Nobel Lecture: Background story of the invention of efficient blue InGaN light emitting diodes

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(published 5 October 2015)

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I. INTRODUCTION AND IMPACT OF WHITE LIGHT EMITTING DIODES

The basic structure of an efficient double-heterostructure (DH) light emitting diode (LED) is summarized in Fig. [1.](#page-0-0) This optoelectronic device is composed of semiconductor materials and is fabricated by sandwiching an active, emitting layer between an *n*-type and *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 band gap of the material. For DH LEDs, the band gap of the active layer is smaller than that of the n-type and p-type layers.

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 layers, respectively. The electrons and holes recombine radiatively in the active layer, thereby emitting photons. This act is very efficient for DH LEDs as the electrons and holes are confined to the active layer due to the smaller band gap of the active layer with respect to the n -type and p-type cladding layers (see also Fig. [7\)](#page-4-0). The resulting photon has an energy approximately equal to the band gap of the active layer material. Modifying the band gap 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 negating the possibility of creating an efficient blue LED. Gallium nitride (GaN) was one possible candidate, although, 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, Mukai, and Senoh \(1994\)](#page-12-0). Figure [2](#page-1-0) shows a close-up image of a bare and packaged blue GaN LED.

Using blue LEDs, highly efficient white light sources become possible. This can be achieved by converting part of the blue light emitted from the LED to yellow using a phosphor [\(Nakamura, Pearton, and Fasol, 2000](#page-12-1)). 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 Fig. [3](#page-2-0)). Higher quality white light can also be created by mixing blue light with other colors as well, including red and green [\(Pimputkar](#page-12-2) et al., 2009).

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 lm/W) in the 15 000 s B.C., incandescent bulbs (16 lm/W) in the 19th century, fluorescent lamps (70 lm/W) in the 20th century, and LEDs (300 lm/W) in the 21st century (see also Fig. [15](#page-9-0)).

FIG. 1 (color). Schematic depiction of a double-heterostructure (DH) light emitting diode (LED) in operation while being powered by a 2.8 V battery. Within the active, emitting layer, electrons and holes recombine and emit light equal to the band gap of said 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.

^{*}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.

FIG. 2 (color). (a) Image of a blue GaN LED with attached gold wire contacts (size of diode 0.4×0.4 mm²) and (b) the same LED packaged as a commercial product. From [Nakamura,](#page-12-0) [Mukai, and Senoh, 1994.](#page-12-0)

With this significant improvement, substantial energy savings are now possible. It is currently estimated that in 2030 approximately 261 TWh of electrical energy will be saved due to widespread use of white $LEDs¹$. 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 185×10^6 tons of CO₂.

II. MATERIAL OF CHOICE: ZnSe VERSUS GaN

In the 1980s, there were two materials considered as possible candidates for efficient blue LEDs: zinc selenide (ZnSe) and GaN ([Ohkawa, 2014\)](#page-12-3). ZnSe could be grown on single crystal gallium arsenide (GaAs) substrates, yielding high structural quality material 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 less than 10^3 cm⁻². It 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 achieve optically functional LEDs with a high efficiency and a long lifetime [\(Ohkawa, 2014](#page-12-3)). Most researchers worked in this field. GaN, however, was grown on sapphire, yielding dislocation densities on the order of 10^9 cm⁻². Not surprisingly, few researchers were working in this field, although, 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 five, 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 material.

III. 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 metal organic chemical vapor deposition (MOCVD) 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 that 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 publishes 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 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 publishing a paper. 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, although 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 ([Amano](#page-11-0) et al., 1986). Their design required exceptionally high carrier gas velocities (around 4.25 m/s) yielding GaN, although the high carrier velocities presented challenges pertaining to uniformity, scalability, and reproducibility. Furthermore, their reactor design could be used only for small area growths, thereby lacking the necessary properties for commercialization. Since I was working for a company, I had to find a way to grow high quality GaN on large area, 2-in. 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 mirrorlike surface morphology [\(Amano](#page-11-0) *et al.*, 1986), the use of aluminum caused significant problems to the MOCVD reactor

¹"Energy Savings Forecast of Solid-State Lighting in General Illumination Applications, " DOE Report, August 2014, [http://](http://apps1.eere.energy.gov/buildings/publications/pdfs/ssl/energysavingsforecast14.pdf) [apps1.eere.energy.gov/buildings/publications/pdfs/ssl/energysavings](http://apps1.eere.energy.gov/buildings/publications/pdfs/ssl/energysavingsforecast14.pdf) [forecast14.pdf](http://apps1.eere.energy.gov/buildings/publications/pdfs/ssl/energysavingsforecast14.pdf).

FIG. 3 (color). From blue LED to white LED. Part of the blue light emitted from a blue LED is converted to lower energy colors, 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. From [Pimputkar](#page-12-2) et al., 2009.

FIG. 4. (a) Schematic of a two-flow MOCVD for GaN growth and (b) schematic of the effect of the newly introduced subflow on the carrier gases. From [Nakamura, Harada, and Seno, 1991.](#page-12-4)

resulting in poor reproducibility in subsequent GaN growths. 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 growths 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 1.5 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 growths and analyze the result. I would repeat this pattern for 1.5 years until I invented a novel MOCVD reactor design with a low carrier gas flow which I coined a two-flow MOCVD [Fig. [4\(a\)\]](#page-2-1) [\(Nakamura, Harada, and Seno, 1991](#page-12-4)). Using this reactor, I was able to get very uniform and high quality 2-in. GaN growth. The main breakthrough of this reactor was the introduction of a subflow [Fig. [4\(b\)\]](#page-2-1) which 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 due to the elimination of aluminum from the growth system. With the invention of the two-flow MOCVD and the GaN buffer layer, it was possible to achieve 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 enhance overall mobility of the electron. Mobilities for GaN grown directly on sapphire (no buffer layer) by Akasaki and Amano resulted in values around 50 cm²/Vs ([Amano](#page-11-0) *et al.*, 1986), whereas use of the two-flow MOCVD yielded 200 cm^2/Vs [\(Nakamura, Harada,](#page-12-4) [and Seno, 1991\)](#page-12-4). Use of an AlN buffer layer improved the mobility to values as high as $450 \text{ cm}^2/\text{Vs}$ for Akasaki and Amano ([Amano](#page-11-1) et al., 1988). Use of a GaN buffer layer and the two-flow MOCVD values as high as $600 \text{ cm}^2/\text{Vs}$ were measured at room temperature (see Fig. [5](#page-3-0)) [\(Nakamura, 1991](#page-12-5)). 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 commercialization of GaN-based devices.

The next significant development in creating an efficient blue LED occurred in 1992 when I was able to clarify why

FIG. 5. Hall mobility measurements at 77 K (\bullet) and 300 K (\blacksquare) for a 4 μ m thick GaN film grown on sapphire as a function of the GaN buffer layer thickness. From [Nakamura, 1991.](#page-12-5)

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) ([Amano](#page-11-2) et al., 1989), its origin was not understood for another three years. In 1992, I clarified that hydrogen was the source of passivating p -type GaN [\(Nakamura](#page-12-6) et al., 1992). A few years later, theoretical computations by Jörg Neugebauer and Chris Van de Walle confirmed hydrogen passivation in Mg-doped GaN [\(Neugebauer and Van de Walle, 1995](#page-12-7)).

For MOCVD growth of GaN, ammonia $(NH₃)$ 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 to act as an acceptor [\(Nakamura](#page-12-6) et al., 1992). 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 [\(Nakamura, Mukai, Senoh, and Iwasa, 1992\)](#page-12-8) (see Fig. [6](#page-3-1)). As thermal annealing can be performed quickly and simultaneously on multiple substrates of any size in parallel (an act 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 causing the hydrogen to locally diffuse out of the crystal, permitting the affected Mg atoms to act as acceptors yielding p-type GaN.

With the ability to growth *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 demon-strated by [Amano](#page-11-2) et al. (1989) using an AlN buffer layer and their newly developed LEEBI treatment process to obtain

FIG. 6. (a) Change in electrical resistivity of as grown Mg-doped GaN films as a function of annealing temperature in a nitrogen environment. From [Nakamura, Mukai, Senoh, and Iwasa, 1992.](#page-12-8) (b) Change in resistivity of LEEBI-treated Mg-doped GaN films as a function of annealing temperature in a nitrogen (\bullet) or ammonia (\bullet) environment. From [Nakamura](#page-12-6) *et al.*, 1992. Annealing time was 20 min for all samples.

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

p-type GaN). 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 lowtemperature GaN buffer and the LEEBI treatment [\(Nakamura,](#page-12-9) [Mukai, and Senoh, 1991\)](#page-12-9). The output power at 20 mA with a forward voltage of 4 V was 42 μ W. 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. p-n homojunction LEDs cannot reach those levels of output power without generating substantial amounts of waste heat, in large part due to 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 band gap. 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 production of metal-insulator-semiconductor (MIS) GaN LEDs with an output power of 70 μ W on October 20th, $1993.²$ 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 although it side steps 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 Fig. [7](#page-4-0) for the $p-n$ homojunction LED and the doubleheterostructure LED.

In order to understand the advantage a DH LED provides over a p -n homojunction LED, one needs to look at the internal quantum efficiency (IQE)

$$
IQE = \frac{\text{Light generated}}{\text{Electrons injected}}
$$

=
$$
\frac{R_{\text{radiative}}}{R_{\text{radiative}} + R_{\text{nonradiative}}}
$$

=
$$
\frac{Bn^2}{An + Bn^2 + Cn^3}.
$$
 (1)

The IQE is a measure of efficiency and is related to how many electrons 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 $(R_{\text{radiative}},$ emission of a photon, desired), while the other two are nonradiative $(R_{nonradiative},$ emission of phonons, i.e., 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 a n -type layer), *n*. The SRH process increases linearly $(A \cdot n)$, the radiative recombination process quadratically $(B \cdot n^2)$, whereas the Auger recombination process increases as the cube $(C \cdot n^3)$ of *n*. The coefficients *A*, *B*, and *C* are constants.

For low carrier concentrations the SRH term $(A \cdot n)$ dominates leading to poor efficiencies and significant nonradiative recombination. This is the case for p -*n* homojunction LEDs. Because 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 μ m [\(Kumakura](#page-12-10) et al., 2005.) This causes carriers to be spread out over a large region 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 $(B \cdot n^2)$ thereby increasing the efficiency of the LED.

IV. DEVELOPMENT OF InGaN

A. 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 the addition

²"MIS type blue LEDs with a brightness of 200 mcd were developed by Toyoda Gosei," October 20th, 1993, Nikkan Kogyo Shinbun (Japanese newspaper press release).

FIG. 8. Photoluminescence spectra of $In_{0.235}Ga_{0.765}N$ grown at 800 °C using MOCVD on a sapphire substrate. From [Yoshimoto](#page-12-14) et al.[, 1991.](#page-12-14)

of indium into the GaN, the band gap of the material shrinks, thereby providing the ability to confine a carrier in a DH arrangement, and also providing 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 (RT) band-to-band emission, essential for the active layer of a DH LED, could not be achieved given the defective nature of the material.

The reason for this can be traced back to the many challenges associated with InGaN growth, which is in many ways more challenging than growth of p-type or n-type GaN. Indium has such a high vapor pressure, that at typical growth temperatures of GaN (∼1000 °C), it would boil off the surface and not incorporate into the crystal. Growth at lower temperatures yielded poor crystal quality along with numerous defects and impurity incorporation. Growths at intermediate temperatures required uniform and stable growth temperatures 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 achieve exceptionally thin layers of high quality (a layer is typically composed of a few 10s to 100s of atom layer thicknesses in DH LEDs). To make matters even more challenging, introduction of indium into the GaN lattice results in significant strain since 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 InGaN alloy growth was performed by electron beam plasma in 1972 and 1975 by Osamura et al. on sapphire and quartz substrates [\(Osamura](#page-12-11) et al., 1972; [Osamura, Naka, and Murakami, 1975](#page-12-12)). In 1989, Nagatomo et al. grew InGaN on a sapphire substrate using MOCVD at a growth temperature of 500 °C ([Nagatomo](#page-12-13) et al., 1989). In 1991, Yoshimoto et al. demonstrated growth of InGaN layers at a growth temperature of around 800 °C using MOCVD [\(Yoshimoto](#page-12-14) et al., 1991). Despite this achievement, their crystal quality was poor as evidenced by their RT photoluminescence (PL) exhibiting only deep level emission (no band-to-band emission) (Fig. [8](#page-5-0)) and by a full width at half maximum (FWHM) of the double crystal x-ray rocking curve (XRC) of 30 arcmin.

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 [\(Nakamura and](#page-12-15) [Mukai, 1992\)](#page-12-15). 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 RT. The FWHM of the double crystal XRC was around 8 arcmin. Figure [9](#page-5-1) shows the first

FIG. 9. (a) RT PL spectra of InGaN films grown on GaN films under identical growth conditions, except for the InGaN growth temperatures of 830 °C [trace (a)] and 780 °C [trace (b)]. (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. From [Nakamura and Mukai, 1992.](#page-12-15)

FIG. 10. (a) Structure of InGaN/AlGaN double-heterostructure blue LED with (b) resulting output power as a function of forward current. From [Nakamura, Mukai, and Senoh, 1994.](#page-12-0)

observation of band-to-band emission of the InGaN layers at RT described by [Nakamura and Mukai \(1992\).](#page-12-15) With this demonstration, the last remaining barrier for efficient blue LEDs was overcome opening the doors for 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 [\(Nakamura, Senoh,](#page-12-16) [and Mukai, 1993\)](#page-12-16). 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 yielding blue light with a wavelength of 440 nm under forward bias conditions. The output power and the EQE were 125 μ W and 0.22%, respectively, at a forward current of 20 mA.

Further improvements to the device led me to demonstrate 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 (Fig. [10](#page-6-0)) ([Nakamura, Mukai, and](#page-12-0) [Senoh, 1994](#page-12-0)). 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 due to 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 further enhancing radiative recombination.

Simultaneously to my publication, Nichia Chemical Corporation released a press statement mentioning 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 1 candle) on November $30th$, $1993³$ just one month after the press release of MIS-type LEDs with an output power of 70 μ W by Toyoda Gosei Co. Ltd on October 20th, 1993. (Refer to footnote 2.)

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 Fig. [11](#page-7-0)) [\(Nakamura](#page-12-17) et al., 1995a). 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 (a few atom layer thicknesses) versus ∼100 nm for typical DH structures up to this point. This thinning further improves the IQE due to higher carrier concentrations, but also requires even more stringent controls on uniformity and temperature control during MOCVD growth.

Further improvements to growth conditions of the InGaN layers lead to the availability of higher power blue and green single QW (SQW) LEDs. At a 20 mA current, 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 powers of the blue, green, and yellow SQW LEDs are shown in Fig. [11](#page-7-0) [\(Nakamura](#page-12-18) et al., 1995b). This LED epitaxial structure is still the basic foundation for 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 [\(Nakamura](#page-12-17) et al., 1995a, [1995b\)](#page-12-18) with a yellow yttrium aluminum garnet (YAG, $Y_3A_5O_{12}$) based phosphor (Bando et al.[, 1996\)](#page-11-3).

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 in 1996 under pulsed ([Nakamura](#page-12-19) et al.[, 1996b\)](#page-12-19) and continuous wave (CW) ([Nakamura](#page-12-20) et al., [1996a](#page-12-20)) operations. Figure [12](#page-7-1) shows the device structure and light output power versus current $(L-I)$ curve for the first InGaN-based laser diode [\(Nakamura](#page-12-19) et al., 1996b). The structure was composed of an InGaN multiquantum wells (MQW) active layer, GaN waveguide layers, and AlGaN cladding layers.

B. Material properties of InGaN

One mystery still remains to date, namely, why InGaN materials are atypical and luminesce with such high

 3^{3} " p -n junction DH blue LEDs with a brightness of more than 1000 mcd were developed by Nichia Chemical Industries Ltd.," November 30th, 1993, Nikkei Sangyo Shinbun (Japanese newspaper press release).

FIG. 11. (a) Green single quantum well (SQW) LED structure. (b) Output power of a blue, green, and yellow SQW LED at RT as a function of forward current. From [Nakamura](#page-12-17) et al., 1995a, [1995b.](#page-12-18)

FIG. 12. (a) Structure of a violet InGaN MQW laser diode with (b) corresponding $L-I$ characteristics indicating the onset of lasing (30 μ m wide, 1500 μ m long). From [Nakamura](#page-12-19) et al., 1996b.

efficiency despite the high density of dislocations? It was deemed common sense in the 1980s that highly efficient LEDs with a long lifetime required dislocation density less than 10^3 cm⁻². Despite all the improvements in MOCVD growth of GaN, the fundamental lattice mismatch between sapphire and GaN remains, yielding 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, Fig. [13](#page-8-0) 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 be achieved only 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 ([Amano](#page-11-2) et al., 1989). Interesting, InGaN materials

Rev. Mod. Phys., Vol. 87, No. 4, October–December 2015

behave quite differently, exhibiting high efficiencies despite high dislocation densities (Lester et al.[, 1995\)](#page-12-21).

One explanation for this phenomenon, as proposed by Professor Chichibu from Tohoku University, is the presence of localized states in the InGaN layer [\(Chichibu](#page-11-4) et al., 1996; [Nakamura, 1998\)](#page-12-22). 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 due to 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 Fig. [14](#page-8-1)) ([Browne](#page-11-5) et al., 2015). 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

FIG. 13 (color). Dependence of LED efficiency on dislocation density for various semiconductor materials. From [Lester](#page-12-21) et al., [1995](#page-12-21), [Chichibu](#page-11-4) et al., 1996, and [Nakamura, 1998.](#page-12-22)

FIG. 14 (color). 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. From [Browne](#page-11-5) et al., 2015.

in regions of high and low indium content. The high indium content regions have a smaller band gap 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 if they are truly the reason for the highly efficient nature of InGaN.

V. HISTORICAL DEVELOPMENT OF InGaN-BASED LEDs

A. Luminous efficacy

To provide an overview of the historical development of the luminous efficacy for the red, green, and blue LEDs, Fig. [15](#page-9-0) is provided ([Stringfellow and Craford, 1997](#page-12-23)). 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 the early 1960s ([Wolff,](#page-12-24) [Hebert, and Broder, 1955](#page-12-24); [Holt, Alfrey, and Wiggins, 1958](#page-11-6); [Gershenzon and Mikulyak, 1961;](#page-11-7) [Grimmeiss and Koelmans,](#page-11-8) [1961](#page-11-8); [Starkiewicz and Allen, 1962](#page-12-25)). 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 due to their poor luminous efficacy, although they are included in this depiction. It wasn't 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 ([Nakamura, Mukai,](#page-12-0) [and Senoh, 1994;](#page-12-0) [Nakamura](#page-12-17) et al., 1995a, [1995b;](#page-12-18) see also footnote 3). 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 make efficient blue and green LEDs in the GaN material system. In 1996, Nichia Chemical Corporation developed the first white LED using the efficient blue InGaN QW DH LED and YAG phosphors ([Bando](#page-11-3) et al., [1996](#page-11-3)). Rapid progress after the first commercialization of the white LED by Nichia Chemical Corporation has led to current state-of-the-art white LEDs with a stunning 303 lm/W peak efficacy at RT as announced by Cree Inc. in March 2014.⁴

B. Significant milestones on the journey to the white LED

Table [I](#page-9-1) provides an overview of significant developments that ultimately led to the first high efficiency white LED developed by Nichia Chemical Corporation in 1996 [\(Bando](#page-11-3) et al.[, 1996\)](#page-11-3). The first demonstrated growth of GaN was performed by Maruska et al. in 1969 using hydride vapor phase epitaxy (HVPE) [\(Maruska and Tieljen, 1969\)](#page-12-26). 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 a MIS structure (due to the lack of p-type GaN) by doping the GaN with Mg, which acted as a color center, in 1973 [\(Maruska, Stevenson, and](#page-12-27) [Pankove, 1973\)](#page-12-27).

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 improved quality GaN material ([Yoshida, Misawa, and Gonda, 1983](#page-12-28)). Amano et al. applied the AlN buffer layer idea to MOCVD growth of GaN by growing it at low temperatures in 1986 [\(Amano](#page-11-0) et al., [1986](#page-11-0)). The mirrorlike surface morphology and reduced

⁴"Cree First to Break 300 Lumens-Per-Watt Barrier," March 26, 2014, Cree Inc. (Press Release), [http://www.cree.com/News](http://www.cree.com/News-and-Events/Cree-News/Press-Releases/2014/March/300LPW-LED-barrier)-and-Events/Cree‑News/Press‑[Releases/2014/March/300LPW](http://www.cree.com/News-and-Events/Cree-News/Press-Releases/2014/March/300LPW-LED-barrier)‑LED‑ [barrier.](http://www.cree.com/News-and-Events/Cree-News/Press-Releases/2014/March/300LPW-LED-barrier)

FIG. 15 (color). Evolution of luminous efficacy of red, green, and blue LEDs. From [Stringfellow and Craford, 1997](#page-12-23).

residual carrier concentration, on the order of 10^{17} cm⁻³ for unintentionally doped GaN, was an important milestone.

Subsequently, Amano *et al.* achieved the first *p*-type Mg-doped GaN by using a postgrowth LEEBI treatment in 1989, although they could not explain the origin of the mechanism by which it was achieved ([Amano](#page-11-2) et al., 1989). The hole concentration and mobility was 2×10^{16} cm⁻³ and 8 cm²/V 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 Nichia Chemical Corporation and developed a novel MOCVD, which I called two-flow MOCVD, in 1991 ([Nakamura, Harada, and Seno,](#page-12-4) [1991](#page-12-4)). 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

TABLE I. 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	Maruska and Tieljen (1969)
	1973	First blue Mg-doped GaN MIS LED	Maruska, Stevenson, and Pankove (1973)
	1983	High quality GaN using AlN buffer by MBE	Yoshida, Misawa, and Gonda (1983)
	1985	High quality GaN using AlN buffer by MOCVD	Amano et al. (1986)
	1989	<i>p-type GaN using LEEBI</i> (low hole concentration) First p - <i>n</i> homojunction GaN LED	Amano et al. (1989)
	1991	Invention of Two-flow MOCVD	Nakamura, Harada, and Seno (1991)
		GaN growth using GaN buffer by MBE	Lei <i>et al.</i> (1991)
		High quality GaN using GaN buffer by MOCVD	Nakamura (1991) and Nakamura, Mukai, and Senoh (1992)
	1992	p-type GaN using thermal annealing (high hole concentration)	Nakamura, Mukai, Senoh, and Iwasa (1992)
		Discovery hydrogen passivation	Nakamura et al. (1992)
InGaN	1972	In GaN growth using electron beam plasma	Osamura et al. (1972) and Osamura, Naka, and Murakami (1975)
	1989	InGaN growth by MOCVD	Nagatomo et al. (1989)
	1992	InGaN layers with RT band-to-band emission	Nakamura and Mukai (1992)
	1994	Efficient blue InGaN DH LED (1 Candela)	Nakamura, Senoh, and Mukai (1993), and Nakamura, Mukai, and Senoh (1994) , see also footnote 3
	1995	Efficient yellow, green, and blue InGaN DH QW LEDs	Nakamura et al. (1995a, 1995b)
	1996	First pulsed violet InGaN DH MQW LDs	Nakamura et al. (1996b)
		First CW violet InGaN DH MQW LDs	Nakamura et al. (1996a)
		Commercialization white LED using InGaN DH blue LED	Bando et al. (1996)

FIG. 16 (color). Summary of key contributions to the efficient blue LED.

(Lei et al.[, 1991](#page-12-29)) and MOCVD ([Nakamura, 1991\)](#page-12-5). Lei et al. developed it for the MBE method, although the achieved crystal quality was poor with a rough surface (Lei [et al.](#page-12-29), [1991](#page-12-29)). I developed it for MOCVD growth by employing a low-temperature growth step, yielding high quality GaN films on sapphire ([Nakamura, 1991\)](#page-12-5). Improvements to the growth of the low-temperature GaN buffer layer resulted in electron mobilities of 900 cm²/V s at RT in 1992 ([Nakamura, Mukai,](#page-12-30) [and Senoh, 1992\)](#page-12-30).

With the availability of high crystal quality material, the next major step was my demonstration of p-type GaN films using post thermal annealing under a $NH₃$ free ambient gas, as shown in Fig. [6,](#page-3-1) in 1992 ([Nakamura, Mukai, Senoh, and](#page-12-8) [Iwasa, 1992\)](#page-12-8). The hole concentration and mobility was 3×10^{17} cm⁻³ and 10 cm²/V s, respectively. Following this act, I was able to clarify the observed hole compensation in GaN:Mg being due to hydrogen passivation [\(Nakamura](#page-12-6) et al., [1992](#page-12-6)), a mechanism which 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 [Neugebauer and Van de](#page-12-7) [Walle \(1995\).](#page-12-7)

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 occurred in 1972 by Osamura et al. revealing some of its properties [\(Osamura](#page-12-11) et al., 1972). The first growth by MOCVD occurred in 1989 by [Nagatomo](#page-12-13) et al. [\(1989\),](#page-12-13) opening the door for development using the same growth technique with which high quality GaN could be grown. It was not until 1992, when Mukai and myself were able to demonstrate the first InGaN layer which exhibited strong band-to-band emission at RT [\(Nakamura and Mukai,](#page-12-15) [1992](#page-12-15)) did the option of forming a high efficiency blue LED become a realistic option. Incorporating 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 [\(Nakamura, Senoh, and Mukai, 1993](#page-12-16); [Nakamura, Mukai,](#page-12-0) [and Senoh, 1994](#page-12-0)), the first high efficiency green InGaN DH QW LED in 1995 ([Nakamura](#page-12-18) et al., 1995b), and the first blue/green/yellow InGaN DH QW LEDs in 1995 ([Nakamura](#page-12-17) et al.[, 1995a](#page-12-17)).

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While our group at Nichia Chemical Corporation worked hard on developing the first white LED, I was able to further pursue improving GaN-based optoelectronic devices and eventually demonstrated the first pulsed ([Nakamura](#page-12-19) et al., [1996b](#page-12-19)) and CW operation [\(Nakamura](#page-12-20) et al., 1996a) violet InGaN DH QW laser diode in 1996. Shortly thereafter, Nichia Chemical Corporation released the first white LED, changing the world forever ([Bando](#page-11-3) et al., 1996).

A more detailed account of the history of the GaN-based LED can be found in [Nakamura and Krames \(2013\)](#page-12-31).

C. 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](#page-10-0) 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 due to the use of a sapphire substrate (see also Fig. [13](#page-8-0)).

VI. FORWARD LOOKING

While I have been talking primary 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 which 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 Fig. [17](#page-11-9)). This phenomena, referred to as efficiency droop, forces LED manufacturers 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

FIG. 17 (color). Comparison of external quantum efficiency (EQE) of a commercial LED and laser with increasing current density. From [Pourhashemi](#page-12-34) et al., 2013.

high light output, manufacturers may use multiple LEDs in parallel, effectively increasing the overall active area and hence reducing current density. The primary origin of efficiency droop, which was not discovered until recently, is the Auger recombination process (Shen et al.[, 2007;](#page-12-32) [Iveland](#page-12-33) et al., [2013](#page-12-33)). If you recall the contributions to the IQE of an LED [see Eq. [\(1\)\]](#page-4-1), the cubic term in carrier concentration $(C \cdot n^3)$ was the Auger recombination process. Given the exceedingly high densities of carriers, this term starts to dominant thereby reducing the value of the IQE. Since the Auger recombination process is due to intrinsic properties of GaN, it is exceptionally challenging to overcome.

An alternative method to produce white light is by using a blue laser, as opposed to an LED, in combination with a phosphor. Above the lasing threshold, the carrier density is clamped at threshold, 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, prohibiting it from reaching densities where the Auger recombination process becomes the dominant recombination process. Auger recombination, with the resulting efficiency droop, does not appreciably occur in blue laser diodes [\(Pourhashemi](#page-12-34) et al., 2013).

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 Fig. [17](#page-11-9)). It is therefore of great interest to further pursue lasers as they have the potential of operating at high current densities, 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 manufacturers have already leveraged in their high-end vehicles. Current, high-end vehicles already use laser based white light sources for their head lamps, allowing them to see farther 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.

ACKNOWLEDGMENTS

While it has been a wonderful, although sometimes rocky, journey and experience for me to develop and ultimately achieve 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 (especially Masayuki Senoh, Takashi Mukai, Shin-ichi Nagahama, Naruhito Iwasa, Motokazu Yamada, and TakaoYamada) 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 high 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 Professor Steve DenBaars, Professor Jim Speck, and Professor 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.

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