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Optoelectronic Device Phosphors

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Without sun light we cannot assume the life on the earth. The sun is giving energy to our mother earth billions of years. Light is at the origin of all life, it plays a central role in human activities, and has revolutionized society through medicine and communications, entertainment and culture. Industries based on light are major economic drivers; they create jobs, and provide solutions to global challenges in energy, education, agriculture and health. Light is also important to our appreciation of art, and optical technologies are essential in understanding and preserving cultural heritage. As light becomes a key cross-cutting discipline of science in the 21st century, it is essential that its importance is fully appreciated. It is equally vital that the brightest young minds from all areas of the world continue to be attracted to careers in this field.

A light-emitting diode (LED) is a two-lead semiconductor light source. It is a basic pn-junction diode, which emits light when activated. When a fitting voltage is applied to the leads, electrons are able to recombine with holes within the device, releasing energy in the form of photons. This effect is called electroluminescence, and the color of the light (corresponding to the energy of the photon) is determined by the energy band gap of the semiconductor. An LED is often small in area (less than 1 mm2) and integrated optical components may be used to shape its radiation pattern.

Appearing as practical electronic components in 1962, the earliest LEDs emitted low-intensity infrared light. Infrared LEDs are still frequently used as transmitting elements in remote-control circuits, such as those in remote controls for a wide variety of consumer electronics. The first visible-light LEDs were also of low intensity, and limited to red. Modern LEDs are available across the visible, ultraviolet, and infrared wavelengths, with very high brightness.

Early LEDs were often used as indicator lamps for electronic devices, replacing small incandescent bulbs. They were soon packaged into numeric readouts in the form of seven-segment displays, and were commonly seen in digital clocks. Recent developments in LEDs permit them to be used in environmental and task lighting. LEDs have many advantages over incandescent light sources including lower energy consumption, longer lifetime, improved physical robustness, smaller size, and faster switching. Light-emitting diodes are now used in applications as diverse as aviation lighting, automotive headlamps, advertising, general lighting, traffic signals, and camera flashes. However, LEDs powerful enough for room lighting are still relatively expensive, and require more precise current and heat management than compact fluorescent lamp sources of comparable output. LEDs have allowed new text, video displays, and sensors to be developed, while their high switching rates are also useful in advanced communications technology.

On October 7, 2014, the Nobel Prize in Physics was awarded to Isamu Akasaki, Hiroshi Amano and Shuji Nakamura for "the invention of efficient blue lightemitting diodes which has enabled bright and energysaving white light sources" or, less formally, LED lamps. The Nobel Prize in Physics 2014 was awarded jointly to Isamu Akasaki, Hiroshi Amano and Shuji Nakamura "for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources".

Although the invention of the blue LED is only twenty years old, it has already contributed to creating white light in a completely new way that greatly benefits the world. The following is the basics LED operating mechanism



Fig. 1: Basics LED operating mechanism

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1. ELECTROLUMINESCENCE DISPLAY (ELD)

Electroluminescence display layout is shown in figure 8. Phosphor is sand witched between two conducting layers. These are either AC or DC powder or thin film devices. Typical thickness of phosphor layer is about 50 to 100 microns with 2 to 5 micron size particles. Phosphor layer can be either thick film or thin film. Depending on the structure, different phosphors are being employed.

2. BACKLIGHT FOR LIQUID CRYSTAL DISPLAY (LCD) OR LCD BLU

A backlight is the form of illumination used in an LCD. The light source can be incandescent light bulb, or cold cathode fluorescent lamps (CCFL) or hot cathode fluorescent lamps (HCFL) or an array of light emitting diodes (LEDs). Backlight usually employs a diffuser to provide uniform light through the display. Color LCD displays using white light that cover most of color spectrum. CCFL are being used on large display for color monitors and TVs. The backlight in hand held and small TV LCDs is generated by an array of LEDs with or without phosphors. Cross section of LCD backlight with edge lighting and bottom lighting are shown in figure 8.

3. LED BASED TVS

With the announcement of World's First Laser-Based Television (Laser Vue) by Mitsubishi Electric on October 28, 2008, there is a huge opportunity and need for better phosphors. In this system, millions of colors are achieved from RGB laser diodes. NEC is developing a 3D system by employing RGB phosphors on near UV laser diode (395nm). The phosphors, we are working is excitable with 395nm wavelength and emit in RGB wavelengths with specific decay times suitable 3D applications.

The first commercial LEDs were commonly used as replacements for incandescent and neon indicator lamps, and in seven-segment displays, first in expensive equipment such as laboratory and electronics test equipment, then later in such appliances as TVs, radios, telephones, calculators, as well as watches. The Monsanto Company was the first organization to mass-produce visible LEDs, using gallium arsenide phosphide (GaAsP) in 1968 to produce red LEDs suitable for indicators. Hewlett Packard (HP) introduced LEDs in 1968, initially using GaAsP supplied by Monsanto. These red LEDs were bright enough only for use as indicators, as the light output was not enough to illuminate an area. Readouts in calculators were so small that plastic lenses were built over each digit to make them legible. Later, other colors became widely available and appeared in appliances and equipment. In the 1970s commercially successful LED devices at less than five cents each were produced by Fairchild Optoelectronics. LED display of a TI-30 scientific calculator (ca. 1978), which uses plastic lenses to increase the visible digit size

As LED materials technology grew more advanced, light output rose, while maintaining efficiency and reliability at acceptable levels. The invention and development of the high-power white-light LED led to use for illumination, and is slowly replacing incandescent and fluorescent lighting recently.

Most LEDs were made in the very common 5 mm $T1\frac{3}{4}$ and 3 mm T1 packages, but with rising power output, it has grown increasingly necessary to shed excess heat to maintain reliability, so more complex packages have been adapted for efficient heat dissipation. Packages for stateof-the-art high-power LEDs bear little resemblance to early LEDs.

The blue and white LED: Illustration of Haitz's law. Light output per LED per production year, with a logarithmic scale on the vertical axis. The first high-brightness blue LED was demonstrated by Shuji Nakamura of Nichia Corporation in 1994 and was based on InGaN. Its development built on critical developments in GaN nucleation on sapphire substrates and the demonstration of p-type doping of GaN, developed by Isamu Akasaki and Hiroshi Amano. In 1995, Alberto Barbieri at the Cardiff University Laboratory (GB) investigated the efficiency and reliability of high-brightness LEDs and demonstrated a "transparent contact" LED using indium tin oxide (ITO) on (AlGaInP/GaAs). The existence of blue LEDs and high-efficiency LEDs quickly led to the development of the first white LED, which employed a Y3Al5O12:Ce, or "YAG", phosphor coating to mix down-converted yellow light with blue to produce light that appears white. Nakamura was awarded the 2006 Millennium Technology Prize for his invention. Akasaki, Amano, and Nakamura were awarded the 2014 Nobel prize in physics for the invention of the blue LED.

The development of LED technology has caused their efficiency and light output to rise exponentially, with a doubling occurring approximately every 36 months since the 1960s, in a way similar to Moore's law. This trend is generally attributed to the parallel development of other semiconductor technologies and advances in optics and material science, and has been called Haitz's law after Dr. Roland Haitz.

The LED consists of a chip of semiconducting material doped with impurities to create a p-n junction. As in other diodes, current flows easily from the p-side, or anode, to the n-side, or cathode, but not in the reverse direction. Charge-carriers—electrons and holes—flow into the junction from electrodes with different voltages. When an electron meets a hole, it falls into a lower energy level and releases energy in the form of a photon.

The wavelength of the light emitted, and thus its color, depends on the band gap energy of the materials forming the p-n junction. In silicon or germanium diodes, the electrons and holes usually recombine by a non-radiative transition, which produces no optical emission, because these are indirect band gap materials. The materials used for the LED have a direct band gap with energies corresponding to near-infrared, visible, or near-ultraviolet light.

LED development began with infrared and red devices made with gallium arsenide. Advances in materials science have enabled making devices with ever-shorter wavelengths, emitting light in a variety of colors.

LEDs are usually built on an n-type substrate, with an electrode attached to the p-type layer deposited on its surface. P-type substrates, while less common, occur as well. Many commercial LEDs, especially GaN/InGaN, also use sapphire substrate.

Most materials used for LED production have very high refractive indices. This means that much light will be reflected back into the material at the material/air surface interface. Thus, light extraction in LEDs is an important aspect of LED production, subject to much research and development.

The light emission cones of a real LED wafer are far more complex than a single point-source light emission. The light emission zone is typically a two-dimensional plane between the wafers. Every atom across this plane has an individual set of emission cones. Drawing the billions of overlapping cones is impossible, so this is a simplified diagram showing the extents of all the emission cones combined. The larger side cones are clipped to show the interior features and reduce image complexity; they would extend to the opposite edges of the twodimensional emission plane.

Bare uncoated semiconductors such as silicon exhibit a very high refractive index relative to open air, which prevents passage of photons arriving at sharp angles relative to the air-contacting surface of the semiconductor. This property affects both the light-emission efficiency of LEDs as well as the light-absorption efficiency of photovoltaic cells. Internal reflections can escape through other crystalline faces, if the incidence angle is low enough and the crystal is sufficiently transparent to not reabsorb the photon emission. But for a simple square LED with 90-degree angled surfaces on all sides, the faces all act as equal angle mirrors. In this case most of the light can not escape and is lost as waste heat in the crystal. A convoluted chip surface with angled facets similar to a jewel or fresnel lens can increase light output by allowing light to be emitted perpendicular to the chip surface while far to the sides of the photon emission point.

The ideal shape of a semiconductor with maximum light output would be a microsphere with the photon emission occurring at the exact center, with electrodes penetrating to the center to contact at the emission point. All light rays emanating from the center would be perpendicular to the entire surface of the sphere, resulting in no internal reflections. A hemispherical semiconductor would also work, with the flat back-surface serving as a mirror to back-scattered photons.Many LED semiconductor chips are encapsulated or potted in clear or colored molded plastic shells. The plastic shell has three purposes:

Efficiency and operational parameters: Typical indicator LEDs are designed to operate with no more than 30–60 milliwatts (mW) of electrical power. Around 1999, Philips Lumileds introduced power LEDs capable of continuous use at one watt. These LEDs used much larger semiconductor die sizes to handle the large power inputs. Also, the semiconductor dies were mounted onto metal slugs to allow for heat removal from the LED die. One of the key advantages of LED-based lighting sources is high luminous efficacy. White LEDs quickly matched and overtook the efficacy of standard incandescent lighting systems. In 2002, Lumileds made five-watt LEDs available with a luminous efficacy of 18-22 lumens per (lm/W). For comparison, a conventional watt incandescent light bulb of 60-100 watts emits around 15 lm/W, and standard fluorescent lights emit up to 100 lm/W.

In September 2003, a new type of blue LED was demonstrated by the company Cree Inc. to provide 24 mW at 20 milli amperes (mA). This produced a commercially packaged white light giving 65 lm/W at 20 mA, becoming the brightest white LED commercially available at the time, and more than four times as efficient as standard incandescents. In 2006, they demonstrated a prototype with a record white LED luminous efficacy of 131 lm/W at 20 mA. Nichia Corporation has developed a white LED with luminous efficacy of 150 lm/W at a forward current of 20 mA Cree's X Lamp XM-L LEDs, commercially available in 2011, produce 100 lm/W at their full power of 10 W, and up to 160 lm/W at around 2 W input power. In 2012, Cree announced a white LED giving 254 lm/W,[50] and 303 lm/W in March 2014. Practical general lighting needs high-power LEDs, of one watt or more. Typical operating currents for such devices begin at 350 mA. Note that these efficiencies are for the LED chip only, held at low temperature in a lab. Lighting works at higher temperature and with drive circuit losses, so efficiencies are much lower. United States Department of Energy (DOE) testing of commercial LED lamps designed to replace incandescent lamps or CFLs showed that average efficacy was still about 46 lm/W in 2009 (tested performance ranged from 17 lm/W to 79 lm/W).

The term "efficiency droop" refers to a decrease (up to 20%[citation needed]) in luminous efficacy of LEDs as the electrical current increases above tens of milliamps (mA). Instead of increasing current levels, luminance is usually increased by combining multiple LEDs in one bulb. Solving the problem of efficiency droop would

| Infrared | $\lambda > 760$ | $\Delta V < 1.63$ | Gallium arsenide (GaAs) |
|----------|-----------------------|----------------------------|---|
| Red | $610 < \lambda < 760$ | $1.63 < \Delta V < 2.03$ | Aluminium gallium arsenide (AlGaAs) |
| Orange | $590 < \lambda < 610$ | $2.03 < \Delta V < 2.10$ | Gallium arsenide phosphide (GaAsP) |
| Yellow | $570 < \lambda < 590$ | $2.10 < \Delta V < 2.18$ | Gallium arsenide phosphide (GaAsP) |
| Green | $500 < \lambda < 570$ | $1.9 \le \Delta V \le 4.0$ | Traditional green: Gallium(III) phosphide (GaP) |
| Blue | $450 < \lambda < 500$ | $2.48 < \Delta V < 3.7$ | Zinc selenide (ZnSe) |
| Violet | $400 < \lambda < 450$ | $2.76 < \Delta V < 4.0$ | Indium gallium nitride (InGaN) |
| Purple | Multiple types | $2.48 < \Delta V < 3.7$ | Dual blue/red LEDs, |

Table 1

mean that household LED light bulbs would need fewer LEDs, which would significantly reduce costs.

In addition to being less efficient, operating LEDs at higher electrical currents creates higher heat levels which compromise the lifetime of the LED. Because of this increased heating at higher currents, high-brightness LEDs have an industry standard of operating at only 350 mA, which is a good compromise between light output, efficiency, and longevity.

Solid-state devices such as LEDs are subject to very limited wear and tear if operated at low currents and at low temperatures. Many of the LEDs made in the 1970s and 1980s are still in service in the early 21st century. Typical lifetimes quoted are 25,000 to 100,000 hours, but heat and current settings can extend or shorten this time significantly.

The most common symptom of LED (and diode laser) failure is the gradual lowering of light output and loss of efficiency. Sudden failures, although rare, can occur as well. Early red LEDs were notable for their short service life. With the development of high-power LEDs the devices are subjected to higher junction temperatures and higher current densities than traditional devices. This causes stress on the material and may cause early light-output degradation. To quantitatively classify useful lifetime in a standardized manner it has been suggested to use the terms L70 and L50, which is the time it will take a given LED to reach 70% and 50% light output respectively.

LED performance is temperature dependent. Most manufacturers' published ratings of LEDs are for an operating temperature of 25 °C. LEDs used outdoors, such as traffic signals or in-pavement signal lights, and that are utilized in climates where the temperature within the light fixture gets very hot, could result in low signal intensities or even failure.

LED light output rises at lower temperatures, leveling off, depending on type, at around -30 °C.[citation needed] Thus, LED technology may be a good replacement in uses such as supermarket freezer lighting[66][67][68] and will last longer than other technologies. Because LEDs emit less heat than incandescent bulbs, they are an energy-efficient technology for uses such as in freezers and refrigerators. However, because they emit little heat, ice

and snow may build up on the LED light fixture in colder climates. Similarly, this lack of waste heat generation has been observed to sometimes cause significant problems with street traffic signals and airport runway lighting in snow-prone areas. In response to this problem, some LED lighting systems have been designed with an added heating circuit at the expense of reduced overall electrical efficiency of the system; additionally, research has been done to develop heat sink technologies that will transfer heat produced within the junction to appropriate areas of the light fixture.

Conventional LEDs are made from a variety of inorganic semiconductor materials. The above (Table 1) are the available colors with wavelength range, voltage drop and material.

4. BLUE LEDS

Current bright blue LEDs are based on the wide band gap semiconductors GaN (gallium nitride) and InGaN (indium gallium nitride). They can be added to existing red and green LEDs to produce the impression of white light. Modules combining the three colors are used in big video screens and in adjustable-color fixtures.

5. PHOSPHORS

As the picture quality of PDP TV depends mainly on the type of phosphors employed, the selection of the appropriate phosphors is of the utmost importance (12). Currently different combinations of phosphors are used by PDP manufacturers. The emission spectra from three different 42" commercial display panels employing three different green phosphors viz., $ZnSiO_4$:Mn, a $ZnSiO_4$:Mn + Y,GdBO₃:Tb blend and a $BaAl_{12}O_{19}$:Mn + Y.GdBO₃:Tb blend, are shown in Fig. 1.

6. LED PHOSPHORS

Yellow emitting Cerium activated yttrium aluminum garnet (YAG:Ce) phosphor is widely used in solid state lighting to convert the blue light from a blue LED to yellow and ultimately white (close) by blending blue and yellow emissions. Europium activated alkaline earth silicates are also used in designing white LEDs. These phosphors are not popular as they degrade fast in a LED module with duration of operating time and conditions. Recently NIMS (Japan) and Mitsubishi came out with



Fig. 2: CIE diagram and optical characteristics of blue LED for LCD back light applications.

better phosphors based on alkaline earth aluminum nitrides as green, yellow and alkaline earth silicon nitrides as red emitting phosphors. CIE diagram and optical characteristics of blue LED for LCD back light applications are shown bellow.

7. PHOSPHOR-BASED LEDS

Spectrum of a white LED showing blue light directly emitted by the GaN-based LED (peak at about 465 nm) and the more broadband Stokes-shifted light emitted by the Ce^{3+} :YAG phosphor, which emits at roughly 500–700 nm. This method involves coating LEDs of one color (mostly blue LEDs made of InGaN) with phosphors of different colors to form white light; the resultant LEDs are called phosphor-based or phosphor-converted white LEDs (pcLEDs). A fraction of the blue light undergoes the Stokes shift being transformed from shorter wavelengths to longer. Depending on the color of the original LED, phosphors of different colors can be employed. If several phosphor layers of distinct colors are applied, the emitted spectrum is broadened, effectively raising the color rendering index (CRI) value of a given LED.

Phosphor-based LED efficiency losses are due to the heat loss from the Stokes shift and also other phosphor-related degradation issues. Their luminous efficacies compared to normal LEDs depend on the spectral distribution of the resultant light output and the original wavelength of the LED itself. For example, the luminous efficacy of a typical YAG yellow phosphor based white LED ranges from 3 to 5 times the luminous efficacy of the original blue LED because of the human eye's greater sensitivity to yellow than to blue (as modeled in the luminosity function). Due to the simplicity of manufacturing the phosphor method is still the most popular method for making high-intensity white LEDs. The design and production of a light source or light fixture using a monochrome emitter with phosphor conversion is simpler and cheaper than a complex RGB system, and the majority of high-intensity white LEDs presently on the market are manufactured using phosphor light conversion.

Among the challenges being faced to improve the efficiency of LED-based white light sources is the development of more efficient phosphors. As of 2010, the most efficient yellow phosphor is still the YAG phosphor, with less than 10% Stoke shift loss. Losses attributable to internal optical losses due to re-absorption in the LED chip and in the LED packaging itself account typically for another 10% to 30% of efficiency loss. Currently, in the area of phosphor LED development, much effort is being spent on optimizing these devices to higher light output and higher operation temperatures. For instance, the efficiency can be raised by adapting better package design or by using a more suitable type of phosphor. Conformal coating process is frequently used to address the issue of varying phosphor thickness.

Some phosphor-based white LEDs encapsulate InGaN blue LEDs inside phosphor-coated epoxy. Alternatively, the LED might be paired with a remote phosphor, a preformed polycarbonate piece coated with the phosphor material. Remote phosphors provide more diffuse light, which is desirable for many applications. Remote phosphor designs are also more tolerant of variations in the LED emissions spectrum. A common yellow phosphor material is cerium-doped yttrium aluminium garnet (Ce3+:YAG).

White LEDs can also be made by coating near-ultraviolet (NUV) LEDs with a mixture of high-efficiency europiumbased phosphors that emit red and blue, plus copper and aluminium-doped zinc sulfide (ZnS:Cu, Al) that emits green. This is a method analogous to the way fluorescent lamps work. This method is less efficient than blue LEDs with YAG:Ce phosphor, as the Stokes shift is larger, so more energy is converted to heat, but yields light with better spectral characteristics, which render color better. The following are the excitation and emissions of Eu³⁺ doped BaYO phosphor. The phosphor exhibited more than 10 excitations ranging from 250-800nm which includes the UV-NUV-Visible and IR regions.

467 527

450 500 550

535

Fig. 3

467

500

417

395

32

538

580 533

1000

800

600

400

200

0

1000

800

600

400

200

0

PL intensity

200 250 300 350 400

PLE intensity

254



The PL emissions are found from 360-630nm. The emissions around 612nm are out of intensity when excited



The present phosphor BYO:Eu³⁺ is synthesized using solid state reaction. The emissions around 612nm are out of intensity when excited with 254,265,395 and 467 along with other emissions in violet to yellow region. All the emissions are allowed transitions of $\operatorname{Eu}^{3\bar{+}}$ When the phosphor is excited with 649,760 and 787nm the emissions are found at 589, 595 and 613nm. The 613nm emission is highest which is up conversion luminescence. This phosphor can be a future candidate for nUV, blue LED material. This material also a good up conversion material.

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It is a great opportunity to discuss few basics to applied aspects of light emitting diodes which changed the future display industry since 2005. Being the president,



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Luminescence Society of India I, am proud that the UNESCO Executive Board has enthusiastically supported the proposal to declare an International Year of Light in 2015 my sincere congratulations to UNESCO for identifying the importance of light. Our research group consenting of 25 researchers, the activates on display phosphors including LED phosphors and devices expecting to lead to major breakthrough on applications.

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