving white light sources."

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