Gallium-Nitride-Based Light-Emitting Diodes

2014 Nobel Prize in Physics

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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). Here, we provide a perspective of solid-state LEDs that are currently revolutionizing our world through energy-efficient lighting.

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I. Introduction

Light plays a central role in our everyday lives. While natural sources of light enable biological processes such as photosynthesis, cellular reactions, and other key life-sustaining processes, artificial sources of light have changed human lives in many ways by allowing us to be productive beyond sunrise and sunset. In addition, these man-made sources of light have dramatically transformed our society through a variety of applications in lighting, communications, transportation, healthcare, and other areas. Starting with fire as a source of light and heat, to the invention of the incandescent bulb and present day solid-state lighting – the energy efficiency of man-made light sources have improved exponentially.

The incandescent lamp, invented by Henry Woodward and Mathew Evans, is based on the emission of photons (fundamental light particles) through the heating up of an electric-current conducting filament [1, 2]. *Figure* 1 shows the picture of the incandescent lamp built by Edison in 1870s (a), and the schematic of an incandescent and fluorescent lamp (b). While these inventions have dramatically transformed human society, a lot more needed to be done to improve the energy efficiency of artificial sources of light. The incandescent bulb produces only about

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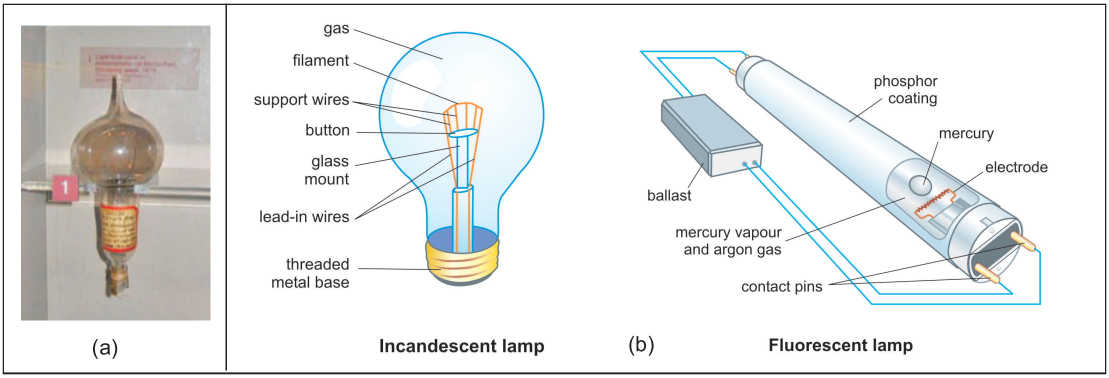


Figure 1. a) Picture of the incandescent lamp built by Edison in 1870s. (Courtesy: Wikipedia, [11]). **b**) Schematic of an incandescent and fluorescent lamp (adapted from *Encyclopedia Britannica* [12]).

15 lumen/watt (an oil lamp produces 0.1 lumen/watt), as the rest of the energy is lost in the form of heat [3]. With the advent of the fluorescent lamp, whose working principle is based on producing light and heat through a gas discharge , the energy efficiency improved to 70 lumen/watt [4]. However, these lamps are quite large and have safety concerns as the incandescent lamp is subject to breakdown due to overheating and fluorescent lamps use mercury as the discharge element.

The advent of the semiconductor light-emitting diode (LED) emerged as a key component in our modern lighting technologies. While LEDs of various colors have been invented since 1950s, the blue LED was elusive till the 1990s. Blue light, with blue being one of the primary colors, is essential for white light emission. White light is essential for lighting in order to perceive objects in their natural colors that are visible to the human eye. The inventions of the blue LED by the Akasaki, Amano and Nakamura, have led to solid-state lighting technologies with energy efficiencies in range of 200–300 lumen/watt. The key to the enablement of the blue LEDs were due to the breakthroughs, by the 2014 Nobel Laureates in Physics, in crystalline and uniform surface growth of GaN and realization of p-type GaN through controlled doping [5–10].

With limited energy resources available to humans, it is inevitable to adopt energy efficient technologies for a sustainable world. Lighting uses 20 % of the world's total energy production, of 15 Tera watts, and this consumption is exponentially increasing [13]. Hence, energy efficiency of lighting devices becomes extremely important and this is where LEDs are creating a revolution. In this article, we describe the evolution of the LED technology, which has a rich history of about 100 years of scientific and technology developments [14].

Light emission from solid state devices have been known since early 1900s.

2. Solid-State Lighting – Advent of the LED

Light emission from solid-state devices have been known since the early works of H J Round of Marconi Electronics in 1907 and Oleg Losev working at Soviet Radio Laboratories in 1920s [15, 16]. Light emission from solid-state devices was understood based on the band theory of semiconductors and p–n junctions[17, 18]. Lehovec and colleagues at the Signal Corps Engineering Laboratory, in 1951, were able to explain the phenomena observed by Round and Losev, through the process of electroluminescence, where light is emitted through a radiative recombination of electrons and holes on the application of electric field in solid-state materials [19]. This basic understanding of light emission, through electroluminescence, led to a flurry of inventions of solid-state light-emitting devices in various optically active materials [20, 21].

Holonyak built the first visible-spectrum semiconductor laser in 1962, and a practical LED based on $GaAs_{1-x}P_x$ alloy to produce red light [22]. Later, a variety of LEDs and lasers based on GaAs (infrared) and doped alloys of Ga, As, and P (covering the visible spectrum from red to green) were invented in 1960s by various groups at Philips Central Laboratories, Services Electronics Laboratories, Bell Labs and General Electric Laboratory [23, 24, 25, 26]. A comprehensive and pedagogical perspective of the LED evolution is provided in the scientific background article on 2014 Nobel Prize in Physics [27].

2.1. *Working Principle of a LED*

An LED consists of a sandwich of a p-type and n-type semiconductors [28]. P- and n-type semiconductors are produced by doping a semiconductor material with donor and acceptor atoms respectively. For example, p-type silicon (Si) is produced by doping Si

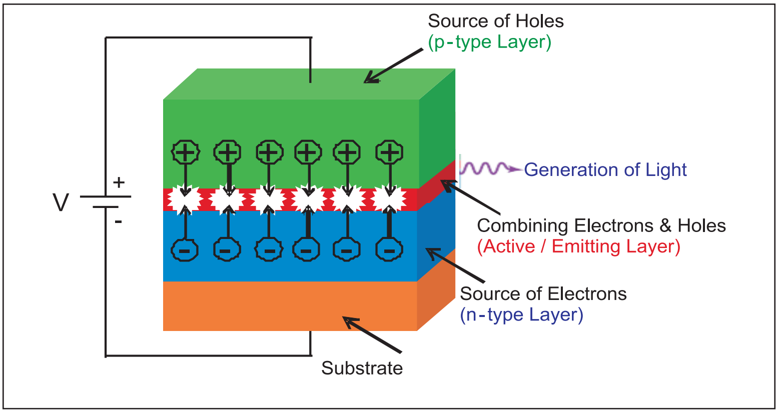
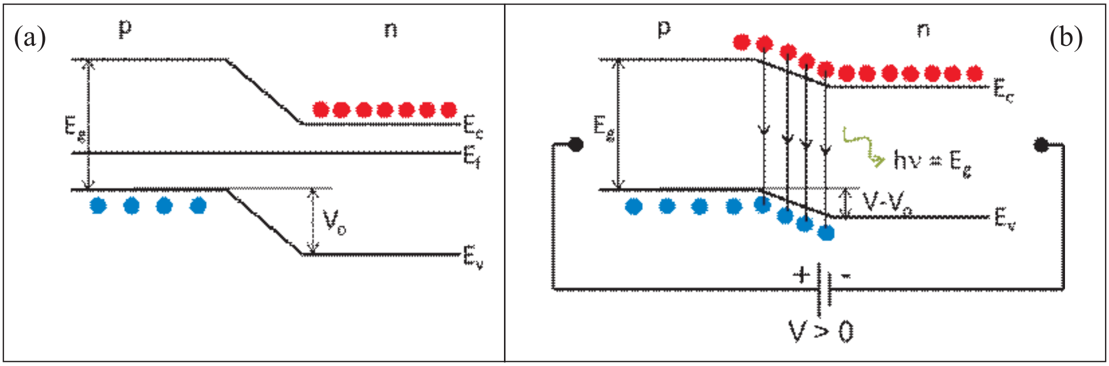


Figure 2. Schematic of a semiconductor-based LED. A p–n junction is formed at the interface of p and n semiconductor layers. Electrons are injected from the n-layer and holes are injected from the p-layer on the application of an electric field; these injected electrons and holes recombine to emit photons.

with acceptor materials like Boron (B) and n-type Si is produced by doping with donor materials like Phosphorus (P) [28]. *Figure* 2 shows a schematic of a semiconductor based LED consisting of p-n junction at the interface of the p and n semiconductor layers. When an electric field (in forward bias condition) is applied across the p–n junction, electrons from the n-type and holes from the p-type semiconductor are injected into the p–n junction region. These electrons and holes can recombine, there by emitting light corresponding to the bandgap (energy difference between the conduction band and valence band) of the semiconductor material or dopant energy levels in the case of doped semiconductor LEDs [23, 24, 25, 26, 28].

To understand the working principle of a light-emitting diode, let us consider an unbiased p–n junction shown in *Figure* 3a and its corresponding forward-biased energy band diagram in *Figure* 3b. The depletion region is formed at the p–n junction due to diffusion

Figure 3. (a) Energy band diagram of p–n junction in the absense of any external electric bias. Built-in voltage V_0 prevents electrons and holes to diffuse from n to p and p to n regions, respectively. (b) The applied bias V reduces V_0 and allows the electrons and holes to be injected into p–n junction region. The recombination of electrons and holes leads to emission of photons, with frequency corresponding to the bandgap.



of electrons into the p-layer and holes into the n-layer, thereby creating a built-in potential V_0. This built-in potential prevents excess free electrons in the n-layer from diffusing into the p-layer, and similarly preventing the holes from p-layer diffusing into the n-layer. When a forward bias voltage (V) is applied across the junction (*Figure* 3b), the potential barrier is reduced from V_0 to (V_0– V). This reduction in the potential barrier allows the electrons and holes to be injected from n to p and p to n layers, respectively. These injected electrons and holes can recombine in the close vicinity of the p–n junction region to emit photons of the frequency corresponding to the bandgap of the material. This recombination results in the spontaneous emission of photons (light) and this phenomenon is known as electroluminescence. The electron and hole recombination can be classified into the following two kinds: (a) direct recombination and (b) indirect recombination as shown in *Figure* 4.

The process of electron and hole recombination through the application of an electric fields is known electroluminescence.

A wide spectrum of red to green LEDs were invented through bandgap engineering and doping of materials based on Ga, As, P and dopants such as Zn, Mg, O, etc. [23, 24, 25, 26]. But blue LEDs remained elusive for decades, and this is where the inventions of GaN-based blue LEDs by Akasaki, Amano and Nakamura in early 1990s led to the creation of white-light-emitting LEDs. These inventions have also changed the energy efficiency of the lighting world [5, 8, 9, 10].

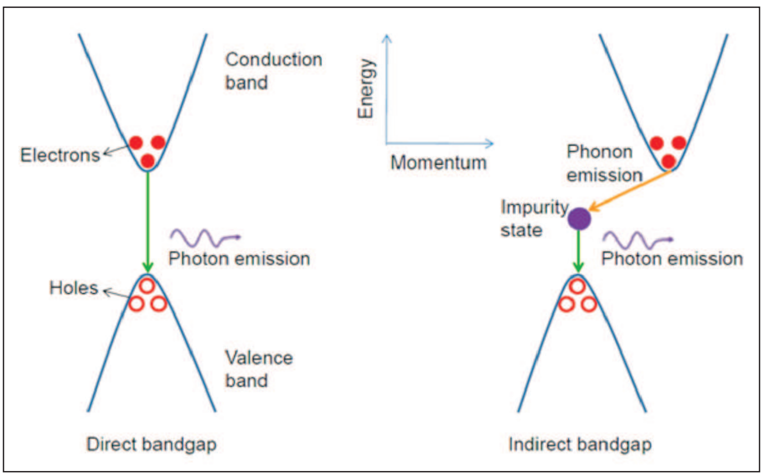


Figure 4. Schematic of radiative recombination in direct and indirect bandgap semiconductors. An impurity energy state is needed to facilitate recombination in indirect bandgap materials [29].

2.2. *GaN-based LEDs for Blue Light Emission*

An ideal material for blue light emission is the one that has a direct bandgap corresponding to blue light (Eg ~ 2.6 eV). The invention of blue LED is extremely important because it is 'the final piece of the puzzle' to create LEDs of all primary colors i.e., R-G-B (Red-Green-Blue). These primary color sources can be combined to produce any wavelength in the visible spectrum including white light. *Figure* 5 shows a schematic of the production of white light using a blue LED in combination with a yellow phosphor.

Historically, various materials including ZnSe, GaN, etc., were being considered for blue light emission. Crystalline GaN with controlled surface roughness was hard to grow on known substrates [30]. Also, doping this material, especially to make a p-type GaN, was extremely difficult as adding dopants introduces defects into the host material [30]. Akasaki, Amano and Nakamura won the 2014 Nobel Prize in physics for enabling the growth of highly crystalline and uniform GaN and effectively doping it in order to create highly energy efficient blue LEDs [5, 8, 9, 10].

3. Challenges with Crystalline GaN growth and its Doping

The possibility of producing blue light using GaN was considered seriously at the end of the 1950s, but the major difficulty was in the development of techniques for the growth of high-quality GaN crystals on a substrate with good lattice matching as well as

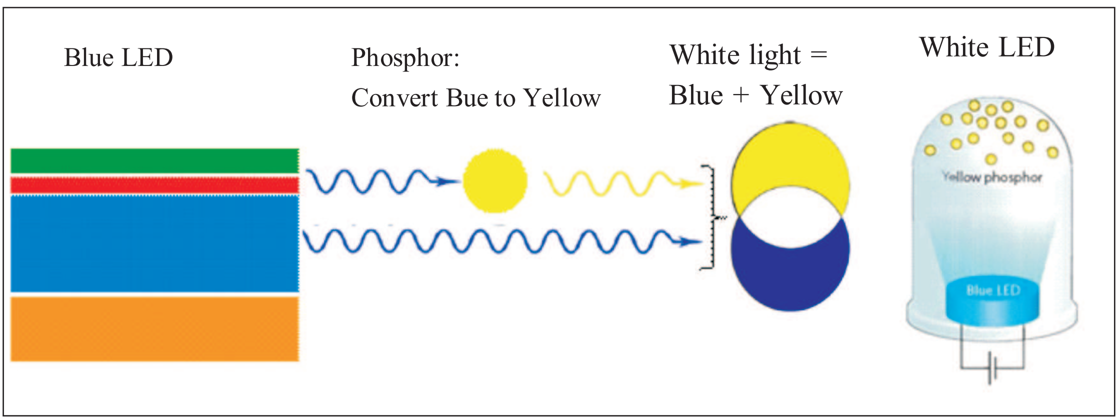


Figure 5. A schematic showing the production of white light using a blue LED in combination with a yellow phosphor. The blue light, coming directly from the blue LED when mixed with the yellow light (produced by exciting a yellow phosphor with blue light) produces white light.
Courtesy: S Nakamura, [31, 36].

the ability to control p-doping in GaN. In 1960s, GaN crystals were produced by growing GaN on a substrate using the HVPE (Hydride Vapor Phase Epitaxy) technique. However, growing high quality crystalline GaN was challenging because it required: (1) A good substrate underneath, which could lead to small lattice mismatch to avoid dislocations, cracking etc. (2) An uniform surface to have low defect density [32]. Also, the p-type doping was a challenge due to deactiviation of the dopants [33].

The Nobel Prize winning work of Hiroshi Amano and Shuji Nakamura was carried out during their PhD.

In the 1970s, several research groups put in efforts to grow GaN using newly developed crystal growth techniques such as MBE (Molecular Beam Epitaxy) and MOVPE (Metalorganic Vapour Phase Epitaxy) [34]. Akasaki, Amano and other co-workers were successful in producing high quality crystalline GaN with good optical properties by introducing a buffer of polycrystalline AlN (30 nm) on sapphire. At the same time, Shuji Nakamura (at Nichia

Isamu Akasaki

"Hold on to your dream. Don't be afraid to make mistakes – experience is the best teacher."
(http://www.insidescience.org/blog/2014/10/07/quotes-notes-and-links-about-2014-physics-nobel-prize)

Hiroshi Amano

"When I was a child I could not understand why I should study."
(http://www.nobelprize.org/nobel_ prizes/physics/laureates/2014/amano-interview.html)

Shuji Nakamura

"I had no confidence in inventing the blue LED, I just wanted my PhD"
(http://www.nobelprize.org/nobel_prizes/physics/laureates/2014/nakamura-lecture.html)

The efficient and uniform growth of crystalline GaN and p-type doping of GaN, paved the way for the development of the blue LED.

Chemical Corporation) used a MOCVD (Metalorganic Chemical Vapor Deposition) technique to produce high quality GaN, with significantly lower background n-doping, by replacing AlN with a thin layer of GaN grown at low temperature [35]. This low temperature GaN buffer growth method, invented by Nakamura, has become popular for volume production as there is no need to change material (i.e., AlN) during the growth process. These high quality crystals of GaN with clean interfaces proved to be the cornerstone of blue LED development [34].

Another important invention by Amano, Akasaki and Nakamura was the p-doping of GaN. Although it was well understood that Mg doping of GaN would lead to p-type GaN, it was experimentally unsuccessful till Amano, Akasaki and colleagues showed that electron irradiation of Mg-doped GaN would make it a p-type material [33]. Nakamura and colleagues then realized that Mg-doped GaN would invariably makes Mg-H complexes leading to inactivity of Mg in GaN. When Mg-doped GaN is irradiated with electrons or thermal annealing in N_2 ambient, Mg frees up from Mg-H complexes, thus enabling p-type doping in GaN [9]. This method of activating dopants through the thermal annealing of Mg-doped GaN, invented by Nakamura, enabled mass production of p-type GaN. This was an important step towards fabrication of GaN-based blue LEDs. *Figure* 6 shows a schematic of the

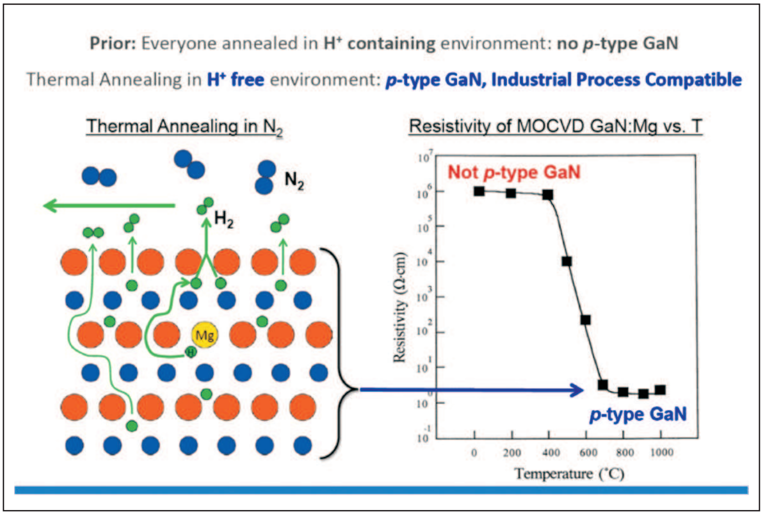


Figure 6. a) Schematic of the activation of Mg in GaN by annealing in N_2 environment. **b**) Resistivity of Mg-doped GaN as a function of temperature. Annealing beyond 600° C in N_2 atmosphere leads to purging of H_2 from GaN, thus freeing up Mg from H and activating Mg in GaN. Courtesy: S Nakamura, [36].

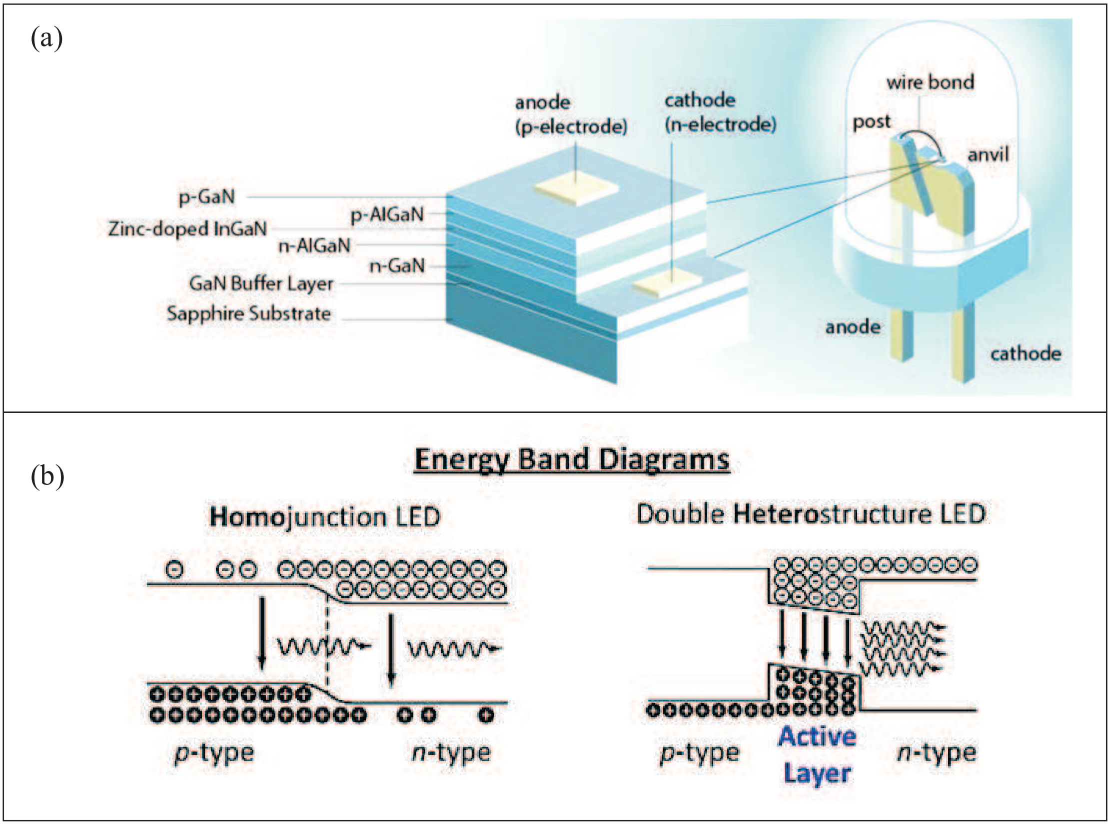


Figure 7: a) Schematic of a blue LED based on double heterostructure formed by a superlattice of GaN/AlGaN/ InGaN/AlGaN/GaN structure. **b**) Band diagrams for a homojunction LED versus double heterostructure LED, where quantum confinement in double heterostructures leads to highly efficient photon emission compared to homojunction LEDs
Courtesy: S Nakamura, [36].

activation of Mg in GaN (a), and the associated resistivity of Mg-doped GaN as a function of annealing temperature (b).

The above inventions, i.e., the efficient and uniform growth of crystalline GaN and p-type doping of GaN, paved the way for the development of the blue LED. The first reported p–n junction GaN blue LED had almost ten times higher luminous intensity than commercially available SiC blue LEDs [37].

Later, in 1993, the InGaN/AlGaN-based double heterostructure LEDs were invented for highly efficient blue light emission [38, 39, 40]. *Figure* 7a shows the double heterostructure based LED device and *Figure* 7b compares the band diagrams of a double heterostructure and homojunction LEDs. 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, workers have created remarkable scientific and technological breakthroughs that are enabling energy efficient lighting in our everyday world.

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