Light Emitting Diodes: A Journey to Blue LED

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Abstract – LEDs have become nowadays most important display devices because they are energy-efficient and environment-friendly light sources and also used in instrumentation [1]. In the present paper, the properties and fabrication of LEDs of different colours have been discussed. Their performance and characteristics have also been reviewed.

Keyword – LED; injection luminescence;

1. INTRODUCTION

LED is an active display device operating on the principle of injection luminescence. Basically, it is a semiconductor pn junction device, capable of emission of electromagnetic (EM) radiations under forward bias condition. The radiation emitted by LEDs can either be in the visible region or infra-red region, which depend on the properties of the semiconductor used [2]. In either case, LEDs are useful for electronic displays. Major benefits of using LEDs display are:

- 1. They are highly miniature devices and can be considered as point source of light.
- The light output from LED is a function of current flows through it. Therefore, the light intensity of LED displays can be smoothly controlled by varying the current.
- 3. They are highly efficient emitters of EM radiations. They require only moderate input power.
- Their switching time is very small due to which they can be turned ON and OFF even in less than 1 nanosecond.
- 5. Their low supply voltage and current requirements make them compatible with DTL and TTL ICs.
- Being solid state devices, they are rugged and can be used safely in shock and vibration environments.
 Moreover, they can be operated reliably over a wide temperature range up to 70°C.

These factors have paved the way for the use of LEDs as displays in professional grade equipment as well. It is of interest to note that red, green and yellow emissions are directly realizable from LEDs through injection luminescence but initially blue emission was possible only through up-conversion of IR emission [3, 4].

2.THEORY OF LED

The basic theory of operation of pn junction diode is: under thermal equilibrium condition when the diode is at zero bias, its depletion layer potential prevents the cross-

over of large concentrations of electrons and holes across the junction. Under forward bias the magnitude of this potential barrier is reduced and diffusion of electrons and holes across the junction takes place thus increasing the minority carrier concentrations on both sides by a considerable amount, due to which enhancement of their rate of recombination take place. The rate of recombination is given by

where Rc is recombination coefficient, Δn is the excess minority carrier electron concentration injected into the p-side of a pn junction diode and p is the concentration of holes.

The emission of photon is possible only when both energy and momentum are conserved. The most probable recombination of electrons and holes requires same value of momentum. This situation exists in many Group III-V compound semiconductors which are of the direct band gap type with the conduction band minimum and the valence band maximum being at the zero momentum position. This recombination process is of the direct type. In contrast to this, during recombination in indirect band gap semiconductors, to conserve momentum a third particle is added, wherein the conduction band minimum and valence band maximum occurs at different values of momentum. The probability of recombination in this case much lower than that for direct band gap semiconductors. Typically Rc for indirect band gap semiconductors such as GaP, is about four orders of magnitude lower than that for direct band gap semiconductors, e.g. GaAs.

The wavelength of emitted radiation may be written as

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For visible radiations, the energy should be in the range 1.75 - 3.15 eV.

The semiconductors having direct band gap and commonly used for the purpose of LED are GaAs, GaSb, InAs, InSb and InP but they have band gap values less than 1.75 eV which result infrared radiations. Therefore it is necessary to use some alternative techniques for getting visible radiations, two of which are described in brief here:

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(i) Up-conversion method: - Infra-red emitting LEDs are coated with a suitable up-converting phosphor. The light output is governed by the characteristic of the phosphor. The phosphors are usually based on mixed rare-earth fluorides such as YOCl (Yb, Er), YF3 (Yb, Er) and YF3 (Yb, Tm). When the diode is turned ON, the infra red emission excites certain trivalent rare-earth ions present in the phosphor to visible emitting state, thereby providing light output with low efficiency.

(ii)Ternary Alloy: - These can be formed between a binary compound with small direct band-gap and another binary compound with large indirect band-gap. Such alloys have band-gap which can be varied monotonically between the band-gap values of the constituents by controlling their proportion. In GaAs1-xPx, band gap value can smoothly be varied from band gap of GaAs i.e. 1.44 eV to the band gap of GaP i.e. 2.26eV by controlling x from 0 to 1.

Despite of their usefulness, the major disadvantage of these LEDs is their poor external efficiency. The GaAs1-xPx LEDs have external efficiency of the order of 0.5% only due to strong internal absorption of the light generated caused by the crystalline structure of the device. To improve this several methods had been developed but still, it is only 0.5-2%.

It is in this connection that *pn* junctions in indirect bandgap semiconductors assume importance. Because of indirect band gap structure, free holes and electrons in *pn* junctions do not recombine radiatively. Therefore, it is in usual practice to associate impurity centres in indirect band gap semiconductors to realize improved LEDs. In such case, each impurity centre assists in localizing one of the charge carriers and then attracting the oppositely charged carrier; which improves the value of *R* and in turn increases internal efficiency. Typically, external efficiencies of Red emitting GaP LEDs are in the range 3-7% and of Green emitting GaP LEDs are about 0.6%.

Based on the above discussion, Red, Green and Yellow emissions are possible through injection luminescence but blue emission is possible only through up-conversion of IR emission.

3.BLUE LED

Blue electroluminescence was first reported in 1923. It was based on light emission from particles of SiC which contained accidental *pn* junction. By the late 1960's, SiC films had been prepared by more careful processes and *pn* junction devices were fabricated, leading to blue LED's with a very low up-conversion efficiency of about 0.005% [5]. In the ensuing decades blue LED's were never substantially improved, because SiC is an indirect band gap material. In the early 1990's, SiC LEDs were actually sold commercially with the best efficiency of 0.03% for wavelength 470 nm [6].

In 1968, Tietjen and Herbert Maruska started working on to find a method for growing single crystal films of GaN, which would yield blue LEDs. GaN had been prepared as a powder by reacting ammonia with liquid gallium metal at elevated temperatures. Various dopants had been introduced into these powder samples.

In 1969, Maruska developed the first single crystal film of GaN as revealed by Laue pattern. He noticed that it is n-type dopant without intentional doping whereas a *pn* junction with p-type dopant was needed which was not an easy task. Zinc seemed to be an appropriate acceptor because it worked for GaAs and GaP. With heavy Zn concentrations, GaN films proved to be insulating and even became orange in color. But the films never became conducting p-type.

After the study of optical absorption photoluminescence of thin film GaN [7] by Maruska and Pankove, in 1971 Pankove and Miller reported electroluminescence from GaN. They made a sample consisted of an insulating Zn-doped layer with two surface contact probes, from this sample a peak at 475 nm of blue colour was observed. Later they made a device consisting of an undoped n-type region, an insulating Zndoped layer, and an indium surface contact. This was the first actual GaN light-emitting diode emitting green light. Later in 1972 while growing Mg-doped GaN films Maruska got a "bright" violet LED emitting at 430 nm [4]. They were able to devise a model for the operation of these devices based on Fowler-Nordheim tunneling of electrons through a triangular potential barrier, because the characteristics were virtually independent of temperature [8-10]. They proposed that the blue luminescence was due to impact excitation of filled Mg acceptors by hot electrons, followed by recombination. But these tunneling devices were never very efficient, and no successful commercial product ever appeared.

In the subsequent years work on GaN was virtually ceased everywhere. Later after a long time, in 1989 Akasaki, solved the p-type doping dilemma, achieving conducting material with electron-beam annealed Mg-doped GaN [11]. In 1995, Nakamura developed blue and green GaN hetero-structure LEDs with efficiencies exceeding 10% [12]. It is important to note that *for this invention of efficient blue LEDs* Akasaki jointly with Hiroshi Amano and Nakamura awarded Nobel Prize in Physics in 2014.

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