Blue LEDs

International Edition: DOI: 10.1002/anie.201500591
German Edition: DOI: 10.1002/ange.201500591

Background Story of the Invention of Efficient InGaN Blue-Light-Emitting Diodes (Nobel Lecture)**

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Blue LEDs · gallium nitride · light-emitting diodes · organometallic CVD · two-flow MOCVD

1. Introduction: Impact of White-Light-Emitting Diodes

The basic structure of an efficient double-heterostructure (DH) light-emitting diode (LED) is summarized in Figure 1. This optoelectronic device is composed of semiconductor materials and is fabricated by sandwiching an active, emitting layer between an *n*-type and a *p*-type layer. The *n*-type semiconductor layer has an abundance of high-energy electrons, whereas the *p*-type semiconductor has an abundance of available empty sites, in which the electron may reside at a lower energy level. These sites are also referred to as holes, are positively charged, and are mobile. The energy difference between the high- and low-energy electron state is referred to as the bandgap of the material. For DH LEDs, the bandgap of the active layer is smaller than that of the *n*-type and *p*-type layers.

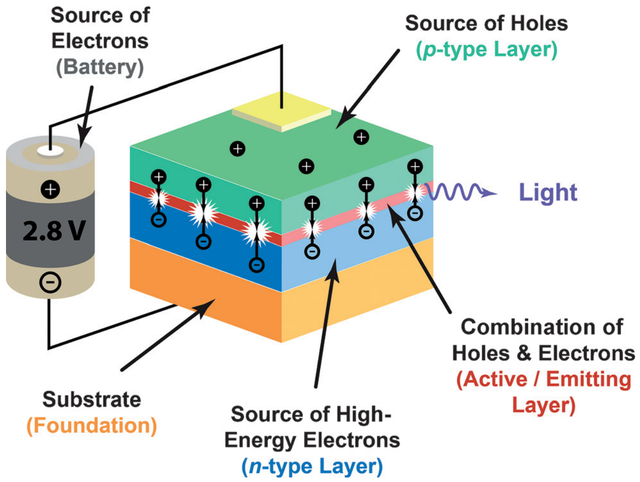

Figure 1. Schematic depiction of a double-heterostructure (DH) light-emitting diode (LED). Within the active layer, electrons and holes recombine and emit light of a wavelength equal to the bandgap of the active layer. High-energy electrons are sourced from the negative terminal of the battery and return to the positive terminal after losing their energy to a photon in the active layer.

When forward biasing a DH LED using a battery (or any other direct current source), electrons and holes are injected into the active layer from *n*-type and *p*-type layer, respectively. The electrons and holes recombine radiatively in the active layer, thereby emitting photons. This process is very efficient for DH LEDs, as the electrons and holes are confined to the active layer as a result of the smaller bandgap of the active layer with respect to the *n*-type and *p*-type cladding layers (see also Figure 7). The resulting photon has an energy that is approximately equal to the bandgap of the active-layer material. Modifying the bandgap of the active layer creates photons of different energies.

In the 1980s, all known material systems possessing the necessary material properties for blue-light emission had shortcomings, thus negating the possibility of creating an efficient blue LED. Gallium nitride (GaN) was one possible candidate, though, at the time, no *p*-type or active layer could be created. These challenges were ultimately overcome, leading to the first efficient blue LED using GaN in 1993 by Nakamura et al.[1] Figure 2 shows a close-up image of a bare and packaged blue GaN LED.

Using blue LEDs, highly efficient white-light sources become possible. White light can be obtained by converting part of the blue light emitted from the LED to yellow using a phosphor.[2] To the human eye, the combination of blue and yellow light is perceived as white. A white LED can be created by embedding phosphors in a plastic cap, which surrounds a blue LED (see Figure 3). Higher-quality white light can also be obtained by mixing blue light with other colors, including red and green.[3]

With the availability of white LEDs, a variety of applications can be significantly improved, if not enabled all together. But arguably, the most important impact of the white LED is its ability to generate white light at an efficiency that was previously impossible. The efficacy, a measure of perceived light power relative to the provided electrical power, of white light improved over the centuries, starting with oil lamps (0.1 $\mathrm{lm\,W^{-1}}$) in the 15000s B.C., incandescent bulbs (16 $\mathrm{lm\,W^{-1}}$) in the 19th century, fluorescent lamps (70 $\mathrm{lm\,W^{-1}}$) in the 20th century, and LEDs (300 $\mathrm{lm\,W^{-1}}$) in the 21st century (see also Figure 15).

With this significant improvement, substantial energy savings are now possible. It is currently estimated that in 2030

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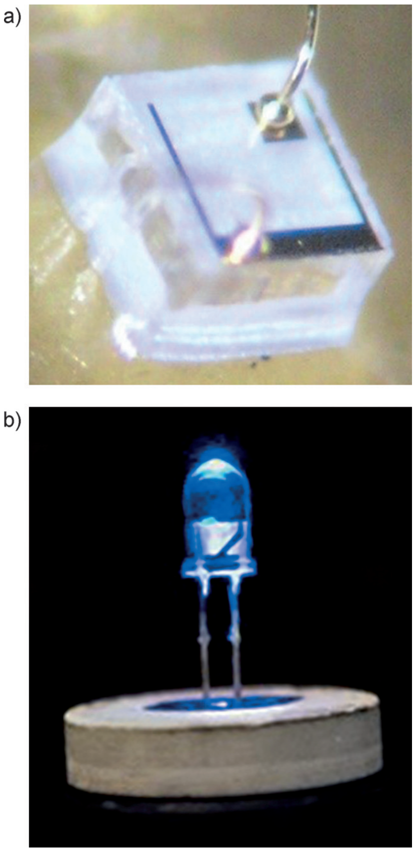

Figure 2. a) Image of a blue GaN LED with attached gold-wire contacts (size of diode: 0.4×0.4 mm), and b) the same LED packaged as a commercial product.[1]

approximately 261 TWh of electrical energy will be saved because of the widespread use of white LEDs.[4] This corresponds to an electricity savings of approximately 40% in 2030. Furthermore, this reduction in energy usage eliminates the need for at least 30 1-GW power plants by 2030 and avoids generating 185 million tons of CO_2.

2. Material of Choice: ZnSe versus GaN

In the 1980s, two materials were considered as possible candidates for efficient blue LEDs: zinc selenide (ZnSe) and GaN[5].

ZnSe could be grown on single-crystal gallium arsenide (GaAs) substrates, resulting materials of high structural quality, given the very small lattice mismatch of 0.3% between ZnSe and GaAs. For GaN on the other hand, no lattice-matched substrate was available and researchers were forced to grow on sapphire. The large lattice mismatch (≈16%) resulted in heavily defected material with a high density of dislocations.

When I joined the field in 1989, ZnSe was grown on GaAs with dislocation densities of less than $10^3\,cm^{-2}$. This was very popular among scientists, given the high crystal quality and the prevailing notion that a dislocation density below $10^3\,cm^{-2}$ is needed to obtain optically functional LEDs with a high efficiency and a long lifetime.[5] Most researchers worked in this field. GaN, however, was grown on sapphire, resulting in dislocation densities in the order of $10^9\,cm^{-2}$. Unsurprisingly, few researchers were working in this field, though, most notably, fellow Nobel Laureates Professor Isamu Akasaki and his graduate student, Hiroshi Amano.

A striking example to highlight the popularity of ZnSe as compared to GaN is provided by looking at the attendance of researchers at the most popular conference for applied physics in Japan. At the Japan Society of Applied Physics (JSAP) conference in 1992, there were approximately 500 individuals attending the ZnSe sessions, whereas for GaN, there were around 5, including the chair Professor Isamu Akasaki, speaker Hiroshi Amano, and myself, as a member of the audience. Not only was ZnSe more popular at the time, GaN was actively discouraged, with researchers stating "GaN has no future" and "GaN people have to move to ZnSe materials".

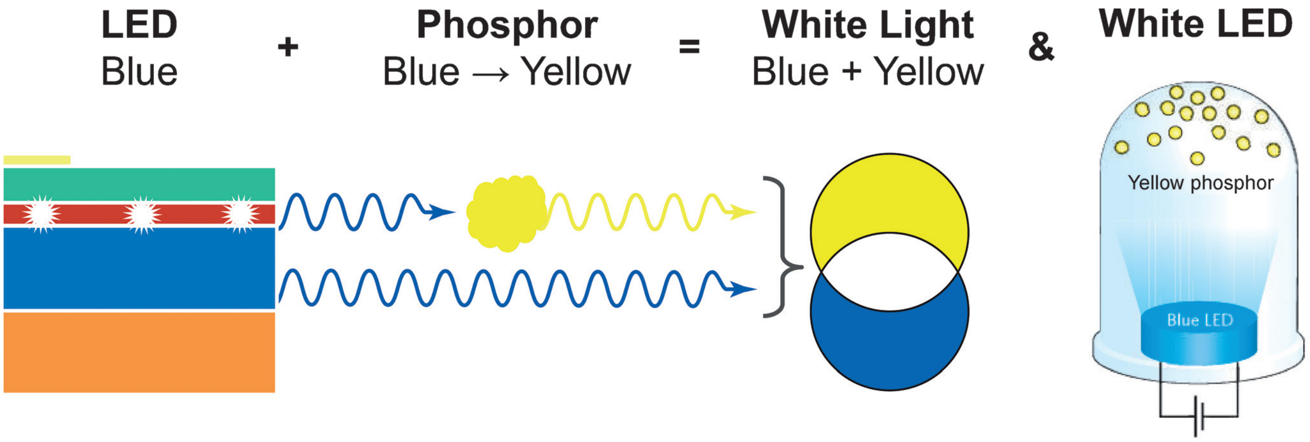

Figure 3. From blue LED to white LED. Part of the blue light emitted from a blue LED is converted to colors of a lower energy, such as yellow, using a phosphor. The combination of blue and yellow light is perceived as white to the human eye. Combining a blue LED with embedded phosphors in the plastic cap creates a white LED.[3]

3. Development of GaN

My entry into the field started in April of 1988, when I went to the University of Florida as a visiting researcher. The main purpose of my visit was to learn how to use a MOCVD (Metal Organic Chemical Vapor Deposition) system to grow GaAs crystals on a silicon substrate, as I had no experience in how to use a MOCVD. During my stay there, I worked together with graduate students and they all asked me if I had a Ph.D. I said no. At the time, I only had a Masters. Next, they asked me if I had published any scientific papers. Again, I said no, I had never published a single paper. Consequently, they treated me as a technician. In the U.S., this meant one has to help the researcher and one's name would not appear on papers or patents. Gradually, I became very frustrated with this arrangement.

One year later, in March of 1989, I came back to Japan. It was my dream to get a Ph.D. degree. In Japan at the time, it was possible to be awarded a Ph.D. if one published five scientific papers. This type of degree was called a paper degree and one did not need to go to the university to get the degree. It was therefore my ultimate dream to publish at least five papers and get a Ph.D.

With this idea in mind, I noted that the ZnSe field was publishing lots of papers. As I had never published a paper, I had no confidence in writing one. In the GaN field, only very few papers had been published, mainly from Professor Isamu Akasaki and Hiroshi Amano. I was therefore confident that I could publish lots of papers, though I had no confidence that I could actually invent the blue LED. My only objective was to get a Ph.D. That's it.

So, after returning to Japan in March of 1989, I wanted to grow GaN using a MOCVD reactor. I purchased a commercially available MOCVD reactor for 2 million U.S. dollars. But this MOCVD reactor was designed for growth of GaAs. At the time, Professor Akasaki and his student Amano had developed a novel, research-scale MOCVD reactor for growth of GaN.[6] Their design required exceptionally high carrier-gas velocities (around $4.25\,\mathrm{m\,s^{-1}}$) giving GaN, though the high carrier-gas velocities presented challenges pertaining to uniformity, scalability, and reproducibility. Furthermore, their reactor design could only be used for small-area growth, thereby lacking the necessary properties for commercialization. As I was working for a company, I had to find a way to grow high-quality GaN on large-area, 2-inch-diameter sapphire substrates.

Another challenge related to growing high-quality GaN was the use of high concentrations of aluminum in the MOCVD reactor. While the development of the aluminum nitride (AlN) buffer layer by Akasaki and Amano was a major breakthrough, providing high-quality GaN film growth with a mirror-like surface morphology,[6] the use of aluminum caused significant problems to the MOCVD reactor, resulting in poor reproducibility in subsequent GaN growth. Eliminating the use of high concentrations of aluminum during growth was strongly desired.

After my purchase of a MOCVD reactor, I attempted a significant number of growth over the course of a few months, but consistently failed. Either no growth of GaN occurred or the grown layer was black. GaN should be transparent. I realized this was a big problem, especially considering the substantial investment in the tool. That is when I decided I had to modify the reactor.

For the next one and a half years I modified the reactor design. In the morning, I would go to work and modify the reactor. In the afternoon, I would perform a couple of growth attempts and analyze the result. I would repeat this pattern for one and a half years, until I invented a novel MOCVD reactor design with a low carrier-gas flow which I coined a two-flow MOCVD (Figure 4a).[7] Using this reactor, I was able to get very uniform and high-quality GaN growth. The main breakthrough of this reactor was the introduction of a subflow (Figure 4b) that gently pushed the carrier gases down to the substrate, thereby also improving the thermal boundary layer.

This was the most important breakthrough in my life and was instrumental toward all future breakthroughs in GaN research. One significant advancement this tool immediately enabled was the development of a GaN buffer layer which was superior to the AlN buffer layer, in part because of the elimination of aluminum from the growth system. With the

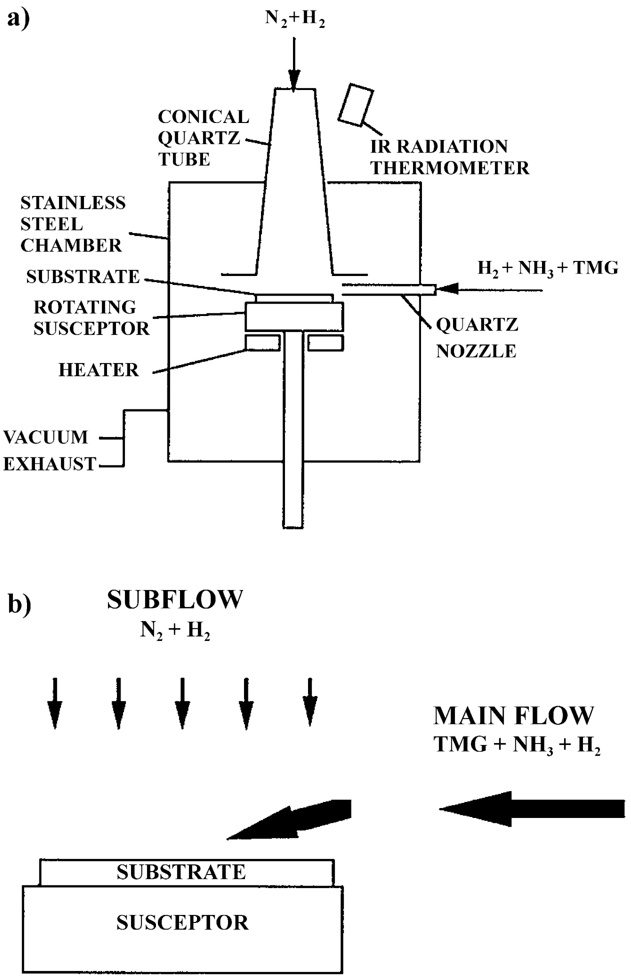

Figure 4. a) Schematic of a two-flow MOCVD for GaN growth, and b) effect of the newly introduced subflow on the carrier gases.[7] (Reprinted with permission. Copyright 1991, AIP Publishing LLC.)

invention of the two-flow MOCVD and the GaN buffer layer, it was possible to obtain the highest-quality GaN material in the world. One measure for crystal quality is the value of the electron mobility in the crystal. Fewer defects result in fewer scattering events, which enhances overall mobility of the electron. Mobilities for GaN grown directly on sapphire (no buffer layer) by Akasaki and Amano resulted in values around $50\,cm^2V^{-1}s^{-1}$,[6] whereas use of the two-flow MOCVD led to $200\,cm^2V^{-1}s^{-1}$.[7] Use of an AlN buffer layer improved the mobility to values as high as $450\,cm^2V^{-1}s^{-1}$ for Akasaki and Amano.[8] Use of a GaN buffer layer and the two-flow MOCVD values as high as $600\,cm^2V^{-1}s^{-1}$ were measured at room temperature (see Figure 5).[9] This was a clear sign that the two-flow MOCVD was producing GaN material of higher quality on larger-area substrates, a key step toward the commercialization of GaN-based devices.

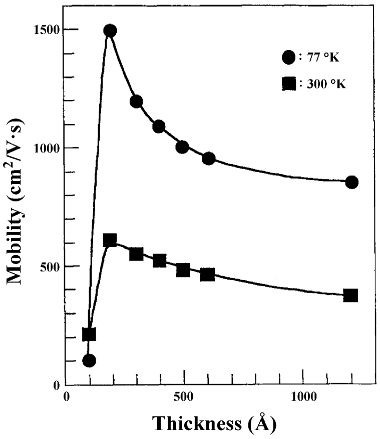

Figure 5. Hall mobility measurements at 77 K (●) and 300 K (■) for a 4 μm thick GaN film grown on sapphire as a function of the GaN buffer layer thickness.[9] (Reprinted with permission. Copyright 1991, The Japan Society of Applied Physics)

The next significant development in creating an efficient blue LED occurred in 1992 when I was able to clarify why *p*-type GaN had remained so elusive for 20 years. While Akasaki and Amano achieved a major breakthrough in 1989 by demonstrating local *p*-type GaN after treating magnesium-doped GaN (GaN:Mg) with low-energy electron beam irradiation (LEEBI),[10] its origin was not understood for another three years. In 1992, I clarified that hydrogen was the source of passivating *p*-type GaN.[11] A few years later, theoretical computations by Jörg Neugebauer and Chris Van de Walle confirmed hydrogen passivation in Mg-doped GaN.[12]

For MOCVD growth of GaN, ammonia (NH_3) is used as the nitrogen source. Ammonia dissociates during growth and atomic hydrogen is introduced into the GaN crystal. If Mg is present in the crystal, the hydrogen atom forms a magnesium hydrogen complex (Mg-H), thereby preventing Mg from acting as an acceptor.[11] Thermal annealing of the GaN:Mg sample in a hydrogen-free environment above approximately 400 °C permits hydrogen to diffuse out of the crystal, thereby breaking up the Mg-H complex.[13] As thermal annealing can be performed quickly and simultaneously on multiple substrates of any size in parallel (a process that is not achievable using LEEBI), it has become the industrial standard process for *p*-type activation of GaN. The formation of local *p*-type GaN using LEEBI treatments can be explained by local heating of the GaN:Mg by the electron beam, which causes the hydrogen to locally diffuse out of the crystal, thus permitting the affected Mg atoms to act as acceptors, thus giving *p*-type GaN.

With the ability to grow *n*-type and *p*-type GaN, *p*-*n* homojunction LEDs (DH LEDs lacking an active layer) can be formed. The first *p*-*n* homojunction LED was demonstrated by Amano et al. in 1989 using an AlN buffer layer and their newly developed LEEBI treatment process to obtain *p*-type GaN.[10] They reported on the observed current–voltage (*I*–*V*) relationship and electroluminescence (EL) of the manufactured LEDs, but did not mention the output power or the efficiency of the LEDs. In 1991, Nakamura et al. demonstrated a *p*-*n* homojunction GaN LED using a low-temperature GaN buffer and the LEEBI treatment.[14] The

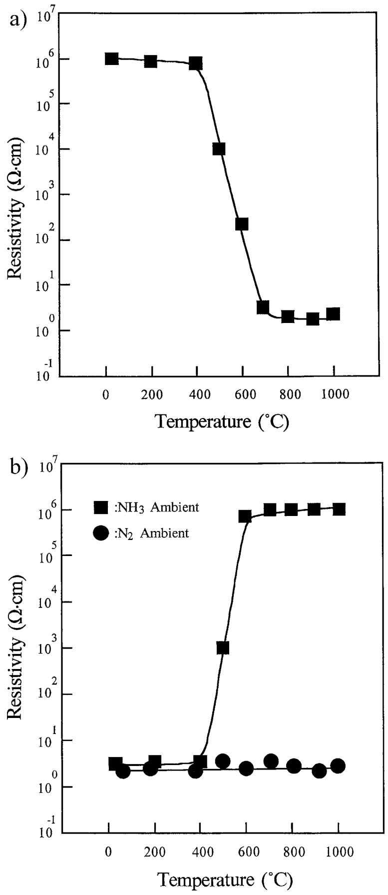

Figure 6. a) Change in electrical resistivity of as grown Mg-doped GaN films as a function of annealing temperature in a nitrogen environment.[13] b) Change in resistivity of LEEBI-treated Mg-doped GaN films as a function of annealing temperature in a nitrogen (●) or ammonia (■) environment.[11] Annealing time was 20 min for all samples. (Reprinted with permission. Copyright 1992, The Japan Society of Applied Physics)

output power at 20 mA with a forward voltage of 4 V was 42 µW. The external quantum efficiency (EQE) and peak emission wavelength were 0.18 % and 430 nm, respectively.

For LEDs to be useful for real-world applications, the light output power needs to be well in excess of 1 mW. The *p-n* homojunction LEDs cannot reach those levels of output power without generating substantial amounts of heat, in large part because of the inefficient device structure. Additionally, *p-n* homojunction LEDs produce light of a fixed wavelength, given the exclusive use of GaN, which has a fixed bandgap. In spite of the achievement by Akasaki and Amano to produce optically active GaN *p-n* homojunction LEDs, Toyoda Gosei Co., Ltd. issued a press release for the production of metal-insulator-semiconductor (MIS) GaN LEDs with an output power of 70 µW on October 20th, 1993.[15] MIS-type LEDs use a semi-insulating layer instead of a *p*-type layer and are also a relatively inefficient device design. The complete omission of *p*-type GaN is advantageous though, as it sidesteps various challenges associated with large-area *p*-type activation using the LEEBI process.

Arguably the most efficient LED designs make use of a DH. The concept and invention of the heterostructure in semiconductor materials was so significant that it was awarded the Nobel Prize in Physics to Zhores Ivanovich Alferov and Herbert Kroemer in 2000. The energy-band diagram is shown in Figure 7 for the *p-n* homojunction LED and the double-heterostructure LED.

In order to understand the advantage that a DH LED provides over a *p-n* homojunction LED, one needs to look at the internal quantum efficiency (IQE) [Eq. (1)].

$$\mathrm{IQE} = \frac{\mathrm{Lightgenerated}}{\mathrm{Electronsinjected}} = \frac{R_{\mathrm{radiative}}}{R_{\mathrm{radiative}} + R_{\mathrm{non-radiative}}} = \frac{Bn^2}{An + Bn^2 + Cn^3} \qquad (1)$$

The IQE is a measure of efficiency and is related to the number of electrons that are converted into photons within the active region. There are three mechanisms by which a high-energy electron may decay to a lower energy state. One of them is a radiative process ($R_{\mathrm{radiative}}$, emission of a photon, desired), while the other two are nonradiative ($R_{\mathrm{nonradiative}}$, emission of phonons, that is, heat, undesired) and include the Shockley-Read-Hall (SRH) process and Auger recombination process. All of these processes are dependent on the minority carrier concentration (electrons in a *p*-type layer, holes in an *n*-type layer), n. The SRH process increases linearly (An), the radiative recombination process quadratically (Bn^2), whereas the Auger recombination process increases as the cube (Cn^3) of n. The coefficients A, B, and C are constants.

For low carrier concentrations, the SRH term (An) dominates, thus leading to poor efficiencies and significant nonradiative recombination. This is the case for *p-n* homojunction LEDs. As a result of the *p-n* structure of the LED, electrons diffuse into the *p*-type layer and holes diffuse into the *n*-type layer. The diffusion length for minority carriers in GaN is approximately 1 µm.[16] This causes the carriers to be spread out over a large region, thus reducing their concentration. The DH LED, on the other hand, confines the carriers to within the active layer, which is typically around 3–200 nm thick. This confinement significantly increases their concentration under the same current density and enhances the probability of radiative recombination (Bn^2), thereby increasing the efficiency of the LED.

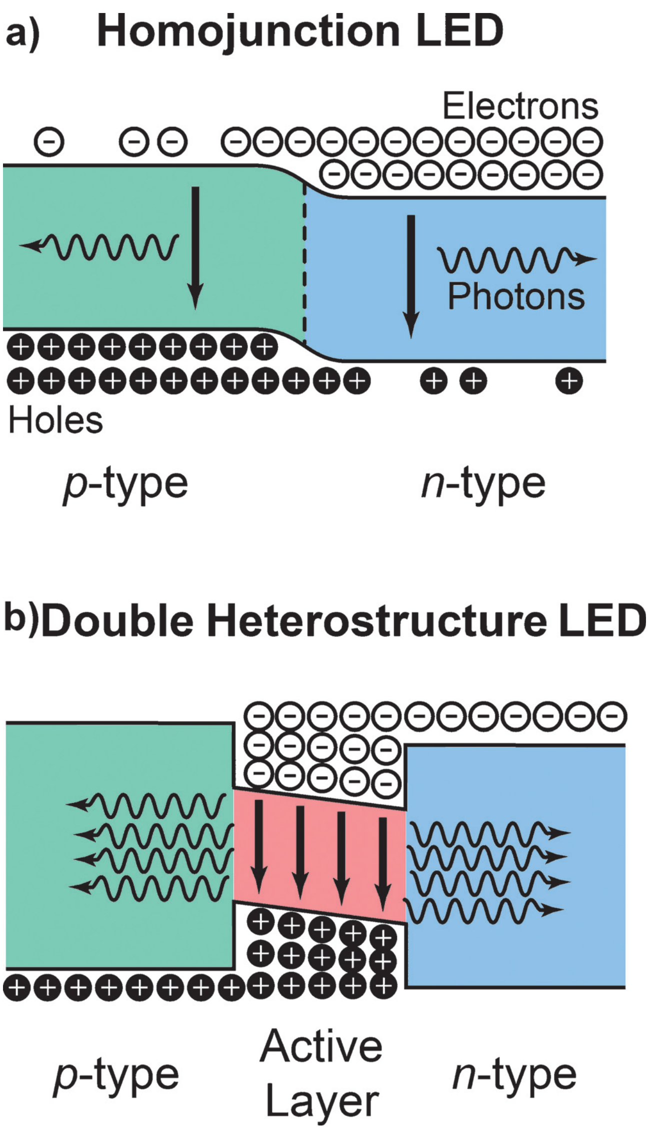

Figure 7. Schematic energy band diagram structure for a a) homojunction LED and b) double-heterostructure LED.

4. Development of InGaN

4.1. InGaN based devices

Achieving a high-quality active layer with the necessary properties to form a DH LED is the last and, arguably, the most critical step toward achieving a commercializable and efficient LED. Indium gallium nitride (InGaN) was identified as the ideal candidate for the active layer. Through addition of indium into the GaN, the bandgap of the material shrinks, thereby providing both the ability to confine the carriers in a DH arrangement, but also to provide the ability to tune the color of the light by changing the amount of indium in the InGaN alloy.

Despite this realization, high-quality layers of InGaN could not be realized in the 1970s–1980s. Room-temperature band-to-band emission, which is essential for the active layer of a DH LED, could not be achieved given the defective nature of the material.

The reason for these defects can be traced back to the many challenges associated with InGaN growth, which is in many ways more challenging than the growth of *p*-type or *n*-type GaN. Indium has such a high vapor pressure that, at typical growth temperatures of GaN ($\approx 1000\,^{\circ}$C), it would boil off the surface and not incorporate into the crystal. Growth at lower temperatures resulted in a poor crystal quality along with numerous defects and incorporation of impurities. At intermediate temperatures, uniform and stable growth temperatures were required, as the incorporation of indium is strongly dependent on the temperature, with a few degrees differences across the substrates, resulting in noticeable variations in output color across the wafer.

Furthermore, in order to effectively use InGaN in a DH LED, excellent control over the various growth parameters is required as the interface between GaN and InGaN needs to be smooth on an atomic level. In addition to a smooth surface morphology, the MOCVD reactor requires precise control over all growth parameters and superior uniformity across the entire surface to obtain exceptionally thin layers of high quality (a layer in DH LEDs is typically composed of a few tens to hundreds of atom layers). To make matters even more challenging, introduction of indium into the GaN lattice results in significant strain, as indium is roughly 20 % bigger in size than gallium. Managing this strain and preventing the formation of defects within the layer is important.

The first recorded growth of an InGaN alloy was performed using electron beam plasma in 1972 and 1975 by Osamura et al. on sapphire and quartz substrates.[17,18] In 1989, Nagatomo et al. grew InGaN on a sapphire substrate using MOCVD at a growth temperature of 500 °C.[19] In 1991, Yoshimoto et al. demonstrated the growth of InGaN layers at a growth temperature of around 800 °C using MOCVD.[20] Despite this achievement, their crystal quality was poor, as evidenced by their room-temperature photoluminescence (RT PL) exhibiting only deep-level emission (no band-to-band emission) (Figure 8) and by a full width at half maximum (FWHM) of the double-crystal X-ray rocking curve (XRC) of 30 arcmin.

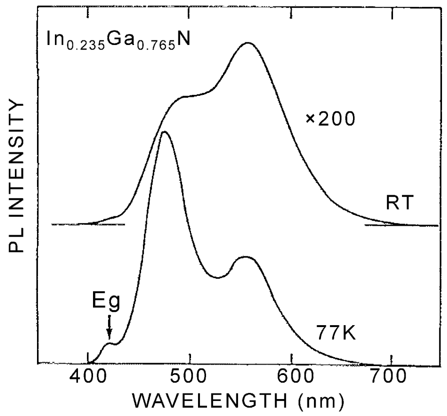

Figure 8. Photoluminescence spectra of $In_{0.235}Ga_{0.765}N$ grown at 800 °C using MOCVD on a sapphire substrate.[20] (Reprinted with permission. Copyright 1991, AIP Publishing LLC.)

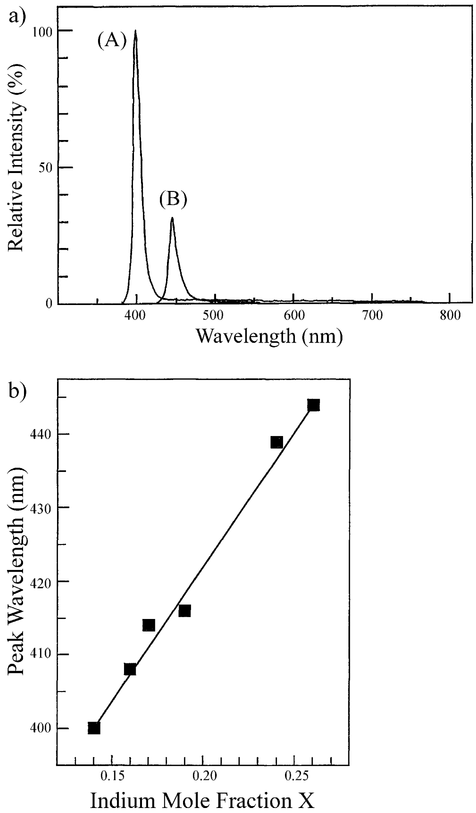

Figure 9. a) Room-temperature photoluminescence (RT PL) spectra of InGaN films grown on GaN films under identical growth conditions, except for the InGaN growth temperatures: trace (A): 830 °C, trace (B): 780 °C. b) Change in peak wavelength of PL spectra as a function of indium mole fraction (*x*) in $In_xGa_{1-x}N$ films. Indium fraction was determined by X-ray diffraction measurements.[21] (Reprinted with permission. Copyright 1992, The Japan Society of Applied Physics)

In 1992, Mukai and myself succeeded in growing a high-quality InGaN layer using the two-flow MOCVD on a GaN template grown on a sapphire substrate.[21] RT PL showed a strong band-to-band emission from violet to blue, depending on the indium composition of the InGaN layers. This was the first report of band-to-band emission of InGaN layers at room temperature. The FWHM of the double-crystal XRC was around 8 arcmin. Figure 9 shows the first reported observation of band-to-band emission of the InGaN layers at room temperature.[21] With this demonstration, the last remaining barrier for efficient blue LEDs was overcome, thus opening the doors for the rapid development of high-brightness, high-power, high-efficiency blue LEDs using the DH structure.

Building on this success, I immediately investigated embedding these InGaN layers within a DH LED structure. The first demonstration of a blue DH LED occurred in 1993 with a *p*-GaN/*n*-InGaN/*n*-GaN structure.[22] The active layer was a Si-doped InGaN layer with a thickness of 20 nm. The LED showed strong band-edge emission in the InGaN layer, resulting in blue light with a wavelength of 440 nm under forward bias conditions. The output power and the EQE were 125 μW and 0.22 %, respectively, at a forward current of 20 mA.

After further improvements to the device, I demonstrated in 1994 the first commercially available blue LED with an output power of 1.5 mW, an EQE of 2.7 %, and the emission wavelength of 450 nm (Figure 10).[23] The structure of this DH LED was *p*-GaN/*p*-AlGaN/Zn-doped InGaN/*n*-GaN. The Zn-doped InGaN active layer had a thickness of 45 nm and was used because of an observed increase in luminous efficiency. For the first time, an electron-blocking layer was introduced into the structure. The *p*-AlGaN prevented electrons from overflowing the electron confinement provided by the active layer, thus further enhancing radiative recombination.

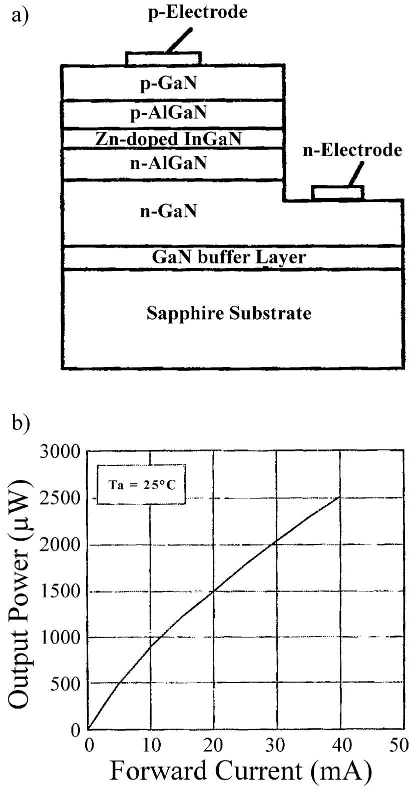

Figure 10. a) Structure of InGaN/AlGaN double-heterostructure blue LED with b) resulting output power as a function of forward current.[23] (Reprinted with permission. Copyright 1994, AIP Publishing LLC.)

Simultaneously to my publication, Nichia Chemical Corporation released a press statement, mentioning the production of high-brightness blue DH LEDs with *p*-type layers, an output power of 1.5 mW, and a brightness of more than 1000 mcd (roughly equal to the luminous intensity of one candle) on November 30th, 1993,[24] just one month after the press release about MIS-type LEDs with an output power of 70 μW by Toyoda Gosei Co. Ltd on October 20th, 1993.[15]

Further improvements to the growth conditions allowed me to demonstrate high-brightness blue, green, and yellow LEDs with InGaN quantum-well (QW) structures in 1995 (see Figure 11).[25] QW structures are DH structures with a very thin active layer, so thin that quantum confinement effects need to be considered. Layer thicknesses for QW structures are on the order of a few nanometers (thicknesses of a few atom layers) versus around 100 nm for typical DH structures up to this point. This thinning further improves the IQE as a result of higher carrier concentrations, but also requires even more stringent controls on uniformity and temperature control during MOCVD growth.

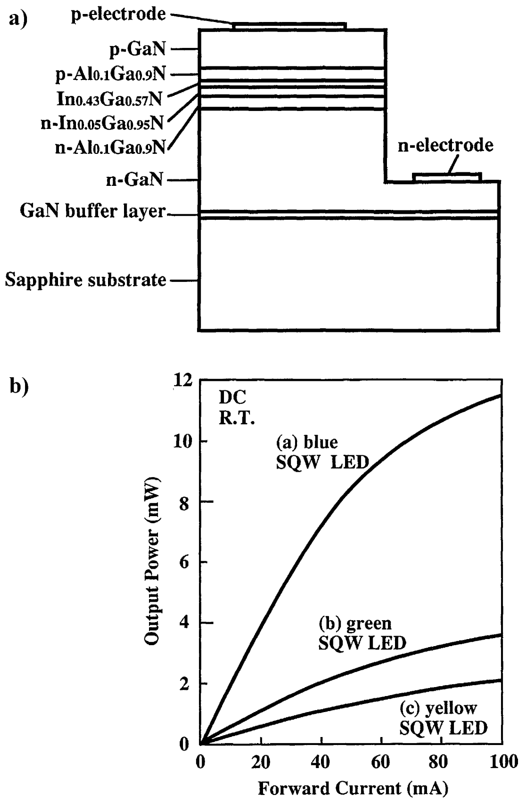

Figure 11. a) Structure of a green single-quantum-well (SQW) LED. b) Output power of a blue, green, and yellow SQW LED at room temperature as a function of forward current.[25,26] (Reprinted with permission. Copyright 1995, The Japan Society of Applied Physics)

Further improvements to the growth conditions of the InGaN layers led to the availability of higher-power blue and green single-quantum-well (SQW) LEDs. At a current of 20 mA, the output power and the EQE of the blue SQW LEDs were 5 mW and 9.1 %, respectively. Those of green SQW LEDs were 3 mW and 6.3 %, respectively. The structure of the green SQW LED and output power of the blue, green, and yellow SQW LEDs are shown in Figure 11.[26] This epitaxial structure of LEDs is still the basic concept applied to all currently commercially available blue and green LEDs.

With the success of the developed high-efficiency, high-power blue LED, Nichia Chemical Corporation commercialized the first white LEDs by combining the blue InGaN QW

DH LED[25,26] with a yellow yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$) based phosphor.[27]

Having excelled at achieving high-efficiency blue LEDs, the next step for me was to demonstrate the first InGaN-based laser diode. I achieved this goal in 1996 under pulsed-[28] and continuous-wave (CW)[29] operations. Figure 12 shows the device structure and light output power versus the current (*L–I*) curve for the first InGaN-based laser diode.[28] The structure was composed of an InGaN multi-quantum-well (MQW) active layer, GaN waveguide layers, and AlGaN cladding layers.

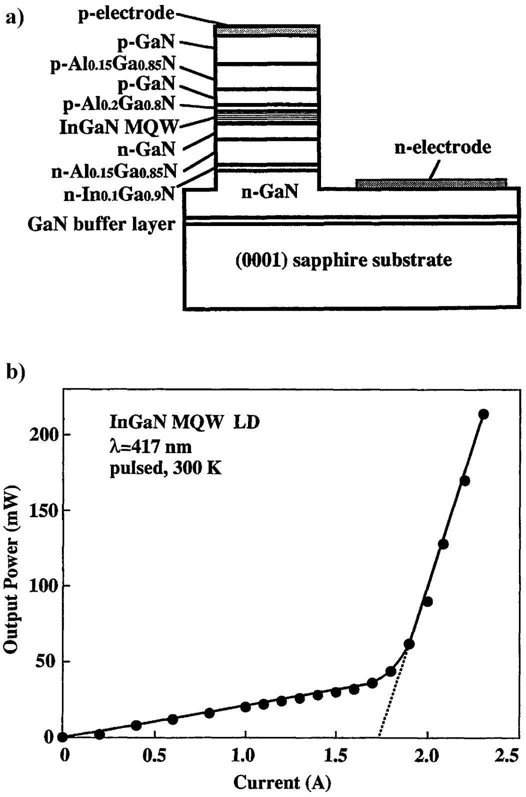

Figure 12. a) Structure of a violet InGaN MQW laser diode with b) corresponding *L–I* characteristics, indicating the onset of lasing (30 μm wide, 1500 μm long)[28] (Reprinted with permission. Copyright 1996, The Japan Society of Applied Physics)

4.2. Material Properties of InGaN

One mystery still remains to date, namely why InGaN materials are atypical and luminesce with such high efficiency, despite the high density of dislocations. It was deemed common sense in the 1980s that highly efficient LEDs with a long lifetime required a dislocation density of less than 10^3 cm^{-2}. Despite all the improvements in MOCVD growth of GaN, the fundamental lattice mismatch between sapphire and GaN remains, resulting in 10^9 cm^{-2} dislocations in the GaN and InGaN layers, even for the high-efficiency devices demonstrated in the 1990s. To highlight the stark difference between InGaN and other semiconductors, Figure 13 depicts the approximate dependence of the LED efficiency on the dislocation density for various semiconductor materials. As can be seen, highly efficient arsenide- and phosphide-based LEDs could only be obtained for dislocation densities below 10^3–10^5 cm^{-2}. This observation led to the erroneous statements that dislocation densities below 10^3 cm^{-2} are needed for efficient LED operation. Pure GaN LEDs behave comparable to the other arsenide and phosphide LEDs, as demonstrated by dim *p-n* GaN homojunction LEDs developed by Akasaki and Amano in 1989.[10] Interestingly, InGaN materials behave quite differently, exhibiting high efficiencies despite high dislocation densities.[30]

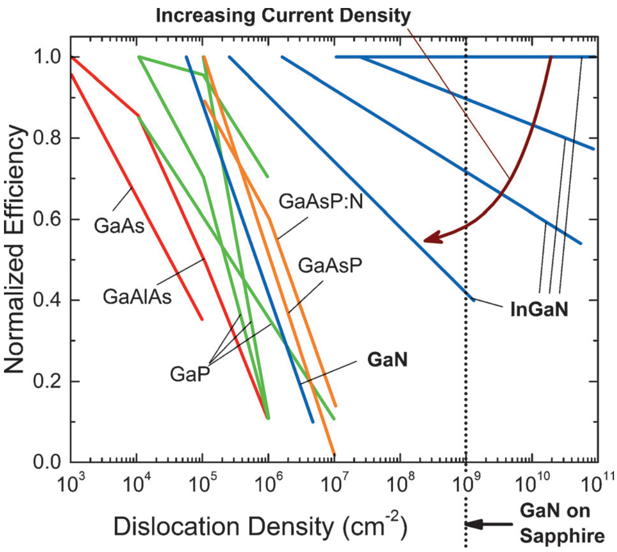

Figure 13. Dependence of LED efficiency on dislocation density for various semiconductor materials. (based on [30–32])

One explanation for this phenomenon, as proposed by Professor Chichibu from Tohoku University, is the presence of localized states in the InGaN layer.[31,32] When electrons and holes are injected into the active layer, they are captured by localized states within the layer and radiatively recombine before they are captured by crystal defects (dislocations), which would provide nonradiative recombination pathways. The localized centers can be thought of as enhanced emission centers of light.

Localized states may emerge as a result of the natural fluctuation of indium within the InGaN layers. Atom probe tomography measurements of the InGaN layers have provided atomic level resolution of the chemical and spatial distribution of atoms within the layer (see Figure 14).[33] The statistical analysis of the indium distribution in the layer yields a random binomial distribution on the Group III site about some average indium concentration. This naturally occurring random binomial distribution provides fluctuations resulting in regions of high and low indium content. Regions with a high indium content have a smaller bandgap and hence could act as localized sites. As fluctuations occur on the nanometer scale, there are a significant number of localized sites, comparable, if not greater, to the number of defects present. It is important to keep in mind that this is just one possible explanation for localized sites. We currently still do not understand their origin and whether they are truly the reason for the highly efficient nature of InGaN.

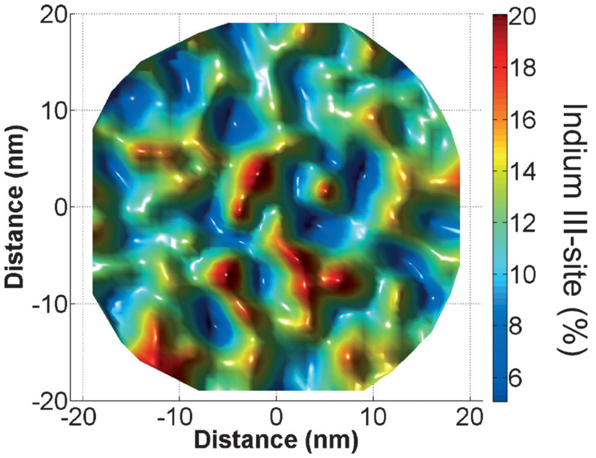

Figure 14. Atom probe tomography analysis provided as a 2D plot of the lateral compositional variations within a 3 nm InGaN quantum well at nominal 14% indium composition showing local indium fluctuations.[33]

5. Historical Development of InGaN-based LEDs

5.1. Luminous Efficacy

Figure 15 shows an overview of the historical development of the luminous efficacy for red, green, and blue LEDs.[34] This figure has been used by many scientists at numerous conferences to explain the historic developments of red, green, and blue LEDs. The first visible-light LEDs were based on GaP and developed in the late 1950s through early 1960s.[35–39] Over time, the red LED gradually improved in efficacy as shown in the figure.

The first violet/blue LEDs, the MIS LED developed by Maruska et al. in 1973 and the *p-n* homojunction LED developed by Akasaki and Amano in 1989, have typically not been included in the figure, probably because of their poor luminous efficacy, though are included in this depiction. Not until 1992, when high-quality InGaN became available and could be incorporated into a DH LED structure, did rapid progress ensue, leading to the first efficient yellow, green, and blue LEDS in 1992–1995.[23–26] The rapid progress that occurred could not have been possible without the atypical properties of high-quality InGaN. Without InGaN, I argue, it would not have been possible to produce efficient blue and green LEDs in the GaN material system. In 1996, the Nichia Chemical Corporation developed the first white LED using the efficient blue InGaN QW DH LED and YAG phosphors.[27] Rapid progress after the first commercialization of the white LED by the Nichia Chemical Corporation has led to the current state-of-the-art white LED with a stunning 303 $\mathrm{lm\,W^{-1}}$ peak efficacy at room temperature, as announced by Cree Inc. in March, 2014[40].

5.2. Significant Milestones on the Journey to the White LED

Table 1 provides an overview of significant developments that ultimately led to the first high-efficiency white LED developed by the Nichia Chemical Corporation in 1996.[27] The first demonstrated growth of GaN was performed by Maruska et al. in 1969 using hydride vapor-phase epitaxy (HVPE).[41] A great thanks goes out to Dr. Maruska for opening the door to GaN research and crystal growth. Not only did Maruska et al. perform the first GaN growth, he also demonstrated the first violet GaN-based LED using an MIS structure (because of the lack of *p*-type GaN) by doping the GaN with Mg, which acted as a color center, in 1973.[42]

The next significant development was the demonstration by Yoshida et al. to grow GaN films using an AlN buffer on a sapphire substrate by reactive molecular beam epitaxy (MBE) in 1983, providing a pathway to GaN materials with improved quality.[43] In 1986, Amano et al. applied the idea of an AlN buffer layer to MOCVD growth of GaN by growing it at low temperatures.[6] The mirror-like surface morphology and reduced residual carrier concentration, in the order of $10^{17}\,\mathrm{cm^{-3}}$ for unintentionally doped GaN, was an important milestone.

Subsequently, Amano et al. obtained the first *p*-type Mg-doped GaN by using a post-growth LEEBI treatment in 1989, though could not explain the origin of the mechanism by which it was obtained.[10] The hole concentration and mobility was $2\times10^{16}\,\mathrm{cm^{-3}}$ and $8\,\mathrm{cm^2V^{-1}s}$, respectively, and output power of the *p-n* homojunction GaN LED was not reported.

The next major milestone in the development of the blue LED occurred when I was working for the Nichia Chemical Corporation

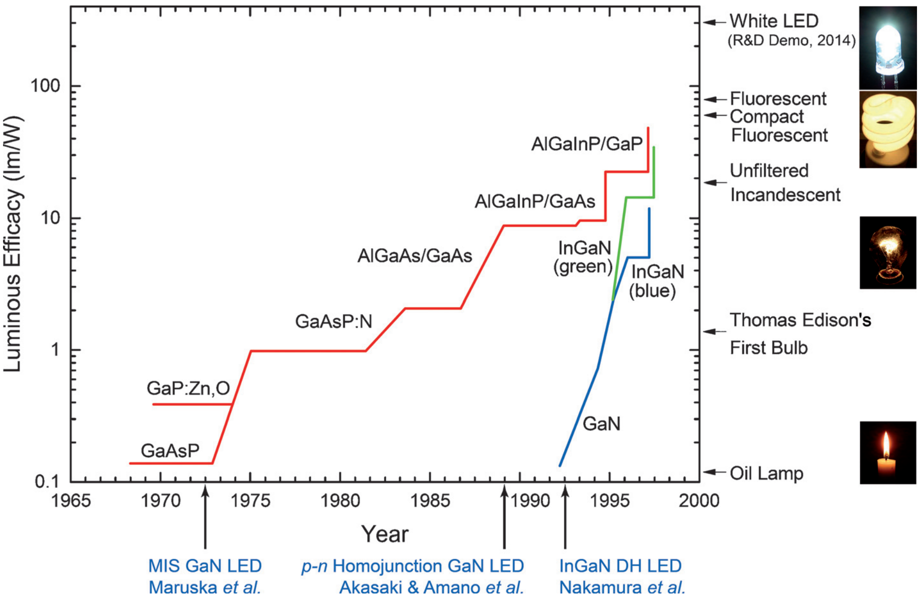

Figure 15. Evolution of luminous efficacy of red, green, and blue LEDs (After [34]).

Table 1: Significant developments ultimately leading to the white LED for GaN and InGaN on sapphire.

Material	Year	Achievement	Reference
GaN	1969	GaN epitaxial layer by HVPE	[41]
	1973	first blue Mg-doped GaN MIS LED	[42]
	1983	high-quality GaN using AlN buffer by MBE	[43]
	1985	high-quality GaN using AlN buffer by MOCVD	[6]
	1989	p-GaN using LEEBI (low hole concentration)	[10]
	1989	first *p-n* homojunction GaN LED	
	1991	invention of two-flow MOCVD	[7]
	1991	GaN growth using GaN buffer by MBE	[44]
	1991	high-quality GaN using GaN buffer by MOCVD	[9,45]
	1992	p-GaN using thermal annealing (high hole concentration)	[13]
	1992	discovery of hydrogen passivation	[11]
InGaN	1972	InGaN growth using electron beam plasma	[17,18]
	1989	InGaN growth by MOCVD	[19]
	1992	InGaN layers with room-temperature band-to-band emission	[21]
	1994	efficient blue InGaN DH LED (1 Candela)	[22–24]
	1995	efficient yellow, green, and blue InGaN DH QW LEDs	[25,26]
	1996	first pulsed violet InGaN DH MQW LDs	[28]
	1996	first CW violet InGaN DH MQW LDs	[29]
	1996	commercialization of the white LED using blue InGaN DH LED	[27]

and developed a novel MOCVD, which I called two-flow MOCVD, in 1991.[7] Introducing a new subflow to the system provided a significant improvement in reproducibility and uniform growth over large-area substrates.

Shortly thereafter, in 1991, the GaN buffer layer was developed for GaN growth on sapphire using MBE[44] and MOCVD.[9] Lei et al. developed it for the MBE method, though the achieved crystal quality was poor with a rough surface.[44] I developed it for MOCVD growth by employing a low-temperature growth step, which led to high-quality GaN films on sapphire.[9] In 1992, improvements to the growth of the low-temperature GaN buffer layer resulted in electron mobilities of 900 $cm^2 V^{-1} s$ at room temperature.[45]

With the availability of materials with high crystal quality, the next major step was my demonstration of *p*-type GaN films using post-thermal annealing under a NH_3-free ambient gas, as shown in Figure 6, in 1992.[13] The hole concentration and mobility were 3×10^{17} cm^{-3} and 10 $cm^2 V^{-1} s$, respectively. Following this demonstration, I was able to determine that the observed hole compensation in GaN:Mg was due to hydrogen passivation,[11] a mechanism that had been a mystery since the early 1970s. A hydrogenation model, wherein acceptor–hydrogen (Mg-H) complexes were formed in *p*-type GaN, was proposed and theoretically confirmed by Neugenbauer and Van de Walle in 1995.[12]

Having overcome the major hurdles for GaN, the next major advance occurred for InGaN materials, arguably the most important layer in the efficient blue LED. Its first growth using electron beam plasma was accomplished in 1972 by Osamura et al., who also investigated some of its properties.[17] The first growth by MOCVD was achieved in 1989 by Nagatomo et al.,[19] opening the door for the development using the same growth technique with which high-quality GaN could be grown. Not until 1992, when Mukai and I were able to demonstrate the first InGaN layer that exhibited strong band-to-band emission at room temperature,[21] did the option of forming a high-efficiency blue LED become a realistic option. The incorporation of the material in a DH LED structure rapidly led to a slew of developments, most notably, the first highly efficient blue InGaN DH LED in 1994,[22,23] the first high-efficiency green InGaN DH QW LED in 1995,[26] and the first blue/green/yellow InGaN DH QW LEDs in 1995.[25]

While our group at Nichia Chemical Corporation worked hard on developing the first white LED, I was able to further pursue improving GaN-based optoelectrontic devices, and eventually demonstrated the first pulsed[28] and CW operation[29] violet InGaN DH QW laser diode in 1996. Shortly thereafter, the Nichia Chemical Corporation released the first white LED, changing the world forever.[27]

A more detailed account of the history of the GaN-based LED can be found in Ref. [46].[46]

5.3. Contributions to the Efficient Blue LED

Of all the contributions that eventually led to the efficient blue and white LED, only a select few were highlighted in the Nobel Prize announcement. Figure 16 provides a visual summary of the key inventions and contributions to the efficient blue LED. While the demonstration and explanation of *p*-type GaN and the inclusion of buffer layers were important, the development and incorporation of high-quality InGaN material was just as, if not even more, vital to achieving the efficient blue LED. A pure GaN *p-n* homojunction LED structure is too inefficient and would never have led to the development of the high-efficiency LED, especially when also considering the high dislocation densities that are present as a result of the use of a sapphire substrate (see also Figure 13).

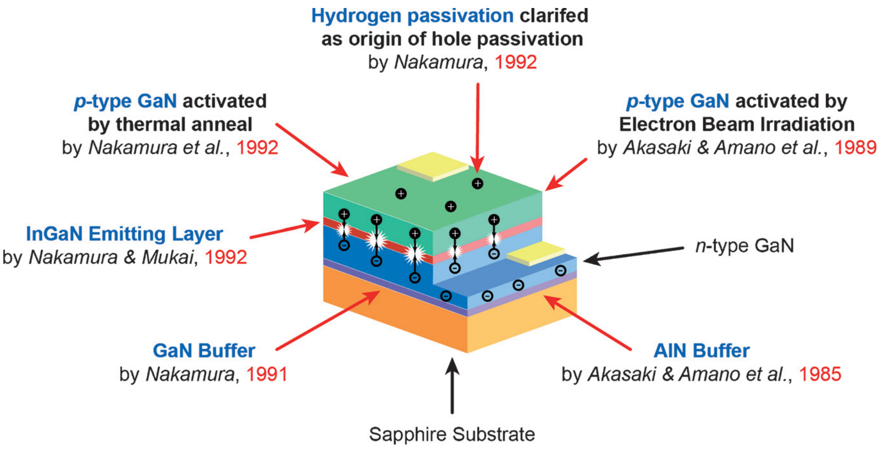

Figure 16. Summary of key contributions to the efficient blue LED.

6. Future Challenges

While I have been talking primarily about LEDs, there is an intrinsic problem that cannot be easily overcome. Given the highly efficient nature of LEDs, it is of interest to maximize the light output per device. This is most easily achieved by increasing the current density that runs through the device. Higher efficiencies permit higher current densities, as the device does not heat up as much. With increasing current density though, the carrier densities within the QW increases. We can now push the current densities so high that we are seeing a reduction in efficiency with increasing current density (see Figure 17). This phenomenon, referred to as efficiency droop, forces LED manufactures to operate LEDs at lower current densities (and hence reduced light output) than would be possible to prevent excess heating of the device. To maintain high light output, manufactures may use multiple LEDs in parallel, effectively increasing the overall active area and hence reducing current density. The primary origin of the efficiency droop, which was not discovered until recently, is the Auger recombination process.[47,48] If you recall the contributions to the IQE of an LED [see Eq. (1)], the cubic term in carrier concentration (Cn^3) was the Auger recombination process. Given the exceedingly high densities of carriers, this term starts to become dominant, thereby reducing the value of the IQE. As the Auger recombination process is a result of the intrinsic properties of GaN, it is exceptionally challenging to overcome.

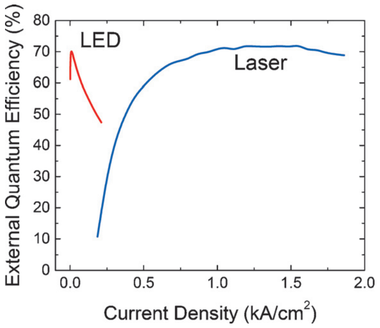

Figure 17. Comparison of external quantum efficiency (EQE) of a commercial LED and laser with increasing current density.[49]

An alternative method to produce white light is the use of a blue laser, as opposed to an LED, in combination with a phosphor. Above the lasing threshold, the carrier density is clamped at threshold, thus fixing its density. Increases in carrier density beyond the threshold density immediately contribute to stimulated emission, or lasing. Thus, the carrier density is maintained at the lower threshold density, thus prohibiting it from reaching densities at which the Auger recombination process becomes the dominant recombination process. Auger recombination, with the resulting efficiency droop, does not appreciably occur in blue laser diodes.[49]

Current commercial blue lasers have already demonstrated comparable external quantum efficiencies to those of blue LEDs at significantly higher current densities, and hence light output (see Figure 17). It is therefore of great interest to further pursue lasers as they have the potential of operating at high current densities, thus resulting in white-light sources with staggering light output.

While laser-based lighting has the potential of being more efficient with smaller chip sizes with a very high current density region, it also offers intrinsic directionality of the light output—a feature that car manufactures have already leveraged in their high-end vehicles. Current, high-end vehicles already use laser-based white-light sources for their headlamps, allowing them to see further ahead on the road without blinding oncoming traffic. Future modifications to the laser-based lighting technology may well enable the next generation of white lighting with higher efficiencies at lower cost.

Appendix: Autobiography

I was born on 22 May 1954 in Oku, a tiny fishing village on the Pacific coast of Shikoku, the smallest of Japan's four main islands. Farming is the principle occupation in Oku. Local farmers grow yams on steps cut into steep hillsides. My maternal grandparents owned such a farm. To get to the nearest town, the villagers relied on a ferry. Inconvenient perhaps, but the village was an idyllic place to grow up in.

My father, Tomokichi (Figure 18), worked as a maintenance man for Shikoku Electric Power. From him, I learned how to make wooden toys, such as catapults and bamboo propellers. I liked "making" things and became good at it, a skill that would stand me in good stead.

At school, I was not academically gifted. My boyhood was typical. I fought constantly with my elder brother. Smaller than my sibling, I always lost. Though physically defeated, mentally I would never give in. My mother was forever

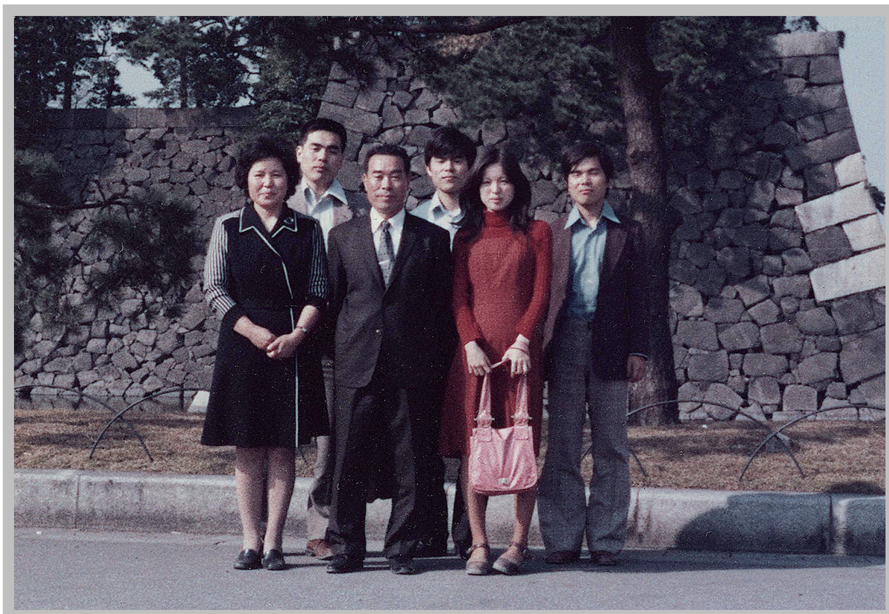

Figure 18. My parents, siblings, and I (far right) in 1979.

chiding us boys to do our homework. But for the most part, we ignored her admonishments.

Throughout primary and high school, my passion was volleyball. There was no gym at the school, so my team had to practice outside in the mud. We tried hard, but rarely won. Fiercely competitive from an early age, I always hated to lose. Volleyball left me little time to study for my high school entrance exams. I was bad at rote learning, but good at math and science. Somehow, I managed to scrape into an academically oriented school.

Here, too, volleyball remained my priority. My classroom teacher told me that to improve my scores, I would have to quit playing. It was time to concentrate on studying for the all-important university entrance exams. But I could not let down my team. I was the only student in the A-stream to continue playing sports until graduation.

However, I paid a price for my dedication to volleyball. My university entrance exam results were not good enough to win myself a place at a prestigious school. My dream was to become a theoretical physicist or a mathematician. But my teacher told me that I could not make a living from physics; I had better choose a course such as engineering so that I could find a job.

I picked electrical engineering because it seemed close to physics. In 1973, aged 19, I entered Tokushima University, a local state school. Many professors there were former high-school teachers. The textbooks were out of date.

My first two years consisted of general studies, including arts courses, which I hated. I couldn't understand why I had to take such irrelevant subjects. Soon I stopped attending classes. All day long I would read books, mostly on physics. But there was a limit to the amount I could absorb by reading alone. Finally, in my third year at Tokushima, I attended a lecture on semiconductors. Fascinated by the physics of solid-state materials, I decided to stay on at the university for a further two years and do a master's degree under Professor Osamu Tada.

As my thesis topic, I chose the conductivity mechanism of barium titanium oxide. My focus was theoretical. But Professor Tada was a dyed-in-the-wool experimentalist. He would catch me reading papers and tell me that knowing theory was no use if I couldn't make actual devices.

Tada's lab was known as "the junk room." It was crammed with broken televisions and old radios that could be cannibalized for spare parts. To build what they needed, students had to acquire manual skills: soldering, cutting, and joining glass, beating and welding sheet metal, and fashioning parts on a lathe.

I remember my days as a master's student as being like a sheet-metal worker in a small factory. What I wanted was to study theory. But most of my time was taken up jury-rigging equipment for experiments. In fact, I was gaining precisely the kind of skills that I would later need in my quest to develop a bright blue LED. As a corporate researcher, I would be forced to make or modify much of my own equipment. Ultimately it would largely be this technical mastery that gave me the edge on my rivals.

As a 25-year-old graduate student with a master's degree in electrical engineering, I expected that one of Japan's consumer appliance manufacturers would hire me. But the likes of Sony tend not to recruit graduates from local universities.

In my interview at Matsushita, I made the mistake of discussing the theoretical aspects of my thesis research. "We don't need theoreticians", the firm's recruiters told me. At Kyocera, I did better, emphasizing the practical applications of my work. The company offered me a job. But as the day on which I was due to report for work in Kyoto neared, I had second thoughts. Prior to my job-hunting trips, I had rarely left Shikoku.

At the same time, I really wanted to work in a proper research laboratory at a major company. Torn between two paths, I asked Professor Tada what I should do. Tada pointed out that in Tokushima, there were no jobs for electrical engineers. If I elected to stay on the island, I would have to give up a career in my chosen field. Eventually I decided to remain in Tokushima.

My professor introduced me to Nobuo Ogawa, the founder and president of an obscure local chemical firm called Nichia. The company was initially reluctant to hire me, but I refused to take no for an answer.

When I joined in April 1979, Nichia had fewer than 200 employees (Figure 19). The firm made phosphors for color televisions and fluorescent lamps. These were mature markets. If Nichia was to grow, it needed new products.

Figure 19. My first day at Nichia in April 1979.

I was assigned to the company's two-man development section. My first job was to refine high-purity gallium metal. This turned out to be a dead end. The company ordered me to produce gallium phosphide, a material used to make red and green LEDs. Knowing next to nothing about LED materials, I had to start from scratch.

There was no budget for equipment. I had to scavenge, fixing broken parts by hand. To build my reactor, I scrounged heat-proof bricks, cables, a vacuum pump, and an old electric furnace. I had to order quartz tubes. To seal the open-ended tubes so they could be evacuated, I had to learn how to weld quartz.

To make gallium phosphide, phosphorus is heated in a tube. If the tube gets too hot, the phosphorus vapor expands, causing the quartz to crack. This lets in oxygen, which reacts with the phosphorus, causing an explosion. Such explosions became a feature of my time at Nichia. My lab would fill with white smoke. Ignited phosphorus would fly everywhere, along with shards of broken quartz. I would run around pouring water over the burning phosphorus, desperately trying to douse the flames.

The blasts happened several times a month, often in the evening. The shock wave would hit my fellow workers as they were heading for their cars in the parking lot. The first few times it happened, they dashed into my lab to see if I was alright. By the fifth or sixth time, however, they had become so used to the bangs they no longer came to check.

Eventually, I succeeded in developing commercial-grade gallium phosphide. More satisfying than producing the material was how I felt when the company's salesmen told me we had made a sale. It gave me pleasure to think that I had finally managed to contribute to the company's bottom line. But only a little: the market for gallium phosphide was already crowded. As a late entrant, Nichia was only able to win a sliver of the pie.

My next assignment was to produce gallium arsenide, which is also used to make LEDs, typically infrared ones such as those found in television remote controls. But GaAs also has other applications, for example in the semiconductor lasers used in optical fiber communications. Thus, the potential market for the material was much larger.

Happily, unlike phosphorus, arsenic is not inflammable. Unhappily, the material is poisonous, releasing lethal arsenic oxide gas every time the furnace blew up. I had to wear a home-made "space-suit" and breathe through a respirator. Miraculously, I was never adversely affected by having to work in such a toxic environment.

By 1985, I was producing gallium arsenide in bulk. But when it came to selling the product, the market's response was the same. There were plenty of existing suppliers, so why buy from an untried latecomer such as Nichia? The next idea the salesmen brought back was, instead of making the starting materials for LEDs, why not make the devices themselves? To fabricate a simple LED required mastering a technique known as liquid-phase epitaxy.

I performed countless experiments. I discovered that small differences in thickness could make a big difference in brightness and lifetime. As usual, the company pressured me to produce a saleable product quickly; as usual, there was no budget for equipment. Eventually I managed to fabricate some prototype LEDs. Samples were delivered to a client for evaluation. Not having my own measuring equipment meant I was dependent on such external evaluations. I had to wait months to get data back before I could start making improvements.

I felt strongly that if the company was going to enter the LED business, then I should be able to conduct my own evaluations. I presented the case to my boss, but was told that there was no budget, so it was not possible. Previously, I would have accepted this answer and given up. By now, I had realized that Nichia was run on the say-so of its president and founder, Nobuo Ogawa. I went directly to Ogawa to ask for the equipment I needed. To my surprise, the old man immediately agreed to my request.

I had made many friends among Nichia's employees. When work finished they would often ask me to make up the numbers for a game of softball. Afterwards, we would drop by a local bar. There, my workmates would implore me to develop products that would make the company grow. Knowing that I had yet to produce anything that had a significant impact on the company's bottom line, I would hang my head. Others, especially older employees, were critical. They asked me what I had been doing for the past five years. In their opinion, I was just wasting the company's money.

The only way a corporate researcher can contribute directly to the bottom line is through patent royalties. But fearful of losing trade secrets, Nichia did not permit patent applications. My apparent sales were thus zero. In ten years, I had not published a single scientific paper, because of Nichia's policy of keeping its technical know-how secret. From a professional point of view, I had no achievements.

Finally, in desperation, I approached the president with an audacious proposal: to develop the world's first bright blue LED. To do this I would need around five hundred million yen (then worth about US$ 4 million). This was equivalent to 2% of the company's sales that year, an unbelievably large amount. Nonetheless, Ogawa gave me his blessing.

Two thirds of the money would go to equipment, together with the laboratory and clean-room facilities to house it. Of the remaining third, the largest item was mastering metal-organic chemical-vapor deposition, the crystal-growth technology needed to make bright blue LEDs.

I selected MOCVD because it could be applied to the factory floor. Shiro Sakai, an expert on the technique, was an old acquaintance from Tokushima University. Now a professor at Tokushima, Sakai was on sabbatical at the University of Florida. I invited him to visit Nichia. There I outlined the significance of MOCVD. Blue LEDs were not mentioned. Sakai recommended that Nichia should send me to Florida for a year to learn the technique.

In March 1988, I flew to Gainesville. It was the first time I, the country boy, had boarded an airplane. As many first-time fliers, I feared it might fall from the sky. It was also my first trip abroad. I worried that my rudimentary English would not enable me to communicate with Americans.

I was 34 years old, rather long in the tooth for a student. My fellow researchers at the University of Florida were mostly in their mid-twenties. All of them were PhD students. My status was ambiguous. As I was not studying for a degree, I was obviously not a student. Nor, as I did not have a PhD, could I be a post-doctoral fellow. As a compromise, I was designated a "guest research associate".

Initially, my fellows treated me as an equal or even, because I was older, as a senior. However, once they discovered that I only had a master's degree and, worse, that I had not published a single paper, their attitude changed. Henceforth they looked down on me, treating me as little more than a technician. It was particularly galling because, from my perspective, these PhDs were mere novices whereas I had years of hands-on experience. They could not do the simplest experiment. Something would go wrong and they would come running to me for help. Their condescending attitude provided me with further motivation. I feel resentful when people look down on me. At that time, I developed more fighting spirit—I would not allow myself to be beaten by such people.

When I arrived at Gainsville, the MOCVD system at the lab to which I had been assigned had not yet been built. I had to spend ten months of my precious year in the US with my sleeves rolled up, connecting pipes and welding quartz, just like back at Nichia. Here again, adversity in the short term would turn out to be a priceless experience in my quest to develop the first bright blue LEDs. I gained an intimate familiarity with the workings of the MOCVD equipment. Having managed to assemble the system, I was only able to do a few device-growing runs. Then it was time to go home.

I returned to Nichia in March 1989. While in the US, I had ordered my own MOCVD equipment, keeping my goal a secret from the supplier. The reactor had arrived. The question was, what material to grow in it? There were three candidates. One, silicon carbide (SiC), despite the fact that it was in limited commercial production, I had already rejected. SiC had an indirect bandgap, meaning that the material would never be able to emit bright blue light.

The other two materials, ZnSe and GaN, both suffered from the same deficiencies. One was that, to make a proper LED, you need to fabricate both negative- and positive-type materials. Thus far, however, it had proved impossible to produce either *p*-type ZnSe or *p*-type GaN. When making my choice, I could not have known it, but this was about to change: in 1989, researchers would succeed in fabricating *p*-type GaN; the following year would see the first *p*-type ZnSe.

The second, more serious, drawback was the lack of a suitable base material on which to fabricate an LED. Gallium arsenide LEDs could be grown on gallium arsenide wafers. But nobody had been able to grow bulk ZnSe or GaN. That meant employing wafers of some "foreign" material as the substrate, which in turn meant a mismatch between substrate and light-emitting layers. The result was defects, which are undesirable because they cause LEDs to dissipate energy in the form of heat instead of light.

With ZnSe, a soft material, the problem seemed much less severe. You could grow ZnSe on a gallium arsenide substrate and the mismatch was only 0.3%, not far off the ideal value of 0.01%. This translated into a defect density of around 1000 per cm^2. With GaN, a rock-hard material, the best available substrate was sapphire. But even sapphire produced a huge mismatch of 16%. That translated into a defect density of ten billion per cm^2. It was plausible to imagine that imperfections in crystal ZnSe could be reduced by one order of magnitude. But ten billion defects? It seemed unlikely that that figure was going to be significantly reduced during any researcher's working lifetime.

GaN had been thoroughly investigated by RCA, Bell Labs, and Matsushita. It was almost universally perceived as a dead end. Few groups were still active in the GaN field. The overwhelming consensus was that ZnSe was the way to go. Yet devices based on ZnSe tended to fall apart when zapped with current. ZnSe simply wasn't strong enough to cope with the stress of producing photons. What nobody could have foreseen in 1989 was that GaN would turn out to behave very differently compared to previously developed light-emitting materials. Any other semiconductor with that density of defects simply would not function. Much to everyone's surprise, however, with GaN, defects just didn't seem to matter.

Having arrived at what I previously described as this "fateful fork in the road", I chose GaN. My reason for placing this apparently reckless bet was not because I was confident that I could do what no one else had done before. Rather, it was because I had repeatedly had the bitter experience of developing products only to find that my company could not sell them. As big companies had several years' head start, history would likely repeat itself if I chose ZnSe. With GaN, in the unlikely event that I did succeed, there would be no competition, because no other company was working on GaN.

Another motivation, following my unhappy experience at the University of Florida, was that I wanted to get a PhD. In Japan it was possible to obtain a PhD by publishing a minimum of five scientific papers. If I had selected ZnSe, it would have been difficult to publish papers because a huge number of papers on ZnSe had already been published. If I selected GaN, it would be easier to publish because only a few papers had been published.

I was able to make this seemingly foolhardy decision by myself without reference to Nichia's senior management because none of them knew anything about semiconductors. All they knew was that my target was to develop a bright blue LED. The choice of methodology to adopt and material to work on was mine alone. Had I been working at a large company, my proposal to work on a known loser material would undoubtedly have been shot down. But as I would later say, "breakthroughs are born out of unusual circumstances".

The quest began. I had no colleagues with whom I could discuss my work. Other than on New Year's Day, I never took time off. My solitary routine seldom varied. I would get into work around 7 AM, leaving around 7 PM. I would go home, eat dinner with my family, have a bath, then go to bed. All the while I would be musing about my work.

Modifying the MOCVD equipment was the key to my success. I took the reactor apart, then put it back together exactly the way I wanted. I bent the steel pipe, changing the height and the angle at which it was attached to the reaction chamber. I welded quartz tubes, cut high-purity carbon, re-did the wiring. I even altered the shape of the gas nozzles.

My motto was "remodel in the morning, experiment in the afternoon". Such urgency was not because I was worried that other researchers might overtake me. Rather, impatient by nature, I was eager to see the results of the changes I had made.

To grow high-quality films of GaN, one major problem had to be solved. Nitrides are vulnerable to parasitic reactions. The gases react with each other spontaneously to form an adduct, in this case, a white powder that researchers call "snow". Flakes of snow fall on the wafer, ruining the film. Much ingenuity therefore goes into designing reactors so that the gases are injected separately, keeping them apart as they flow down to the wafer. I conceived a novel way of doing this, which I dubbed "two-flow" MOCVD.

Still, failure followed failure. Nichia kept demanding to know when I could develop a product. But as time went by and no results emerged, my boss stopped bothering me. Even my friends at the company left me alone. Then, one winter's day, the clouds finally lifted.

Everything was as usual: I arrived at work and grew a thin film of GaN crystal. I hooked up my sample to measure its electron mobility. The figure was surprisingly high: the best result to that point, achieved at Nagoya University by (fellow Nobel Laureates) Professor Isamu Akasaki and his student Hiroshi Amano, was less than half as much. I had succeeded in making the world's best GaN. It was the most exciting day of my life.

Further breakthroughs followed. Akasaki and Amano had blazed the trail, with their buffer layer (1986) and positive-type GaN (1989). The buffer layer was necessary to mitigate the effect of the mismatch between the sapphire substrate and the GaN layers deposited on top. Interposing a buffer enabled the growth of smoother films. For their buffer layer, Akasaki and Amano had used aluminum nitride (AlN). I was determined not to copy my rivals, knowing patent problems would result if I did. I used GaN as the material for my buffer layer. I was able to obtain a smooth, mirror-like surface that had better electrical characteristics than AlN.

But to build a blue LED, first I needed to prepare positive-type GaN. My rivals had produced *p*-type GaN by irradiating the material with an electron beam. This was a wonderful scientific discovery, but impractical technologically because the method was too slow for LED manufacturing.

Akasaki and Amano announced their discovery at a conference in 1989, just after I got back from Florida. I asked them what the hole concentration of their material was. The answer told me that the quality of their material was not high. But at least they had demonstrated that it was possible to make *p*-type GaN. I would thus start my research on GaN, just as the hitherto most intractable problem in the field had been shown solvable. It was an incredible stroke of luck.

In July 1991, armed with both negative- and positive-type materials, I was able to proceed to the next stage, making a simple LED. The device lit up with a violet-blue light. Though not very bright, it was 50% brighter than conventional, SiC LEDs. The outstanding question was longevity. How long would a fragile thin film with ten billion defects per cm^2 continue to emit light? I went home that night, leaving my LED switched on. Next morning, I returned to the lab, my heart thumping, to find that … it was still lit! I measured the output and was elated to discover that it had barely dropped. In fact, on testing, the lifetime turned out to be longer than 1000 h.

Next, I focused on making high-quality *p*-type GaN. My rivals had not figured out why electron beams caused the transformation. I speculated that it was merely heat that turned the material into *p*-type. In December 1991, I tried annealing magnesium-doped films. The resultant material was *p*-type. Thermal annealing was simpler and much faster than the electron-beam method, hence applicable to the production line. It also produced GaN of a much better quality. Electron-beam penetration was very shallow, with only a very thin surface layer of the material becoming *p*-type. Thermal annealing converted the material to *p*-type all the way through. This was a major breakthrough.

I also clarified the mechanism of hole compensation, which had been a mystery for twenty years. Atomic hydrogen, produced from the dissociation of ammonia gas, forms Mg-H complexes. This formation prevents magnesium from behaving as an acceptor. Using thermal annealing removes atomic hydrogen from the Mg-H complexes, thus activating the Mg acceptors. The material then becomes *p*-type GaN.

The world's first conference on nitrides was held in St Louis in 1992. I gave a talk on my prototype blue LED. I revealed that its lifetime was more than 1000 h. The audience reacted by giving me a standing ovation. Encouraged by the response, on my return to Japan, I embarked on the final stage of what I called my "climb to the summit of Mount Fuji".

To produce a bright blue LED, I had to take two further steps. First, to make the light bright, I had to build a more complex device, called a double heterostructure. Second, in order to make the light pure blue, as opposed to violet-blue, I had to prepare alloys that incorporated indium, whose slightly narrower bandwidth would produce light of a longer wavelength.

Thus far, no one had been able to make InGaN of sufficiently high quality for practical use. The difficulty is that the InGaN layer has to be grown at a much lower temperature than the confining layers of GaN. The bonds between indium and nitrogen are weak. Increase the temperature too quickly and the indium atoms disassociate from their nitrogen neighbors. How to move on to grow the next layer at a higher temperature without destroying the thin layer of InGaN in the process? It was at this final hurdle that Akasaki and Amano failed.

I solved the disassociation problem in two ways. First, by brute force, turning the indium tap on my system all the way open, using ten times as much indium as would turn out to be needed, attempting to get at least some of the stuff to stick. Second, by guile, adding an extra "blocking" layer to cap the InGaN layer, thus preventing the material from disassociating.

In September 1992, I succeeded in fabricating a double-heterostructure LED. Its wavelength was still too short to qualify as true blue. By the end of the year, I had adjusted the growth program, increasing the amount of indium and reducing the thickness of the active layer. This time, there was no doubting the result. Thus far, the output of blue LEDs had been given in millicandelas, that is, a thousandth part of the brightness of a candle. Now, for the first time, my device crossed into the candela class. It shone with a dazzling sky-blue light, a hundred times brighter than blue SiC LEDs, bright enough to be clearly seen in broad daylight. I felt like I had reached the top of Mount Fuji.

On 29 November 1993, at a press conference in Tokyo, Nichia announced the world's first bright blue LED. The initial reaction was incredulity. Once the disbelief subsided, however, orders for Nichia's LEDs started pouring in.

I continued making breakthroughs. In May 1994, I demonstrated blue and blue-green LEDs capable of emitting two candelas, double the brightness of my original devices. Next year, Nichia commercialized bright emerald-green light emitters, the first true green LEDs. In September 1995, I announced the first quantum-well-based blue and green LEDs. These featured a brightness of up to ten candelas. Also in 1995, at my suggestion, the company developed white LEDs. They worked by placing a yellow phosphor in front of a bright blue LED, converting its light to white. Wavelength conversion opened up huge new markets, in particular in general illumination.

Figure 20. My colleagues (from left to right) James Speck, Umesh Mishra, and Steven DenBaars, and I at UCSB after the announcement of the 2014 Nobel Prize in Physics.

Perhaps my biggest coup was the development of a blue laser diode. Many people thought such devices would be impossible, given that GaN crystals were riddled with micro-cracks. To amplify light, a laser needs a more complicated structure than an LED; it also has to be pumped with more current. The structural defects in the material should have scattered the light, preventing optical amplification. Under high current, the defect-ridden layers should have caused instantaneous catastrophic failure.

In the mid 1990s, blue lasers were seen as more significant than blue LEDs. The reason for this perception was that, whereas it was hard to imagine all the applications that would emerge for bright blue LEDs, it was clear what the big application for a blue laser would be: data storage. That was why consumer electronics and disk-drive-producing companies were pouring resources into the development of blue lasers. In 1996, I unveiled a prototype violet-blue laser at a conference in Berlin, using the laser as a pointer in my presentation. By the end of the year, I and my group at Nichia announced an improved blue laser that operated for 1000 h.

In December 1999, I left Nichia to join the University of California at Santa Barbara (UCSB) as a professor of materials and electrical & computer engineering. Since then I have continued to push the boundaries in solid-state lighting and associated crystal-growth methods with my colleagues Professors James Speck, Umesh Mishra, and Steven DenBaars (Figure 20).

As the Research Director of the Solid State Lighting & Energy Electronics Center (SSLEEC; Figure 21) and the Cree Chair in Solid State Lighting & Displays, I am overseeing the research enabling the next-generation optoelectronic devices. Of the various research topics, I am a strong advocate of developing and using native GaN substrates, which offer

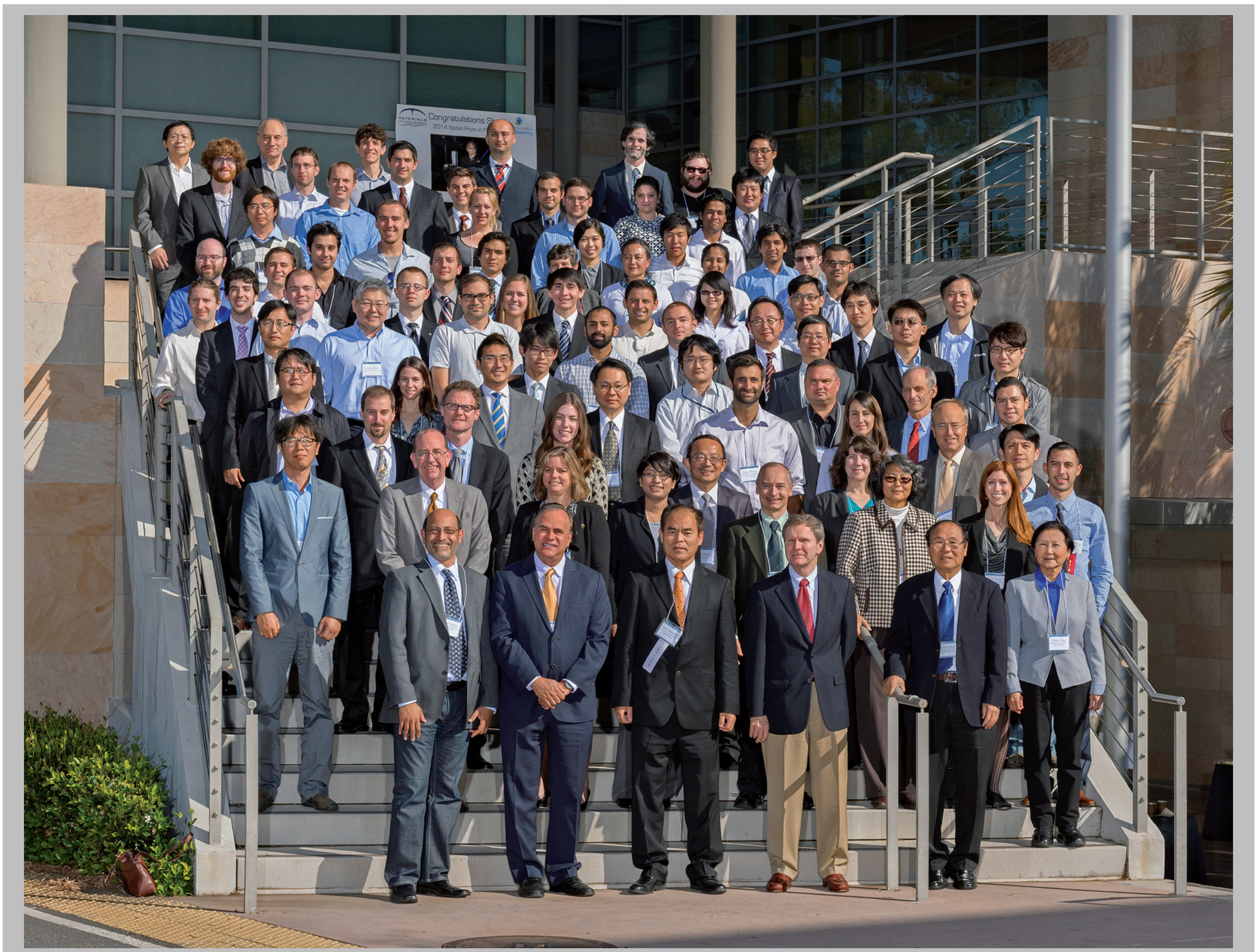

Figure 21. Group photograph at the Solid State Lighting and Energy Electronics Center (SSLEEC) in 2014.

Figure 22. My researchers Paul Von Dollen (middle) and Siddha Pimputkar (right), and I (left) in one of the bulk-single-crystal GaN growth laboratories.

significant improvements toward efficient operation at high current. Furthermore, it opens the door to investigating the use of laser-based solid-state lighting because of the superior performance of lasers over LEDs at very high current densities, and hence light output. To enable this future, I am heavily invested in pursuing bulk-single-crystal growth of GaN boules using the ammonothermal method, which grows single crystals from a supercritical ammonia solution under extreme conditions (thousands of atmospheres pressure and hundreds of degrees Celsius; Figure 22).

I currently hold more than 200 US patents and over 300 Japanese patents, and I have published more than 550 papers in my field. Since coming to UCSB, I have become a fellow of the National Academy of Engineering (NAE) and the National Academy of Inventors (NAI), and have won numerous awards. They include the Charles Stark Draper Prize (2015), the Order of Culture Award (2014), the Inventor of the Year Award from the Silicon Valley Intellectual Property Law Association (2012), the Technical and Engineering Emmy Award (2011), the Harvey Prize from Technion, the Israel Institute of Technology (2009), the Japan Science of Applied Physics Outstanding Paper Award (2008), the Prince of Asturias Award for Technical Scientific Research (2008), the Czochralski Award (2007), the Santa Barbara Region Chamber of Commerce Innovator of the Year Award (2007), Finland's Millennium Technology Prize (2006), and the Global Leader Award, Optical Media Global Industry Awards (2006).

Acknowledgements

While it has been a wonderful, though sometimes rocky, journey and experience for me to develop and ultimately to achieve the production of a blue LED, I would like to acknowledge the many individuals that helped and supported me along the way. Most notably, I would like to thank the founder of Nichia Chemical Corporation, Nobuo Ogawa, who trusted me and invested a lot of money in my research, despite the initial lack of results. I would also like to acknowledge the current president, Eiji Ogawa, my colleagues of the R&D department during 1989—1999 and all current employees of Nichia for their help, as I would not have been able to make the highly efficient blue LED without them. I would also like to stress my gratitude toward Chancellor Henry Yang of the University of California, Santa Barbara (UCSB), for his personal support and encouragement to come to UCSB and further pursue my research there. During my years at UCSB, I have been able to experience and appreciate the tremendous support provided to me by Dean Rod Alferness and former Dean Matthew Tirrell. Last, but certainly not least, I would like to send my sincere gratitude and warmest thanks to my colleagues and friends at UCSB, most notably Professors Steve DenBaars, Jim Speck, and Umesh Mishra, who make it a great pleasure and experience to work and excel at UCSB. I would also like to thank Dr. Siddha Pimputkar for his substantial help in writing this article. Thank you very much.

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 7770–7788
Angew. Chem. **2015**, *127*, 7880–7899

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Received: January 22, 2015