



Scientific Background on the Nobel Prize in Physics 2014

EFFICIENT BLUE LIGHT-EMITTING DIODES LEADING  
TO BRIGHT AND ENERGY-SAVING WHITE LIGHT SOURCES

compiled by the Class for Physics of the Royal Swedish Academy of Sciences



## **Efficient blue light-emitting diodes leading to bright and energy-saving white light sources**

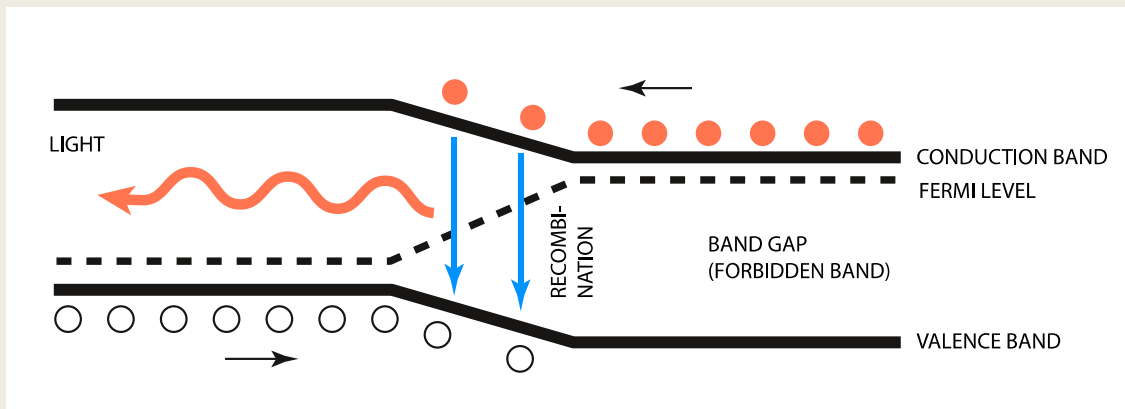
Light-emitting diodes (LEDs) are narrow-band light sources based on semiconductor components, with wavelengths ranging from the infrared to the ultraviolet. The first LEDs were studied and constructed during the 1950s and 1960s in several laboratories. They emitted light at different wavelengths, from the infrared to the green. However, emitting blue light proved to be a difficult task, which took three more decades to achieve. It required the development of techniques for the growth of high-quality crystals as well as the ability to control p-doping of semiconductors with high bandgap, which was achieved with gallium-nitride (GaN) only at the end of the 1980s. The development of efficient blue LEDs also required the production of GaN-based alloys with different compositions and their integration into multilayer structures such as heterojunctions and quantum wells.

The invention of efficient blue LEDs has led to white light sources for illumination. When exciting a phosphor material with a blue LED, light is emitted in the green and red spectral ranges, which, combined with the blue light, appears as white. Alternatively, multiple LEDs of complementary colours (red, green and blue) can be used together. Both of these technologies are used in today's high-efficiency white electroluminescent light sources. These light sources, with very long lifetimes, have begun to replace incandescent and fluorescent lamps for general lighting purposes. Since lighting represents 20-30% of our electrical energy consumption, and since these new white light sources require ten times less energy than ordinary light bulbs, the use of efficient blue LEDs leads to significant energy savings, of great benefit to mankind.

This year's Nobel Prize in Physics honours the inventors of efficient blue LEDs: I. Akasaki, H. Amano and S. Nakamura.

### **Early history**

The first report of electrically generated light by emission from a solid-state device came from H.J. Round working at Marconi Electronics in 1907 [1]. He applied voltage across two contacts on a carborundum (SiC) crystal. At low voltages yellow light was observed, but more colours were emitted at higher voltages. Electroluminescence was also studied by O. Losev (1903-1942), a device physicist in the Soviet Union, who in the 1920s and 1930s published several articles in international journals on electroluminescence from carborundum [2]. These developments took place prior to the formulation of the modern theory of electronic structure of solid-state materials.



**Fig. 1.** Principle for light emission in a p-n junction. In a p-n junction biased with a forward voltage, electrons are injected from the n- to the p-side, and holes are injected in the opposite direction. Electrons recombine with holes and light is emitted (spontaneous emission). For efficient diodes it is important that the semi-conductors have direct bandgaps. LEDs with indirect bandgaps require phonon-assisted recombination, which limits the efficiency. The quantum efficiency of a LED is the ratio of the number of emitted photons to the number of electrons passing through the contact in a given time.

The understanding of the physics of semiconductors and p-n junctions progressed during the 1940s, leading to the invention of the transistor at Bell Telephone Laboratories in the USA in 1947 (Nobel Prize 1956 to Shockley, Bardeen and Brattain). It became clear that a p-n junction could be an interesting device for light emission. In 1951, K. Lehovc and co-workers of the Signal Corps Engineering Laboratory in the USA [3] 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. However, the observed photon energy was less than the energy gap of SiC, and they suggested that radiative recombination was likely to occur due to impurities or lattice defects. In 1955, injection electroluminescence was shown in a number of III-V compounds [4, 5]. In 1955 and 1956, J.R. Haynes at Bell Telephone Laboratories demonstrated that electroluminescence observed in germanium and silicon was due to recombination of holes and electrons in a p-n junction [6] (see Fig. 1).

### Infrared LEDs

Techniques to make efficient p-n junctions with GaAs were rapidly developed during the following years. GaAs was attractive because of its direct bandgap, enabling recombination of electrons and holes without involvement of phonons. The bandgap is 1.4 eV corresponding to light in the infrared. In the summer of 1962, the observation of light emission from p-n-junctions was reported [7]. A few months later, laser emission in GaAs at liquid nitrogen temperature (77 K), was demonstrated independently and almost simultaneously by three research groups at General Electric, IBM and the MIT

Lincoln Laboratory, in the U.S. [8-10]. It would be a few years, however, before laser diodes became widely used. Thanks to the development of heterostructures (Nobel Prize 2000 to Z.I. Alferov and H. Kroemer), and later quantum wells, allowing for a better confinement of the carriers while reducing the losses, laser diodes could operate continuously at room temperature, with applications in a large variety of areas.

## Visible LEDs

Following early experiments at the end of the 1950s [11], 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) [12-14]. They 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 ranging from red to green. By the late 1960s a number of manufacturers in different countries were making red and green LEDs based on GaP.

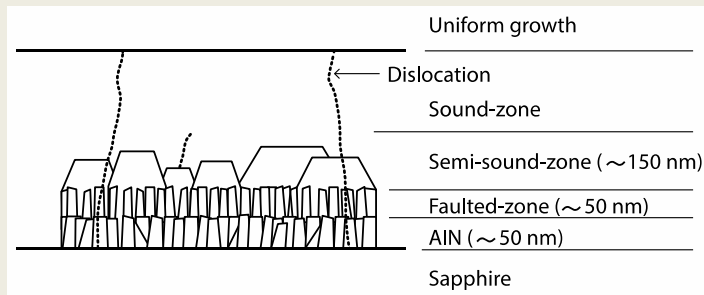
Mixed crystals including Ga, As, and P ( $\text{GaP}_x\text{As}_{1-x}$ ) are interesting since the emission wavelength can be shorter than for GaAs, reaching the visible range while the bandgap is direct for  $x$  below 0.45. N. Holonyak Jr. and co-workers at the General Electric laboratory in the USA, began to work with  $\text{GaP}_x\text{As}_{1-x}$  in the late 1950s, and succeeded in making p-n junctions and observing LED emission. Laser diode emission at 710 nm (red) was reported in 1962 [15].

## Early work on blue LEDs

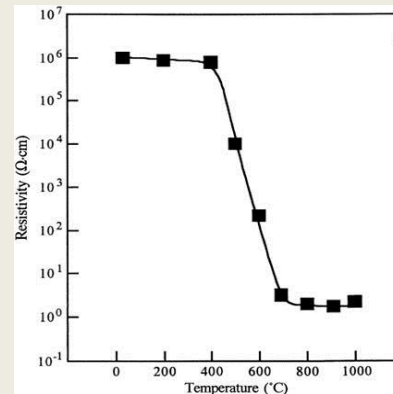
The step to the emission of blue light proved to be considerably more difficult. Early attempts with ZnSe and SiC, with high indirect bandgaps, did not lead to efficient light emission. The material that enabled the development of blue LEDs was GaN (Gallium Nitride).

### Gallium Nitride

GaN is a semiconductor of the III-V class, with Wurtzite crystal structure. It can be grown on a substrate of sapphire ( $\text{Al}_2\text{O}_3$ ) or SiC, despite the difference in lattice constants. 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.



**Fig. 2.**  
a) Growth of GaN on sapphire using an AlN layer [27].



b) Resistivity of Mg doped GaN as a function of annealing temperature [32].

Already 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 [16]. 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 (see above).

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) [17]. A number of laboratories in the United States [18, 19], in Japan [20] and in Europe [21] 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 [22]: "*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: (1) the synthesis of strain-free single crystals, (2) the incorporation of a shallow acceptor in high concentrations*" (to provide effective p-doping). Again the research effort was halted due to lack of progress.

### New growth techniques

In the 1970s, new crystal growth techniques, MBE (Molecular Beam Epitaxy) [23] and MOVPE (Metalorganic Vapour Phase Epitaxy) [24] were developed. Efforts were made to adapt these techniques for growing GaN [25]. Isamu Akasaki began studying GaN as

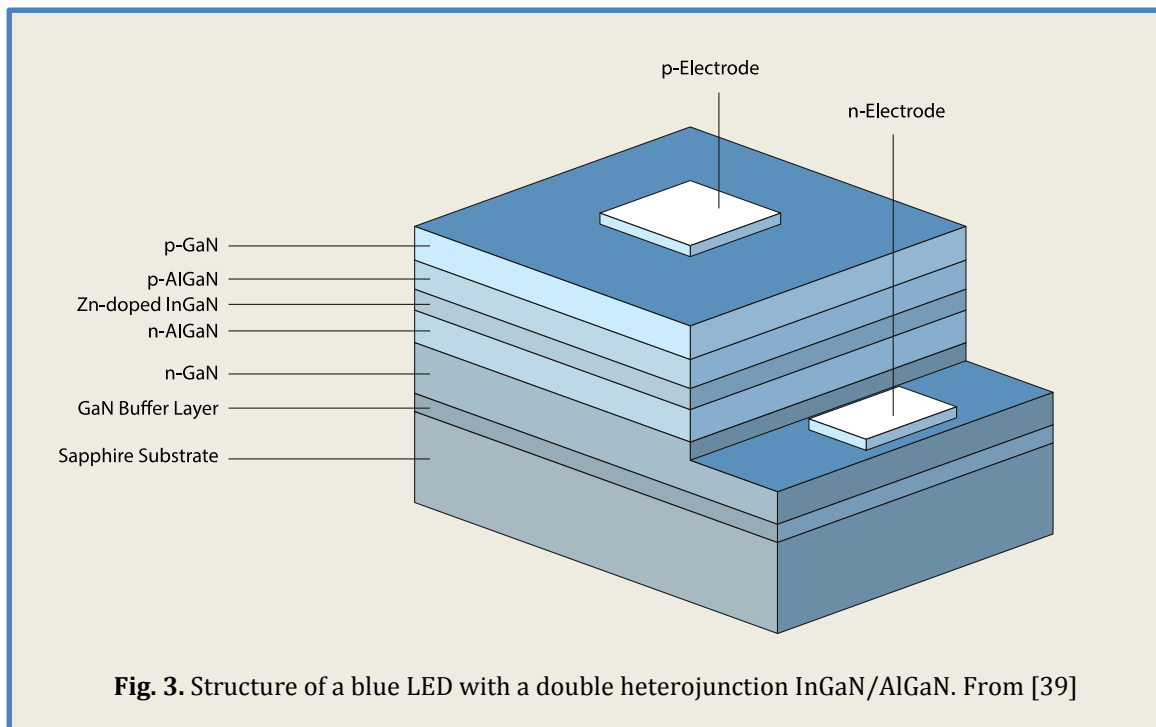
early as 1974, at the time working at the Matsushita Research Institute in Tokyo. In 1981, he took up a professorship at Nagoya University and continued his research on GaN, together with Hiroshi Amano and other co-workers. It would take until 1986 before GaN with high crystal quality and good optical properties could be produced with the MOVPE technique [26]. The breakthrough was 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). During the heating process, the layer develops a texture of small crystallites with a preferred orientation on which GaN can be grown. The density of dislocations of the growing GaN crystal is first high, but decreases rapidly after a few  $\mu\text{m}$  growth. A high quality surface could be obtained, 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 (see Fig. 2a). 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 [28].

### **Doping of GaN**

A major problem for manufacturing 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 [29], 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 [30]. This was an important breakthrough and opened the way to p-n junctions in GaN.

The effect of electron irradiation was explained a few years later, in an article by Nakamura and co-workers [31]. 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 [32], G.F. Neumark Rothschild [33], and others.

A crucial step in developing efficient blue LEDs was the growth and p-doping of alloys (AlGa<sub>N</sub>, InGa<sub>N</sub>), which are necessary in order to produce heterojunctions. Such heterojunctions were realized in the early 90s in both Akasaki's and Nakamura's research groups [34, 35].



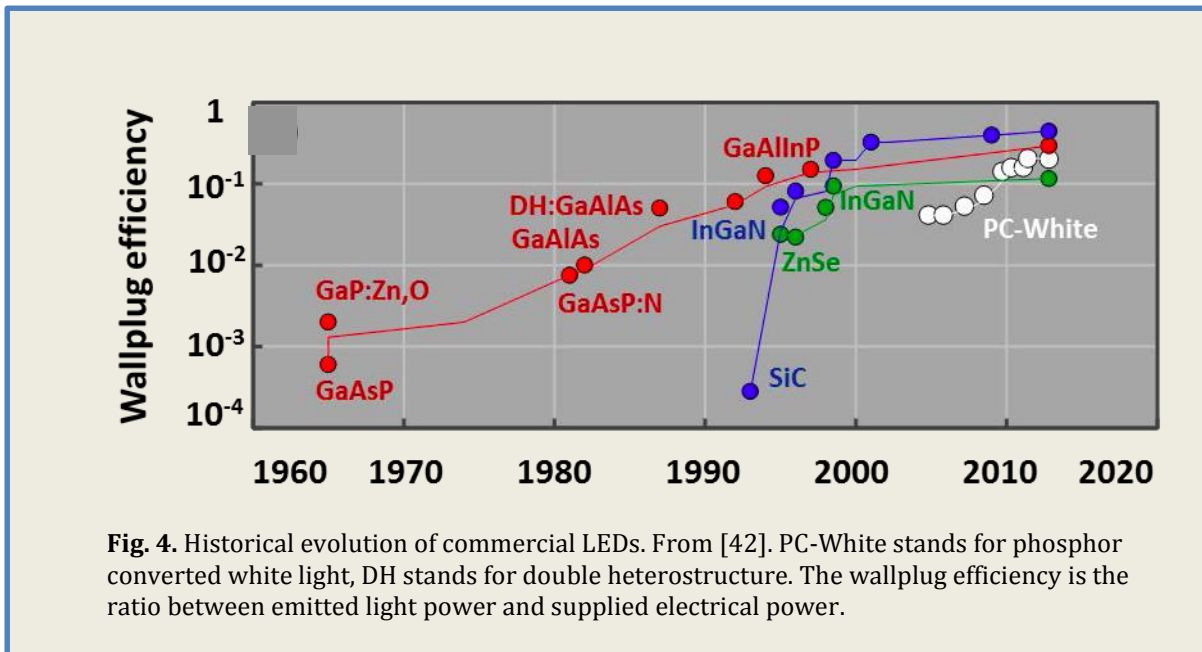
**Fig. 3.** Structure of a blue LED with a double heterojunction InGaN/AlGaN. From [39]

### Double heterostructures and quantum wells

The development of infrared LEDs and laser diodes had shown that heterojunctions and quantum wells were essential to achieve high efficiency. In such structures holes and electrons are injected in a small volume where recombination occurs more efficiently and with minimal losses. Akasaki and co-workers developed structures based on AlGaN/GaN [36, 37] while Nakamura with great success exploited the combinations InGaN/GaN and InGaN/AlGaN for producing heterojunctions, quantum wells and multiple quantum wells [38]. In 1994, Nakamura and co-workers achieved a quantum efficiency of 2.7% using a double heterojunction InGaN/AlGaN (see Fig. 3) [39]. With these important first steps, the path was cleared towards the development of efficient blue LEDs and their application was open. Both teams have continued to develop blue LEDs, aiming towards higher efficiency, versatility and applications. Blue laser emission based on GaN was observed in 1995-1996 by both groups [40, 41].

Today's efficient GaN-based LEDs result 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. The historical development of blue, green, red and "white" LEDs is summarized in the picture below.





## Applications

Illumination technology is presently going through a revolution, namely the transition from light bulbs and fluorescent tubes to LEDs. The light bulb, invented by Thomas Edison in 1879, has a low efficiency  $\approx 16$  lm/W representing approximately 4% energy efficiency from electricity into light. A lumen is a unit used to characterize the light flux, which takes into account the eye's spectral response. The fluorescent tube, containing mercury and invented by P. Cooper Hewitt in 1900, reaches an efficiency of 70 lm/W. White LEDs currently reach more than 300 lm/W, representing more than 50% wallplug efficiency.

White LEDs used for lighting are often based on efficient blue LEDs that excite a phosphor so that the blue light is converted to white light. These high-quality LEDs with their very long lifetime (100 000 hours) are getting cheaper, and the market is currently exploding. A little further on in the future, three-colour LEDs may replace the combination of blue LED and phosphor for efficient lighting. This technology will allow for dynamic control of colour composition.

Replacing light bulbs and fluorescent tubes with LEDs will lead to a drastic reduction of electricity requirements for lighting. Since 20-30% of the electricity consumed in industrial economies is used for lighting, considerable efforts are presently being devoted to replacing old lighting technologies with LEDs.

Today, GaN-based LEDs provide the dominant technology for back-illuminated liquid crystal displays in many mobile phones, tablets, laptops, computer monitors, TV screens, etc. Blue and UV-emitting GaN diode lasers are also used in high-density DVDs, which has advanced the technology for storing music, pictures and movies. Future application may include the use of UV-emitting AlGaIn/GaN LEDs for water purification, as UV light destroys the DNA of bacteria, viruses and microorganisms. In countries with insufficient or non-existent electricity grids, the electricity from solar panels stored in batteries during daylight, powers white LEDs at night. There, we witness a direct transition from kerosene lamps to white LEDs.

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