

BLUE LEDS – FILLING THE WORLD WITH NEW LIGHT

Chandra B.P. †

School of Studies in Physics and Astrophysics, Pt. Ravishankar Shukla University, Raipur 492010 (C.G.), India.

*Corresponding author E-mail: bpchandra4@yahoo.co.in

† Emeritus Professor

ABSTRACT

The 2014 Nobel Prize in Physics was awarded to Isamu Akasaki and Hiroshi Amano of Nagoya University, Japan, and Shuji Nakamura of University of California, Santa Barbara, USA for their pioneering work on blue-light-emitting diodes (LEDs) based on Gallium Nitride (GaN). The inventions made by these Nobel Laureates have revolutionized the field of illumination technology whereby new, more efficient, cheaper and smarter lamps are developed all the time. White LED lamps can be obtained in two different ways. One way is to use blue light to excite a phosphor so that it shines in red and green. When blue, red and green colours come together, then white light is produced. The other way is to construct the lamp out of three LEDs; blue, red and green, and let the eye do the work of combining the three colours into white. The Greenhouse-cultivation using artificial light is already a reality. Furthermore, the LED lamp also holds great promise when it comes to the possibility of increasing the quality of life for the more than 1.5 billion people who currently lack access to electricity grids, because the low power requirements imply that the lamp can be powered by cheap local solar power. Moreover, polluted water can be sterilized using ultraviolet LEDs, a subsequent elaboration of the blue LED. The present paper discusses the construction and working of homojunction, heterojunction, quantum well, and the LEDs used for lighting. Furthermore, applications of LEDs and the present status of LEDs for lighting are also described.

KEYWORDS: Blue LEDs, Light sources, LED applications, Multiquantum well LEDs.

1. Introduction

In 2014, Isamu Akasaki and Hiroshi Amano of Nagoya University, Japan, and Shuji Nakamura of University of California, Santa Barbara, USA were awarded Nobel Prize in Physics for inventing a new energy efficient and environment-friendly light source – the blue light-emitting diodes (LEDs) based on Gallium Nitride (GaN). In the spirit of Alfred Nobel, the Prize is awarded for the invention of greatest benefit to mankind. Using blue LEDs, white light can be created in a new way. With the advent of LED lamps we now have more long-lasting and more efficient alternatives to older light sources. When Akasaki, Amano and Nakamura reached Stockholm in December 2014 to attend the Nobel Prize ceremony, they hardly failed to notice the light from their invention glowing in virtually all the windows of the city. In fact, the white LED lamps are energy-efficient, emit a bright white light and they are long-lasting. Moreover, unlike fluorescent lamps, they do not contain mercury.

Red and green light-emitting diodes have been with the researchers for almost half a century, but blue light was needed to really revolutionize lighting technology. Only the triad of red, green and blue can produce the white light that illuminates the world. Although high stakes and great efforts were undertaken in the research community as well as in industry, the blue light remained a challenge for three decades. Akasaki and Amano worked at Nagoya University while before shifting to USA, Nakamura was employed at Nichia Chemicals, a small company located in Tokushima on the island of Shikoku in Japan. When they obtained bright blue light beams from GaN semiconductors, in reality the gates opened up for a fundamental transformation of illumination technology. In fact, incandescent light bulbs had lit the 20th century; the 21st century will be lit by LED lamps.

A light-emitting diode consists of a number of layered semiconductor materials. In the LED, electricity is directly converted into light particles, called photons, leading to high efficiency gains compared to other light sources in which most of the electricity is converted to heat and only a small amount into light. In incandescent bulbs, as well as in halogen lamps, electric current is used to heat a wire filament, which causes it to glow. In fluorescent lamps

(previously referred to as low-energy lamps, but with the advent of LED lamps that label has lost its meaning) a gas discharge is produced in which both heat and light are created. In this way, the new LEDs require less energy in order to emit light compared to older light sources. Moreover, LEDs are constantly improved, getting more efficient with higher luminous flux (measured in lumen) per unit electrical input power (measured in watt). The most recent record is just over 300 lumen/watt, which can be compared to 16 lumen/watt for regular light bulbs and close to 70 lumen/watt for fluorescent lamps. Since about one-fourth of world electricity consumption is used for lighting purposes, the invention of highly energy-efficient LEDs contributes significantly to saving the Earth's resources. LEDs are also more long-lasting as compared to other lamps. Whereas incandescent bulbs tend to last 1,000 hours, as heat destroys the filament, the fluorescent lamps usually last around 10,000 hours. In fact, LEDs can last for 100,000 hours, and thereby they greatly reduce materials consumption.

The United Nation General Assembly has proclaimed 2015 as the International Year of Light and Light-based Technologies (IYL 2015) with a aim to raise awareness of the achievements of light science and its applications, and its importance to human kind. The present paper discusses the construction and working of homojunction LEDs, heterojunction LEDs, quantum well LEDs, and the LEDs used for lighting. Furthermore, applications of LEDs and the present status of LEDs for lighting are also described.

2. Construction and Working of LEDs

Light-emitting diode (LED) is a p-n junction semiconductor diode in which light emission takes place when it is forward biased (Held 2009, Bhattacharya 1999). It is opposite of solar cells in which incident light causes the generation of voltage. In other words, light emitting diode is an optoelectronics device consisting of semiconductor p-n junction, in which spontaneous emission of incoherent radiation in the ultraviolet, visible and infrared region of electromagnetic spectrum taken place under proper forward bias condition. When a single piece of semiconductor is made p-type in one region and n-type in another region by addition of proper impurities, a junction is formed between the two regions and the device is called p-n junction diode.

During the formation of a p-n junction the diffusion and subsequent recombination of electrons and holes takes place near the junction. In this way, a region is formed across the junction which is deprived of charge carriers and it is called depletion region. The depletion region possesses only fixed rows of oppositely charged ions on its two sides and because of this charged separation, an electric potential V_B is established across the junction even when the junction is not connected to any external source of e.m.f. It is known as junction barrier potential. It stops further flow of carriers across the junction unless supplied by the energy from an external source. At room temperature V_B is about 0.3 V for Ge and 0.73 V for silicon.

Energy band diagram of a p-n junction is as shown in Fig. 2 (a). Under equilibrium the Fermi levels of two homogeneous p- n- type semiconductors brought into contact must be coincident. This causes the bending of energy bands and the formation of a potential barrier as shown in Fig. 2(b). When the diode has zero bias the potential barrier prevents the cross-over of large concentration of conduction band electrons and valence band holes across the junction. However, when the junction is forward biased, reduction in potential barrier takes place and now, electrons are able to flow from n- region to p-region and holes can flow from p-region to n- region. Thus, the majority charge carriers from both sides of the junction cross the internal potential barrier and enter the material at other side, where they are minority type carriers and cause local minority carrier concentration to be larger than normal. This situation is described as minority carrier injection.

The excess minority carriers diffuse away from the junction and consequently, they recombine with majority carriers. In certain material, the recombination of electrons and holes is radiative and energy is emitted in the form of light. LEDs are made of such materials in which radiative recombination probability is high.

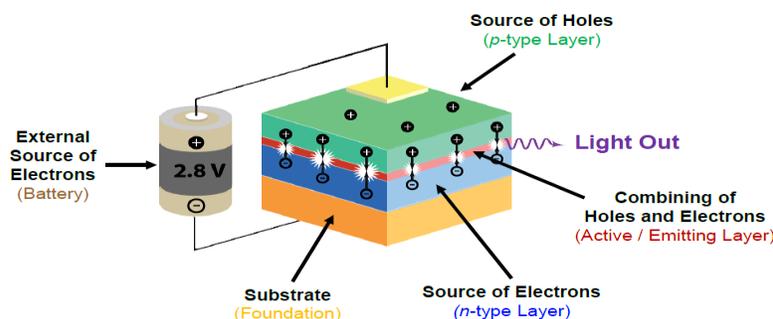


Fig. 1 Construction of an LED.

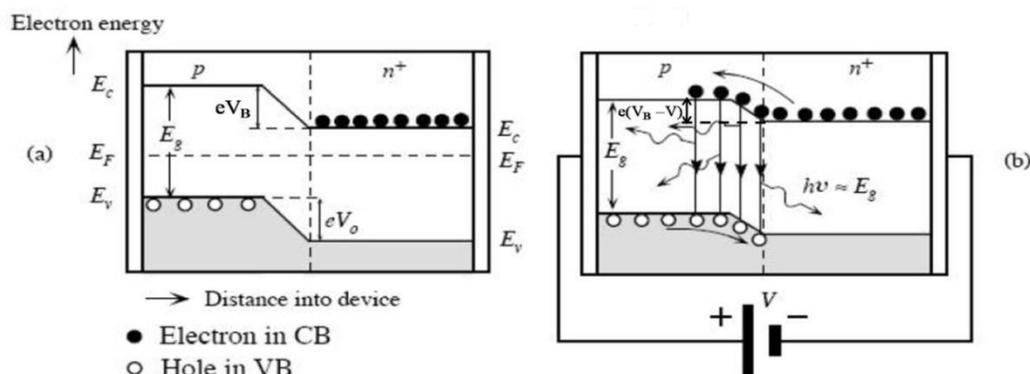


Fig.2 (a)The energy band diagram of a pn^+ (heavily n-type doped) junction without any bias. Built-in potential V_B prevents electron from diffusing n^+ to p side. (b) The applied bias reduces V_B and thereby allows electrons to diffuse or be injected into the p-side. Recombination around the junction and within the diffusion length of the electrons in the n-side leads to photon emission.

A light-emitting diode consists of several layers: an n-type layer with a surplus of negative electrons, and a p-type layer with an insufficient amount of electrons, also referred to as a layer with a surplus of positive holes. Between them is an active layer, to which the negative electrons and the positive holes are driven when an electric voltage is applied to the semiconductor. When electrons and holes meet they recombine and light is created. The wavelength of emitted light depends entirely on the semiconductor; blue light appears at the short-wave end of the rainbow and can only be produced in some materials. The LED efficiency is high for direct band-gap materials, and it is less for indirect band-gap materials. Those materials for which maximum of valence band and minimum of conduction band lie for same value of k (wave vector), are called direct band-gap materials (i.e. satisfies the condition of energy and momentum conservation). For example : GaAs, InP, CdS, etc. are direct band-gap semiconductors. Those materials for which maximum of valence band and minimum of conduction band do not occur at same value of k , are called indirect band-gap materials. For example : Si, Ge., etc. are indirect band-gap semiconductors. Table 1 shows the details of the light emission from homojunction LEDs made using III-V binary compounds.

Table 1: Details of light emission from homojunction LEDs made using III-V binary compounds

	Lattice constant a_0 (Å)	Melting temperature T_m (°C)	Bandgap energy E_g (eV)	Emission wavelength λ (nm)	Band structure
AlP	5.451	2000	2.45	510	indirect
AlAs	5.661	1740	2.16	570	indirect
AlSb	6.135	1050	1.65	750	indirect
GaP	5.451	1467	2.26	550	indirect
GaAs	5.653	1238	1.42	870	direct
GaSb	6.095	706	0.73	1850	direct
InP	5.869	1058	1.34	920	direct
LnAs	6.057	942	0.35	3440	direct
InSb	6.479	530	0.17	730	direct

If η_r is the probability of radiative recombination and η_{nr} is the probability of non-radiative recombination, then the efficiency of radiative recombination is given by

$$\eta = \frac{\eta_r}{\eta_r + \mu_{nr}} \quad (1)$$

For indirect bandgap semiconductors $\eta_{nr} \gg \eta_r$, and therefore, η is much less. On the other hand, for indirect bandgap semiconductors $\eta_r \gg \eta_{nr}$, and therefore, η is high.

The first report of light being emitted from a semiconductor was given in 1907 by Henry J. Round of England, a co-worker of Guglielmo Marconi, Nobel Prize Laureate 1909 (Schubert 2006). At low voltages yellow light was observed, but more colours were emitted at higher voltages. Later on, in the 1920s and 1930s, in the Soviet Union, Oleg V. Losev undertook closer studies of light emission. However, Round and Losev lacked the knowledge to truly understand the phenomenon (Khanna, 2014). These developments took place prior to the formulation of the modern theory of electronic structure of solid-state materials. It took a few decades before the prerequisites for a theoretical description of this so-called electroluminescence were created. The red light-emitting diode was invented in the end of the 1950s. They were used, for instance, in digital watches and calculators, or as indicators of on/off-status in various appliances. At an early stage it was evident that a light-emitting diode with short wavelength, consisting of highly energetic photons – a blue diode – was needed to create white light. Many laboratories tried, but without success.

- In 1907, Henry J. Round reported light emission from a SiC semiconductor.
- In the mid 1920s, Russian Oleg Vladimirovich Losev independently created the first LED, although his research was ignored at that time.
- In 1955, Rubin Braunstein of the Radio Corporation of America reported an infrared emission from gallium arsenide (GaAs) other semiconductor alloys.
- Experimenters at Texas Instruments, Bob Biard and Gary Pittman, found in 1961 that gallium arsenide gave off infrared radiation when electric current was applied. Biard and Pittman received the patent for the infrared light-emitting diode.
- In 1962, Nick Holonyak Jr., of the General Electric Company and later with the University of Illinois at Urbana – Champaign, developed the first practical visible-spectrum LED. He is seen as the “father of the light-emitting diode”.

- In 1972, M. George Craford, Holonyak’s former graduate student, invented the first yellow LED and 10x brighter red and red – orange LEDs.
- Shuji Nakamura of Nichia Corporation of Japan demonstrated the first high- brightness blue LED based on InGaN. The 2006 Millennium Technology Prize was awarded to Nakamura for his invention.

3. Enhancing the Internal Quantum Efficiency of LEDs

As compared to conventional light sources, LEDs are superior in many areas such as longer life span, light weight, vivid color emission and energy saving. Although LEDs have these unbeatable advantages, the implementation requires that LEDs should be more efficient and of high power. In an ideal LED, every electron injected into the active region should generate a photon, thus giving an internal quantum efficiency of unity. The internal quantum efficiency (η_{int}) of LED is defined as (Pui 2007):

Hence, the overall quantum efficiency can be defined as:

$$\eta_{ext} = \frac{\text{number of photons escaped from LED per unit time}}{\text{number of electrons injected to LED per unit time}} \quad (2)$$

The internal quantum efficiency of a LED can be enhanced using the following two possibilities: (i) by enhancing the radiative recombination probability, and (ii) by reducing the non-radiative recombination probability. These results can be achieved by employing good quality nitride films and appropriate device design structures. For the former case, some growth techniques which aim to reduce material defects have been considered. Following section will be mainly on how the advancement of LED structures be employed to enhance the η_{int} .

3.1 p-n homojunction

In GaN-based LEDs at the early stage, the device structure is basically a simple p-n junction which commonly consisted of a single material with different diffusion constants of the carriers. .This p-n homojunction LED structure successfully demonstrated the emission of blue light, but, its overall efficiency was very low and the achieved total light output was even lower than a single candela. Such result is probably attributed to the inherently long diffusion length in the p-n homojunction, of which the minority carriers are distributed over quite a large distance of about several microns. Moreover, the concentration of the minority carriers decreases with the increasing diffusion distance. Thus, the electron-hole recombination process takes place over a large region, which is not beneficial for efficient light emission. These scenarios and the carrier distributions in a p-n junction under zero and under forward bias are schematically illustrated in Fig. 3a and 3b, respectively.

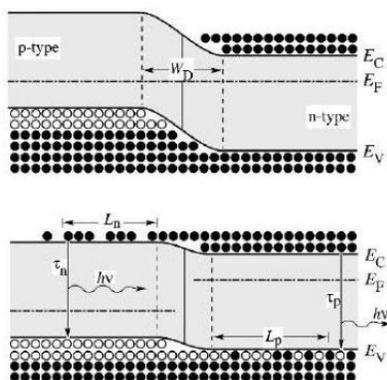


Fig. 3: Schematic diagrams showing a p-n homojunction under a) zero and b) forward bias.

3.2 Heterojunction

It was found that the problems of minority carrier diffusion and inefficient recombination in the p-n homojunction can be overcome by introducing a small bandgap active layer between the p-type and n-type regions, namely heterostructure or quantum well structures. In fact, the employment of heterostructures enables one to improve the efficiency of LEDs by confining carriers to the active region, which is typically much smaller than the diffusion length, and thereby avoiding the diffusion of minority carriers over a long distance and increasing the rate of effective radiative recombination. The effect of the heterojunction on the carrier distribution is shown in Fig. 4. However, it is to be noted that it is not without penalty. In such device, the problem of carrier overflow is severe in the structures with a small active region volume, in which the region is likely to be saturated with the carriers at a certain operating current density. The injection of additional carriers does not contribute to an increase of light output of LEDs.

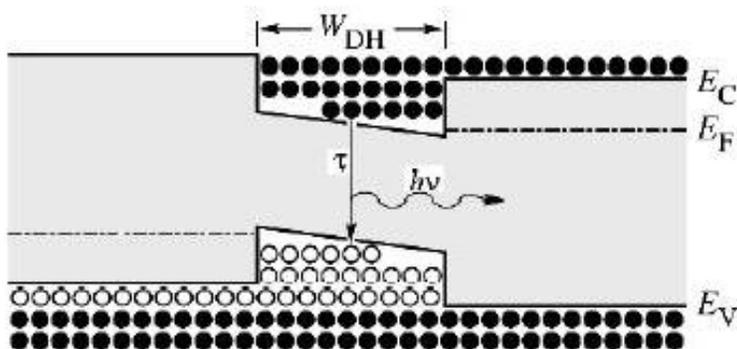


Fig. 4: A schematic diagram showing a p-n diode with a heterostructure and under forward bias.

3.3 Multiple quantum well structures

In fact, the highly desirable drives for obtaining high intensity nitride based LEDs have been the catalyst, and the problem of carrier overflow in the heterostructural active region has become the hottest research topic. In order to cope with this challenge, many different good ideas have been proposed, which include: (i) thickening the heterostructure layer, or employing repeating of the heterostructure active regions, or applying a large injection area. Among these concepts, Hunt *et al.* (1992) studied the phenomena of current saturation in quantum well LEDs, and ascertained that the saturation current level would increase by increasing the number of quantum well pairs. Based on this work, the first commercial GaInN/GaN multiquantum well (MQW) LED with high light intensity output was developed and reported in 1995 (Nakamura 1996). In the past, MQW structure has been employed as an active layer in almost all nitride based LEDs.

Then, the electron blocking layers, which use a high energy bandgap material to confine the active interface, were developed and incorporated into many LED structures to further reduce electron escape from the active region. The structural design of MQW LEDs is shown in Fig. 5.

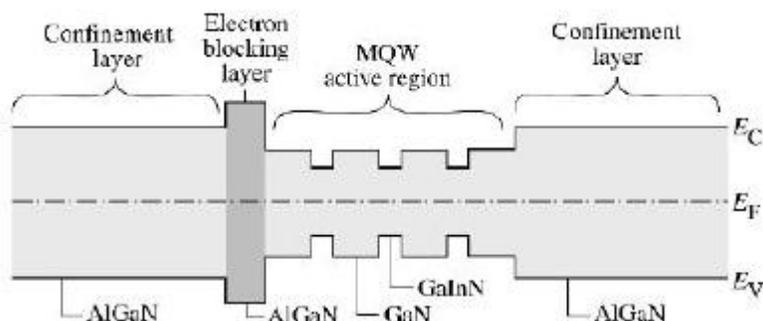


Fig. 5: LED design with MQWs and electron blocking layer structures.

3.2 Light extraction efficiency

In addition to modifying the internal quantum efficiency design, increasing light extraction efficiency (η_{ext}) is another key for further improvement on the overall efficiency of an LED. Due to the large difference in the refractive index between semiconductors and air, a significant portion of light is trapped inside the semiconducting devices because the generated photons are totally reflected internally and will eventually be reabsorbed as heat (Forster 2005). As GaN has a relatively low refractive index of 2.4, roughly only around 10% of the total emitted light can escape from the active region to air. Thus, it is of paramount importance to use promising techniques to effectively enhance photon extraction.

4. Enhancing the Light Extraction Efficiency of LEDs

For getting the full potential of GaN LEDs as a general illuminating source, the overall efficiency of the devices was to be further improved and to achieve an efficacy of 200 lm/W. The followings are some approaches which have been commonly used to improve the light extraction efficiency of the LEDs.,

4.1 Shaping of LED dies

Practically, the geometric shaping of the LED surface has been proven to be an effective method for increasing light extraction from light emitting devices. In fact, the die shaping in the form of truncated-inverted pyramidal structures can redirect the photons inside the LED and has been shown to significantly improve the extraction efficiency of the devices, being particularly successful in GaAs based LEDs (Krames et al. 1999). However, it is difficult for GaN-based LEDs, grown on sapphire and SiC, to employ such a sophisticated geometry because of the hardness of these substrate materials.

4.2 Reflective mirror coatings

In contrast to the laser diodes, photons generated from LED dies could be emitted in different directions. As a result, a large portion of photons emitted from an LED chip could be lost since the angle of the escape cone is usually small for semiconductor materials with high refractive index, particularly for those photons being emitted downward to the substrate. Hence, the output intensity of the LEDs can be significantly enhanced if those downward emitting photons could be effectively reflected. For reflect all the downward emitting photons, a mirror-like coating, such as a thin metallic aluminum or a silver layer, can be deposited on the top or bottom surfaces of the LEDs (Pui 2007; Forster 2005; Chang et al. 2006). In fact, the reflective coating can redirect light reaching the bottom of the LEDs upwardly and the concept employing mirror coatings as light reflectors is also applicable in flip-chip bonded devices.

4.3 Surface texturing

The roughening the surface of an LED can increase the light extraction efficiency of the device and this concept has been successfully applied to both GaAs and nitride based LEDs. The enhancement of efficiency from the surface texturing technique can generally be explained by the scattering of the internally reflected light at the textured surface. Due to the resulting change in its propagation angle, the light experiences multiple chances to escape from the lighting devices

Many approaches such as including dry etching, chemical wet etching or photolithography techniques have been examined to texture the surfaces of the LEDs (Pui 2007; Forster 2005). It is to be noted that, unfortunately, chemical wet etching of nitride materials has been an arduous task as nitrides have stable chemical resistance properties, while photolithography techniques are also relatively complicated to pattern the device surfaces. Hence, almost all the textured surfaces of nitride based LEDs were obtained by plasma etching on the top epilayer. As the thickness of the top p-type GaN layer is usually very thin in a conventional LED structure, it is not desirable to directly etch the p-type GaN layer due to the difficulty in controlling the dry etching depth. The dry etching often partially destroys the junction region, and thus causes reduction in the light emitting area.

5. Some Important Investigations Related to LEDs

A great progress took place in the understanding of the physics of semiconductors and p-n junctions during the 1940s, which led to the invention of the transistor at Bell Telephone Laboratories in the USA in 1947 (Nobel Prize 1956 to Shockley, Bardeen and Brattain). Subsequently, it became clear to the researchers that a p-n junction could prove to be an interesting device for the light emission. In 1951, K. Lehovc and co-workers of the Signal Corporation Engineering Laboratory in the USA (Lehovc et al. 1951) used these ideas to explain the electroluminescence in SiC as resulting from the injection of carriers across a junction followed by radiative recombination of electrons and holes. Because the observed photon energy was less than the energy gap of SiC, they suggested that radiative recombination was likely to occur from the impurities or lattice defects. Later on, in 1955, injection electroluminescence was reported in a number of III-V compounds (Wolff et al. 1955, Braunstein 1955). At the same time, in 1955 and 1956, J.R. Haynes at Bell Telephone Laboratories reported that electroluminescence observed in germanium and silicon was caused by the recombination of holes and electrons in a p-n junction (Haynes 1955).

5.1 Infrared LEDs

Subsequently, suitable techniques for making efficient p-n junctions with GaAs were rapidly developed during the following years. In fact, GaAs was attracting the attention of workers because of its direct bandgap, which enables recombination of electrons and holes without involvement of phonons. As the bandgap of GaAs is 1.4 eV, it corresponds to light in the infrared. In the summer of 1962, the light emission from p-n-junctions was demonstrated (Pankove 1962, Pankove and Berkeyheiser 1962). A few months later, laser emission in GaAs at liquid nitrogen temperature (77 K), was reported independently and almost simultaneously by three research groups at General Electric, IBM and the MIT. Lincoln Laboratory, in the USA (Hall et al, 1962; Nathan et al. 1962; Quist et al. 1962). Subsequently, after a few years, laser diodes became widely used. The development of heterostructures (Nobel Prize 2000 to Z.I. Alferov and H. Kroemer), and later quantum wells, provided a better confinement of the carriers while reducing the losses. The laser diodes could operate continuously at room temperature, and they found applications in a large variety of areas.

5.2 Visible LEDs

Encouraged by the early experiments, at the end of the 1950s (Wolff et al. 1955), progress in making efficient LEDs using GaP (indirect bandgap equal to 2.2 eV) was made in parallel by three research groups from Philips Central Laboratory in Germany (H.G. Grimmeiss), the Services Electronics Laboratories (SERL) in the UK (J.W. Allen) and Bell telephone laboratories in the USA (M. Gershenson) (Grimmeiss and Koelmans 1961; Starkiewicz and Allen 1962; Gershenson and Mikulyak 1961). These groups had different objectives, ranging from communication, lighting

and television to indicator lamps for electronics and telephones. Using different dopants (*e.g.* Zn-O or N) at various concentrations, different wavelengths were generated which ranged from red to green. By the late 1960s a number of manufacturers in different countries were fabricating red and green LEDs based on GaP. Mixed crystals consisting of Ga, As, and P ($\text{GaP}_x\text{As}_{1-x}$) are interesting because the emission wavelength can be shorter than that for GaAs, reaching the visible range while the bandgap is direct for x below 0.45. In the late 1950s, Holonyak Jr. and co-workers at the General Electric laboratory in the USA, started to work with $\text{GaP}_x\text{As}_{1-x}$ and succeeded in making p-n junctions and observing the emission from LED. In 1962, laser diode emission at 710 nm (red) was reported (Holonyak and Bevacqua 1962).

5.3 Early work on blue LEDs

In fact, the step related to the emission of blue light proved to be more difficult. The early attempts with ZnSe and SiC, with high indirect bandgaps, did not lead to efficient light emission. The material that enabled the development of blue LEDs was found to be GaN.

5.4 Gallium Nitride

GaN is a semiconductor of the III-V class, with Wurtzite crystal-structure. Despite the difference in lattice constants GaN can be grown on a substrate of sapphire (Al_2O_3) or SiC. GaN can be doped, *e.g.* with silicon to n-type and with magnesium to p-type. Unfortunately, doping interferes with the growth process so that the GaN becomes fragile. In general, defects in GaN crystals lead to good electron conductivity, *i.e.* the material is naturally of n-type. GaN has a direct bandgap of 3.4 eV, corresponding to a wavelength in the ultraviolet region.

At the end of the 1950s, the possibility of a new lighting technology using GaN, the bandgap of which had just been measured, was seriously considered at Philips Research Laboratories. H.G. Grimmeiss and H. Koelmans obtained efficient photoluminescence from GaN over a wide spectral range using different activators and a patent was filed (Grimmeiss and Koelmans 1959). However, at that time it was very difficult to grow GaN crystals. Only small crystals, forming a powder, could be produced, in which p-n junctions could not be created. The researchers at Philips decided to concentrate on GaP instead. GaN crystals were more efficiently produced at the end of the 1960s by growing GaN on a substrate using the HVPE technique (Hydride Vapour Phase Epitaxy) (Maruska and Tietjen 1969). A number of laboratories in the United States (Dingle et al. 1971; Pankove et al. 1971; Maruska et al. 1973), in Japan (Sano and Aoki 1976) and in Europe (Grimmeiss and Monemar 1970) studied the growth techniques and doping of GaN with the goal of developing blue LEDs, but material problems still seemed insurmountable. The surface roughness was not controlled, the HVPE-grown material was contaminated with transition metal impurities and p-doping was passivated due to the presence of hydrogen, forming complexes with acceptor dopants. The role of hydrogen was not understood at that time. J.I. Pankove, a leading scientist in the field, wrote in a review article from 1973 (Pankove 1973): "*In spite of much progress in the study of GaN over the last two years, much remains to be done. The major goals in the technology of GaN should be: (i) the synthesis of strain-free single crystals, and (ii) the incorporation of a shallow acceptor in high concentrations*" (to provide effective p-doping). Thus, again the research effort was halted due to lack of progress.

5.5 New growth techniques

In fact, in the 1970s, new crystal growth techniques such as MBE (Molecular Beam Epitaxy) (Cho and Arthur 1975) and MOVPE (Metal organic Vapour Phase Epitaxy) (Manasevit et al. 1971) were developed. Then, efforts were made to use these techniques for growing GaN (Yoshida et al. 1983). Isamu Akasaki started studying GaN as early as 1974, at the time working at the Matsushita Research Institute in Tokyo. In 1981, he joined as a professor at Nagoya University and continued his research on GaN, together with Hiroshi Amano and other co-workers. Using MOVPE technique, in 1986 he succeeded to grow GaN with high crystal quality and good optical properties (Amano et al. 1986). The breakthrough came because of the result of a long series of experiments and observations. A thin layer (30 nm) of polycrystalline AlN was first nucleated on a substrate of sapphire at low temperature (500 °C) and then heated

up to the growth temperature of GaN (1000 °C) (Hiramatsu et al. 1991). In fact, during the heating process, the layer develops a texture of small crystallites with a preferred orientation on which GaN can be grown. At first, the density of dislocations of the growing GaN crystal is high, but it decreases rapidly after a few μm growth. Akasaki succeeded to obtain a high quality, which was very important to grow thin multilayer structures in the following steps of the LED development. In this way, high quality device-grade GaN was obtained for the first time. GaN could also be produced with significantly lower background n-doping. Shuji Nakamura at Nichia Chemical Corporation, a small chemical company in Japan, later developed a similar method where AlN was replaced with a thin layer of GaN grown at low temperature (Nakamura 1991; Nakamura et al. 1991).

5.6 Doping of GaN

A major problem for preparing p-n junctions was the difficulty to p-dope GaN in a controlled manner. At the end of the 1980s, Amano, Akasaki and co-workers made an important observation; they noted that when Zn-doped GaN was studied with a scanning electron microscope, it emitted more light (Amano et al. 1988), thus indicating better p-doping. In a similar way, when Mg-doped GaN was irradiated with low energy electrons, it resulted in better p-doping properties (Amano et al. 1988). This observation was an important breakthrough and opened the way to the formation of p-n junctions in GaN. Later on, after a few years Nakamura and co-workers (Nakamura et al. 1992a; Nakamura et al. 1992b) explained the effect of electron irradiation, in an article. Acceptors such as Mg or Zn form complexes with hydrogen and thus become passive. Electron beams dissociate these complexes and activate the acceptors. Nakamura showed that even a simple thermal treatment (annealing) leads to efficient activation of Mg acceptors. The effect of hydrogen on the neutralization of dopants was known from previous work using other materials by Pankove (Pankove et al. 1983), G.F. Neumark Rothschild (Neumark Rothschild 1988), and others. A crucial step in developing efficient blue LEDs was the growth and p-doping of alloys (AlGaIn, InGaIn), which are necessary in order to produce heterojunctions. Such heterojunctions were realized in the early 1990s in both Akasaki's and Nakamura's research groups (Murakami et al. 1991; Nakamura and Mukai 1992).

5.7 Double heterostructures and quantum wells

From the development of infrared LEDs and laser diodes it had become clear that heterojunctions and quantum wells were essential to achieve high efficiency LED. In such heterostructures holes and electrons are injected in a small volume where recombination occurs more efficiently and with minimal losses. Whereas Akasaki and co-workers developed structures based on AlGaIn/GaN (Itoh et al. 1991; Akasaki et al. 1992) while Nakamura with great success exploited the combinations InGaIn/GaN and InGaIn/AlGaIn for producing heterojunctions, quantum wells and multiple quantum wells (Nakamura et al. 1993a; Nakamura et al. 1993b). Nakamura and co-workers, in 1994, obtained a quantum efficiency of 2.7% using a double heterojunction InGaIn/AlGaIn (Nakamura et al. 1994), as shown in Fig. 6. With the achievement of these important first steps, the path was cleared for the development of efficient blue LEDs and their application was also open. Both teams continued to develop blue LEDs, aiming towards higher efficiency, versatility and applications. Interestingly, both groups (Nakamura et al. 1995; Nakamura et al. 1996) observed in 1995-1996 blue laser emission based on GaN. Today's efficient GaN-based LEDs results have been reported from a long series of breakthroughs in basic materials physics and crystal growth, in device physics with advanced heterostructure design, and in optical physics for the optimization of the light out-coupling. Fig.7 (A) shows the Structure of a green single quantum well LED (SQW), and Fig. 7(B) shows the electroluminescence of a blue, green and yellow SQW LED at a forward current of 20 μA . Fig. 8 shows the structure of the InGaIn multiple quantum well (MQW) laser diode (Nakamura et al.1996). Fig. 9 Techniques for making white LEDs.

5.8 Challenging convention

Nobel Laureates, Isamu Akasaki, Hiroshi Amano and Shuji Nakamura challenged established truths; they worked hard and took considerable risks. They built their equipment themselves, learnt the technology, and carried out thousands of experiments. Most of the time they failed, but they did not despair; this was laboratory artistry at the highest level. Gallium nitride was the material of choice for both Akasaki and Amano as well as for Nakamura, and

they eventually succeeded in their efforts, even though others had failed before them. In the beginning of the investigation, the material was considered appropriate for producing blue light, but practically, a number of difficulties were faced. No one was able to grow gallium nitride crystals of high enough quality, since it was seen as a hopeless endeavour to try to produce a fitting surface to grow the gallium nitride crystal on. Moreover, it was virtually impossible to create p-type layers in this material. Nonetheless, Akasaki was convinced by previous experience that the choice of material was correct, and continued working with Amano, who was a Ph.D.-student at Nagoya University. Nakamura at Nichia also chose gallium nitride before the alternative, zinc selenide, which was considered by others to be a more promising material.

6. Blue LEDs for Lighting

6.1 Succeeded in preparing p-type GaN

Akasaki and Amano, in 1986, were the first to succeed in creating a high-quality gallium nitride crystal by placing a layer of aluminium nitride on a sapphire substrate and then growing the high quality gallium nitride on top of it. A few years later, at the end of the 1980s, they made a breakthrough in creating a p-type layer. By coincidence Akasaki and Amano discovered that their material was glowing more intensely when it was studied in a scanning electron microscope. This observation suggested that the electronic beam from the microscope was making the p-type layer more efficient. In 1992 they were able to demonstrate their first diode emitting a bright blue light. Nakamura began developing his blue LED in 1988, and after two years later, he too, succeeded in creating high quality gallium nitride. He found his own clever way of creating the crystal by first growing a thin layer of gallium nitride at low temperature, and growing subsequent layers at a higher temperature.

Nakamura could also explain why Akasaki and Amano had succeeded with their p-type layer: the electron beam removed the hydrogen that was preventing the p-type layer to form. For his part, Nakamura replaced the electron beam with a simpler and cheaper method: by heating the material he managed to create a functional p-type layer in 1992. Thus, Nakamura's solutions were different from those of Akasaki and Amano.

During the 1990s, both research groups succeeded in further improving their blue LEDs, making them more efficient. They created different gallium nitride alloys using aluminium or indium, and the LED's structure became increasingly complex. Akasaki, together with Amano, as well as Nakamura, also invented a blue laser in which the blue LED, the size of a grain of sand, is a crucial component. Contrary to the dispersed light of the LED, a blue laser emits a cutting-sharp beam. Since blue light has a very short wavelength, it can be packed much tighter; with blue light the same area can store four times more information than with infrared light. This increase in storage capacity quickly led to the development of Blue-ray discs with longer playback times, as well as better laser printers. Many home appliances are also equipped with LEDs. They shine their light on LCD-screens in television sets, computers and mobile phones, for which they also provide a lamp and a flash for the camera.

6.2 A bright revolution

The inventions made by the Nobel Laureates, Isamu Akasaki, Hiroshi Amano and Shuji Nakamura revolutionized the field of illumination technology. New, more efficient, cheaper and smarter lamps are developed all the time. White LED lamps can be obtained in two different ways. One way is to use blue light to excite a phosphor so that it shines in red and green. When all colours come together, then white light is produced. The other way is to construct the lamp out of three LEDs, red, green and blue, and let the eye do the work of combining the three colours into white. LED lamps are thus flexible light sources, already with several applications in the field of illumination – millions of different colours can be produced; the colours and intensity can be varied as needed. Colourful light panels, several hundred square metres in size, blink, change colours and patterns, in which everything can be controlled by computers. The possibility to control the colour of light also implies that LED lamps can reproduce the alternations of natural light and follow our biological clock. Greenhouse-cultivation using artificial light is already a reality. The LED lamp also holds great promise when it comes to the possibility of increasing the quality of life for

the more than 1.5 billion people who currently lack access to electricity grids, as the low power requirements imply that the lamp can be powered by cheap local solar power. Moreover, polluted water can be sterilized using ultraviolet LEDs, a subsequent elaboration of the blue LED. The invention of the efficient blue LED is just twenty years old, but it has already contributed to creating white light in an entirely new manner to the benefit of us all.

Table 2: Important inventions made on GaN/InGaN on sapphire substrate

	Researcher (s)	Achievement	
GaN	1969	Maruska and Tietjen	GaN epitaxial layer by HVPE (Hydride vapor phase epitaxy)
	1973	Maruska et al.	1 st blue Mg-doped GaN MIS LED
	1983	Yoshida et al.	High quality GaN using AlN buffer by MBE (Molecular beam epitaxy)
	1985	Akasaki and Amano et al.	Year
	1989	Akasaki and Amano et al.	p-typed GaN using LEEB (p is too low to fabricate devices)
	1991	Nakamura	Invention of Two – Flow MOCVD
	1991	Moustakas et al.	High quality GaN using GaN buffer by MBE
	1991	Nakamura	High quality GaN using GaN buffer by MOCVD
	1992	Nakamura et al.	p-typed GaN using thermal annealing Discovery hydrogen passivation (p is high enough for devices)
InGaN	1992	Nakamura et al.	InGaN layers with RT Band emission
	1994	Nakamura et al.	InGaN Double Heterostructure (DH) Bright Blue LED (1 Candela)
	1995	Nakamura et al.	InGaN DH Bright Green LED
	1996	Nakamura et al.	1 st Pulsed Violet InGaN DH MQW LDs
	1996	Nakamura et al.	1 st CW Violet InGaN DHMQW LDs
	1996	Nichia Corp.	Commercialization White LED using InGaN DH blue LED

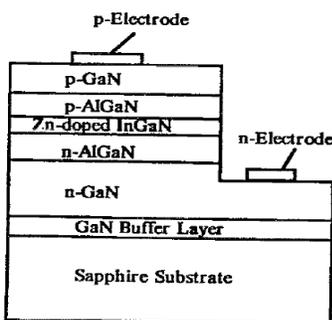


Fig. 6 The structure of the InGaN/AlGaN double-heterostructure blue LED (Nakamura et al. 1994 et al., ref. [47]).

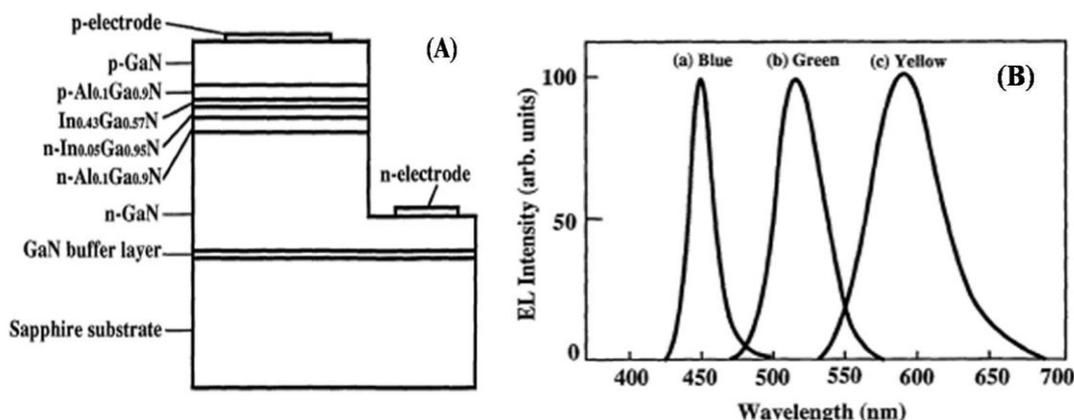


Fig.7 (A) Structure of a green single quantum well LED (SQW), (B) Electroluminescence of a blue, green and yellow SQW LED at a forward current of 20 μ A. (after Nakamura et al. 1995)

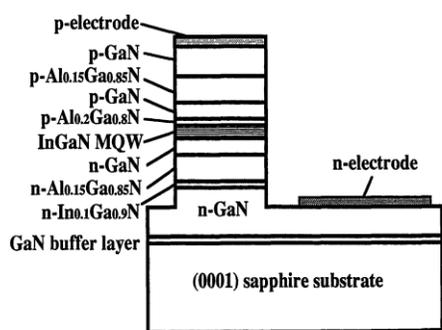


Fig. 8 The structure of the InGaN multiple quantum well (MQW) laser diode (Nakamura et al. (1995).

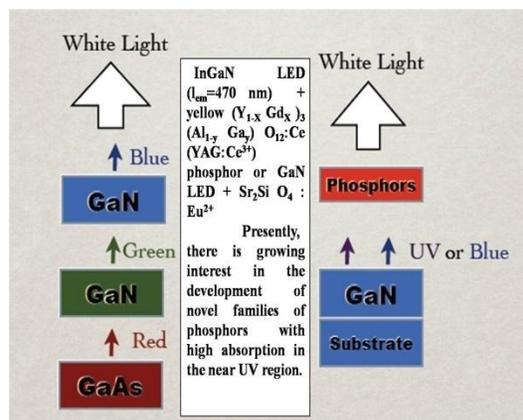


Fig. 9 Techniques for making white LEDs.

7. The Advantages of LED Lighting

The LED lighting have several advantages such as: Long life – lifetimes can exceed 100,000 hours as compared to 1,000 hrs for tungsten bulbs. Robustness – no moving parts, no glass, no filaments. Size – typical package is only 5 mm in diameter. Energy efficiency – 50- 90% less energy used. Translates into smaller power supply. Non-toxicity – no mercury. Versatility – available in a variety of colors; can be pulsed. Cool – less heat radiation than HID or incandescent.



Fig. 10 Changing scenario of lamps.

8. Applications of LEDs

(i) The blue LEDs find applications such as : solid state lighting, decorative lighting, automobile lighting, displays, agriculture, indoor lighting, mobile, signs, traffic signals, LCD backlight, and others. (ii) The blue LEDs find important applications in different types of decoration. (iii) The intensity LEDs are also useful in medical operations. (iv) Different applications in cars. (v) Bus stop light therapy. (vi) Current LED markets are: cellphone, traffic signals, large displays, streetlights, TVs, automotive. (vii) LEDs are also used in architectural lighting. (viii) Used in cellphone camera flash and projector light. (ix) LEDs are used in air/water purification. Fruit and vegetable light storage and UV LEDs are used to kill bacteria. (x) Blue and Green LEDs are used to grow Wasabi at night, It is known that chlorophyll has the second distinct absorption peak in the vicinity of 450nm (blue light region) other than the first peak in the vicinity of 660nm (red light region) in its light absorption spectrum. The blue light is also indispensable to the morphologically healthy growth plant. On the other hand, the red light contributes to the plant photosynthesis.

9. CONCLUSIONS

The LEDs with efficiency $\approx 100\%$, power efficiency = 300 Lumen/Watt, and life = 100,000 hours have been obtained. The LED lamps are eco-friendly and presently, easily available in the markets. Conclusively, scientific developments have proved to be a Boon by providing LED light sources to human beings. The quantum confinement in double heterostructure devices enable much higher electron and hole recombination rates, thereby making them highly efficient for light emission. Building on these inventions, Akasaki, Amano and Nakasaki and their co-workers have created remarkable scientific and technological breakthroughs that are enabling energy efficient lighting in our everyday world.

10. PERSPECTIVES

The important perspectives are as follows:

(i) The efficiency has to be increased. (ii) New materials have to be investigated. (iii) New applications of LED light sources have to be investigated. (iv) Further investigation in architecture of LEDs is required. (v) Pointed light source, hence, diffuse light sources like OLEDs have to be investigated. (vi) Cost has to be reduced.

REFERENCES

- Akasaki I., Amano H., Itoh K., Koide N. and Manabe K. (1992)** “GaN based UV/blue light-emitting devices” GaAs and Related Compounds conference. *Int. Phys. Conf. Ser.* 129: 851.
Amano H., Akasaki I., Kozawa T., Hiramatsu K., Sawaki N., Ikeda K. and Ishii Y. (1988) “Electron beam effects on blue luminescence of zinc-doped GaN” *J. Lumin.* 40 & 41: 121.

- Amano H., Kito M., Hiramatsu K., and Akasaki I. (1989)** “P-type conduction in Mg-doped GaN treated with low-energy electron beam irradiation (LEEBI)”. *Jpn. J. Appl. Phys.* 28: L2112.
- Amano H., Sawaki N., Akasaki I. and Toyoda Y. (1986)** “Metalorganic vapor phase epitaxial growth of a high quality GaN film using an AlN buffer layer”. *Appl. Phys. Lett.* 48: 353.
- Bhattacharya P. (1999)** “Semiconductor Optoelectronics Devices”, *Prentice – Hall of India Private Limited*, New Delhi.
- Braunstein R. (1955)** “Radiative Transitions in Semiconductors” *Phys. Rev.* 99: 1892.
- Chang S.J., Chen W.S., Lin Y.C., Chang C.S., Ko T.K., Hsu Y.P., Shen C.F., Tsai J.M. and Shei S.C., (2006)** “Nitride-based flip-chip LEDs with transparent Ohmic contacts and reflective mirrors” *IEEE Transactions on Advanced Packaging*, 29: 403.
- Cho A. Y. and Arthur J. R. (1975)** “Molecular beam epitaxy. Prog.” *Solid State Chem.* 10: 157.
- Dingle R., Sell D.D., Stokowski S.E. and Ilegems M. (1971)** “Absorption, Reflectance, and Luminescence of GaN Epitaxial Layers”. *Phys. Rev. B* 4: 1211.
- Forster R. (2005)** “Light-emitting diodes: a guide to the technology and its implications”, *Bracknell*, BSRIA.
- Gershenzon M. and Mikulyak R.M. (1961)** “Electroluminescence at p-n Junctions in Gallium Phosphide”. *J. Appl. Phys.* 32: 1338.
- Grimmeiss H. G. and Monemar B. (1970)** “Low-Temperature Luminescence of GaN”. *J. Appl. Phys.* 41:4054.
- Grimmeiss H.G. and Koelmans H. (1961)** “Analysis of p-n Luminescence in Zn-Doped GaP”. *Phys. Rev.* 123:1939.
- Grimmeiss H.G. and Scholz H. (1964)** “Efficiency of recombination radiation in GaP”. *Phys. Lett.* 8: 233.
- Grimmeiss H.G., Koelmans H. and Maak I.B. (1960)** *German patent*, DBP 1 077 330.
- Hall R.N., Fenner G.E., Kingsley J.D., Soltys T.J. and Carlson R.O. (1962)** “Coherent light emission from GaAs junctions”, *Phys. Rev. Lett.* 9: 366.
- Haynes J.R. (1955)** “New radiation resulting from recombination of holes and electrons in germanium”. *Phys. Rev.* 98: 1866.
- Haynes J.R. and Westphal W.C. (1956)** “Radiation Resulting from Recombination of Holes and Electrons in Silicon”. *Phys. Rev.* 101: 1676.
- Held G. (2009)**, Introduction to Light Emitting Diode Technology and Applications, *CRC Press*, New York.
- Hiramatsu K., Itoh S., Amano H., Akasaki I., Kuwano N., Shiraiishi T., Oki K. (1991)** “Growth mechanism of GaN grown on sapphire with AlN buffer layer by MOVPE”. *J. Crystal Growth* 115: 628.
- Holonyak N. and Bevacqua S.F. (1962)** “Coherent (visible) light emission from Ga(As_{1-x}P_x) Junctions”. *Appl. Phys. Lett.* 1: 82.
- Hunt N.E.J., Schubert E.F., Sivco D.L., Cho A.Y., and Zyzdik G.J. (1992)** “Power and efficiency limits in single-mirror light emitting diodes with enhanced intensity”. *Electronics Letters.* 28: 2169.
- Itoh K., Kawamoto T., Amano H., Hiramatsu K. and Akasaki I. (1991)** “Metalorganic Vapor Phase Epitaxial Growth and Properties of GaN/Al_{0.1}Ga_{0.9}N Layered Structures”. *Jpn. J. Appl. Phys.* 30:1924.
- Khanna, V. K. (2014)** “Fundamentals of Solid State Lighting: LEDs, OLEDs, and Their Application in Illumination and Displays”, *CRC Press* New York.
- Krames M.R., Ochiai-Holcomb M., Hoffer G.E., Carter-Coman C., Chen E.I., Tan I.H., Grillo P., Gardner N.F., Chui H.C., Huang J.W., Stockman S.A., Kish F.A., Craford M.G., Tan T.S., Kocot C.P., Hueschen M., Posselt J., Loh B., Sasser G. and Collins D. (1999)** “High-power truncated-invertedpyramid (Al_xGa_{1-x})_{0.5}In_{0.5}P/GaP light emitting diodes exhibiting > 50% external quantum efficiency”, *Appl. Phys. Lett.* 75: 2365.
- Lehovec K., Accardo C.A. and Jamgochian E. (1951)** “Injected Light Emission of Silicon Carbide Crystals”. *Phys. Rev.* 83: 603.
- Manasevit H.M., Erdman F.M. and Simpson W. I. (1971)** “The Use of Metalorganics in the Preparation of Semiconductor Materials: The Nitrides of Aluminum and Gallium”. *J. Electrochem. Soc.* 118: 1864.
- Maruska H.P. and Tietjen J.J. (1969)** “The preparation and properties of vapour-deposited single crystal-line GaN”. *Appl. Phys. Lett.* 15: 327.

- Maruska H.P., Stevenson D.A. and Pankove J.I. (1973)** “Violet luminescence of Mg-doped GaN (light emitting diode properties)”. *Appl. Phys. Lett.* 22: 303.
- Monemar B. (1974)** “Fundamental energy gap of GaN from photoluminescence excitation spectra”. *Phys. Rev. B* 10: 676.
- Murakami H., Asahi T., Amano H., Hiramatsu K., Sawaki N. and Akasaki I. (1991)** “Growth of Si-doped $\text{Al}_x\text{Ga}_{1-x}\text{N}$ on (0001) sapphire substrate by metalorganic vapor phase epitaxy”. *J. Crystal Growth* 115: 648.
- Nakamura S., Iwasa N., Senoh M., and Mukai T. (1992a)** “Hole Compensation Mechanism of P-Type GaN Films”. *Jpn. J. Appl. Phys.* 31: 1258.
- Nakamura S., Mukai T., Senoh M. and Iwasa N. (1992b)** “Thermal Annealing Effects on P-Type Mg-Doped GaN Films”. *Jpn. J. Appl. Phys.* 31: L139.
- Nakamura S. (1991)** “GaN Growth Using GaN Buffer Layer”. *Jpn. J. Appl. Phys.* 30: L1705.
- Nakamura S. (1996)** “High-brightness blue/green LEDs and first III-V nitride based laser diodes”, *Proceedings SPIE – The International Society for Optical Engineering*, 2693: 43.
- Nakamura S., Mukai T. and Senoh M. (1994)** “Candela-class high-brightness InGaN/AlGaIn doubleheterostructure blue-light-emitting diodes”. *Appl. Phys. Lett.* 64: 1687.
- Nakamura S., Senoh M., and Mukai T. (1993a)** “P-GaN/n-InGaIn/n-GaN double-heterostructure bluelight-emitting diodes”. *Jpn. J. Appl. Phys.* 32: L8.
- Nakamura S., Mukai T. Senoh M., Nagahama S., and Iwasa N (1993b)** “ $\text{In}_x\text{Ga}_{(1-x)}\text{N}/\text{In}_y\text{Ga}_{(1-y)}\text{N}$ superlattices grown on GaN films”. *J. Appl. Phys.* 74: 3911.
- Nakamura S., Senoh M. and Mukai T. (1991)** “High-Power GaN P-N Junction Blue-Light-Emitting Diodes”. *Jpn. J. Appl. Phys.* 30: L1998.
- Nakamura S., Senoh M., Iwasa N., and Nagahama S.I. (1995)**, “high-brightness InGaIn/blue, green and yellow light-emitting diodes with quantum well structures” *Jpn. J. Appl. Phys.*, 34: L797.
- Nakamura S., Senoh M., Nagahama S., Iwasa N., Yamada T., Matsushita T., Kiyoku H. and Sugimoto Y. (1996)** “InGaIn-Based Multi-Quantum-Well-Structure Laser Diodes”. *Jpn. J. Appl. Phys.* 35:L74.
- Nathan M.I., Dumke W.P., Burns G., Dill F.H. and Lasher G. (1962)** “Stimulated emission of radiation from GaAs p-n junctions”. *Appl. Phys. Lett.* 1: 62.
- Neumark Rothschild G.F. (1988)** *US patent 5252499.*
- Pankove J.I (1973)** “Luminescence in GaN”. *J. Lumin.* 7: 114.
- Pankove J.I, Miller E.A., Richman D. and Berkeyheiser J.E. (1971)** “Electroluminescence in GaN”. *J. Lumin.*4: 63.
- Pankove J.I. and Berkeyheiser J.E. (1962)** “A light source modulated at microwave frequencies”, *Proc. IRE* 50: 1976.
- Pankove J.I. (1962)** “Tunneling-Assisted Photon Emission in Gallium Arsenide pn Junctions”. *Phys. Rev. Lett.* 9: 283.
- Pankove J.I., Carlson D.E., Berkeyheiser J.E. and Wance R.O. (1983)** “Neutralization of Shallow Acceptor Levels in Silicon by Atomic Hydrogen”. *Phys. Rev. Lett.* 51:2224.
- Pui C.C. (2007)** “Light extraction enhancement on GaN based LEDs using laser assisted debonding and electrodeless photochemical etching”, *Ph.D. Thesis, The Hong Kong Polytechnic University, Hong Kong.*
- Quist T.M., Rediker, R. H., Keyes, R. J., Krag, W. E., Lax, B., McWhorter, A. L., Zeigler, H. J. (1962)** “Semiconductor Maser of GaAs”. *Appl. Phys. Lett.* 1: 91.
- Sano M. and Aoki M. (1976)** “Epitaxial Growth of Undoped and Mg-Doped GaN”. *Jpn. J. Appl. Phys.* 15: 1943.
- Schubert E.F. (2006)** “Light-emitting diodes” *Cambridge University Press, Second Edition, New York.*
- Starkiewicz J. and Allen J.W. (1962)** “Novel metalorganic chemical vapor deposition system for GaN”. *J. Phys. Chem. Solids* 23: 881.
- Wolff G.A. Hebert R.A. and Broder J.D. (1955)** “Electroluminescence of GaP”. *Phys. Rev.* 100: 1144.
- Yoshida S., Misawa S. and Gonda S. (1983)** “Improvements on the electrical and luminescent properties of reactive molecular beam epitaxially grown GaN films by using AlN-coated sapphire substrates”. *Appl. Phys. Lett.* 42: 427.